THE SAMPLING AND IDENTIFICATION OF COMPONENTS IN VOLATILE ORGANIC MIXTURES

by

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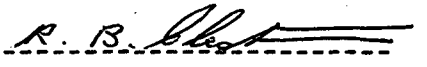

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CONTENTS

ABSTRACT

Public awareness of the toxic effects of some volatile organic compounds present in the working and home environment has created a requirement for the accurate measurement of the concentration of these substances. Similar techniques may be used for the examination of the volatile components of plant material and assist in determining the optimum economic time for harvesting, and also provide useful information in the areas of plant-insect interaction. This thesis examines some of the sampling and analytical aspects for the determination of trace volatile organic compounds present in air.

A brief critical review of the literature is presented describing concentration and trapping techniques, headspace collection, separation and analytical techniques, detection and measurement of the separated components and the sources of error in trace volatile analysis.

The development of an experimental sampling system for volatile organic compounds in air, based on trials conducted with activated carbon and a porous polymer is presented. Two methods of sample desorption are described and the development of sampling equipment based on Tenax GC, thermal elution with secondary trapping and flash injection into the inlet of a gas chromatograph is described.

An investigation was conducted into the nature and origin of an unpleasant lachrimatory component emanating

from an industrial furnace, and a number of trapping and separation techniques were used to determine the nature of the irritant. The experimental methods used are described, and conclusions are drawn concerning the suitability of the various techniques for trace organic volatile sampling.

The steam volatile components of the oil of two Tasmanian native plants, Drimys lanceolata and Prostanthera lasianthos are examined using gas chromatography retention criteria on two columns and mass spectral information. A comparison of the volatile components of Boronia megastigma in the flowers, concrete, and concrete headspace is described and the application of the technique to the determination of the optimum time for harvesting, is outlined.

Changes in the volatile components produced upon injury of Pinus radiata are examined using headspace traps above and below the injury and comparisons are made of the volatile components present in the bark.

ABBREVIATIONS

GC - Gas Chromatograph

FID - Flame Ionisation Detector

MS - Mass Spectrometer

TIC - Total Ion Current

HPLC - High Performance Liquid Chromatography

CW20M - Carbowax 20M Stationary Phase

OV101 - OV Silicone 101 Stationary Phase

GLT - Glass Lined Stainless Steel Tubing

SCOT - Support Coated Open Tubular (Column)

WCOT - Wall Coated Open Tubular (Column)

MIKES - Mass-analysed Ion Kinetic Energy Spectrometer

PMD - Programmed Multiple Development (Chromatography)

TDL - Toxic Dose Level

ppb - Part per billion

ppm - Part per million

Deg.C-Degrees Celsius

INTRODUCTION

The identification of components in complex mixtures of volatile organic substances, plant volatiles, working and living atmospheres, and volatile substances of forensic interest, has been limited by the techniques available for collection and identification.

Identification of compounds in some workday situations has established the presence of a number of carcinogenic, mutagenic and teratogenic agents as well as those known to cause liver and other vital organ malfunctions. An increasing awareness of the influence of some volatile components on human health has created the need for a generally acceptable group of techniques for their separation and identification.

Major problems associated with the investigation of volatile components include the degree of uncertainty of identification due to formation of rearrangement products and artefacts, and to laboratory contamination. Volatile organic materials present in the atmosphere of work places, industrial areas, hospital operating theatres, city streets, waste chemical dumps all present some degree of hazard to human well-being. This thesis examines the concentration, separation and identification of some volatile organic mixtures present in a number of distinct but related areas.

CHAPTER II

EXPERIMENTAL TECHNIQUES FOR THE CONCENTRATION AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS.

Introduction

The sampling of volatile organic materials in a variety of atmospheres ranging from the confined air in a space capsule [1] to background levels in isolated geographical regions of the earth's surface requires collection, concentration and identification techniques with varying degrees of complexity.

Individual component monitoring and identification is essential in an enclosed area, such as an industrial site, where the need to recognise the health hazard that specific compounds have for persons continually exposed to volatile organic materials. The tracing, fingerprinting and identification of odorous volatile components in other areas such as processing plants, sewage treatment works and abattoirs would also provide information on the degree of risk of exposed persons to hazardous compounds. The qualitative and quantitative trapping and identification of components would provide some scientific basis for the measurement of odours and some other parameters affecting what is loosely termed "the quality of life" in an increasingly more crowded environment.

A. Concentration and Trapping Techniques

Techniques for the sampling of volatile organic mixtures in the atmosphere necessitate the concentration of components to a point where separation and measurement is within the capabilities of the analytical instrumentation. The concentration of components by factors of one hundred to ten thousand are often required.

Trapping or concentration techniques may be considered under three major headings: condensation methods, adsorption methods and headspace techniques.

(i) Condensation or Cryogenic Methods

Earlier attempts to concentrate volatile organic materials from air involved the passage of litre quantities of air through a stainless steel or glass U-tube immersed in a freezing mixture of solid carbon dioxide/acetone, or liquid nitrogen [3-5]. Volatiles and semi- volatile components of cigarette smoke [6] and food products [7] have been trapped utilising this technique. Detection limits of 2 $\mu g/m^3$ have been claimed [8]. In 1967 Willis [9] described a trapping system involving the cryogenic collection of a sample in one loop of a gas chromatograph (GC) separating column. Improved resolution was claimed especially for low molecular weight (C1 to C5) hydrocarbons. However, as a rapid routine method of sample trapping there are obvious practical limitations; for example the carriage of cryogenic liquids to remote or awkward situations (such as the inside holds of ships) [8].

Baker in a series of articles [10,11], summarised and reviewed some earlier theoretical and practical aspects of trace organic contaminant concentration by freezing. A major problem associated with cryogenic trapping procedures is the co-condensation of considerable quantities of water and the inherent losses of low molecular weight water soluble compounds upon its removal. Tyson and Carle [12], circumvented this by passing the cryogenically trapped water-organic mixture through a preparative GC to separate the water and then through a gas chromatograph/mass spectrometer (GC/MS) for identification of components (Figure 1). High recovery efficiencies were obtained for a selection of terpenes.

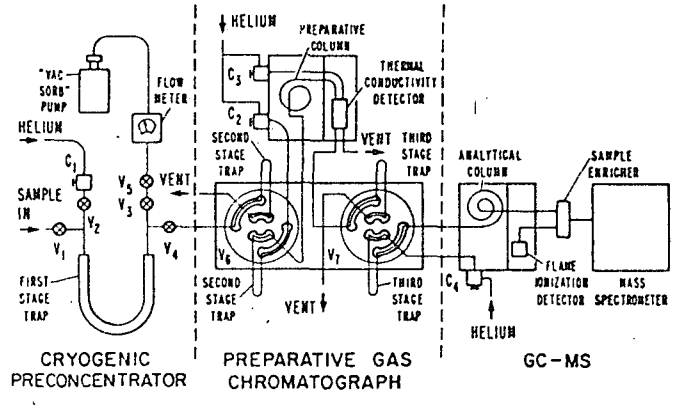

Figure I. Schematic Diagram of a Preconcentration and Analytical System [12].

Cryogenic trapping in conjunction with hydrophobic porous polymers is an effective method for sampling low boiling point organic compounds such as ethylene [15]. Teranishi [13] utilised cryogenic trapping procedures for collection of volatile metabolites from human breath and

urine; and Copier [14] trapped eluent from a GC on cooled glass tubes for subsequent IR analysis.

(ii) Adsorption Methods

(a) Carbon Trapping

Carbon in various forms has been widely used for collecting organic compounds from air [16,17] and water [18,19]. Activated carbon has differing adsorption properties depending upon its source material (coconut, bone, coal or wood), and its particle size. The use of activated carbon for the economic removal of trace organic compounds from water has been of increasing importance following legislation introduced by the U.S. Environmental Protection Authority brought about by the discovery of carcinogenic compounds in New Orleans water [20]. Volatile halogenated hydrocarbon concentrations have been limited by U.S. legislation to 0.5 µg/L.

Small quantities (25mg) of carbon have been used by Grob and Grob [21] to trap microquantities of organic material from the air. However, with small absorbent weights, air flow rates need to be low ca. 2.5 mL/min, and sampling times, as a result, have to be extended to allow collection of sufficient weight of sample. A wide range of molecular weight compounds have been collected and analysed by this method, despite some comment [22], that catalytic changes and irreversilbe absorption of higher molecular weight compounds may occur.

Desorption of trapped components from activated charcoal has been effected by vacuum [23] and steam [24], but the most efficient method appears to be solvent extraction [25,21,26], using dichloromethane or carbon disulphide.

Rubenstein [27] covers some of the theoretical aspects of sorption using activated carbon as an example.

b) Coated Support Trapping

The equilibrium concentration of trace organic compounds upon a liquid stationary phase has been utilised by a number of authors [32,33], for collection of volatiles from air, and other gases, to enable subsequent identification and quantitation by GC. Quantitative trapping of small quantities of organic components at ambient temperatures on a support bonded silicon phases has been described in an excellent paper by Aue [34]. The elution method described involved reflux solvent extraction and concentration of solvent before injection into the GC. Loss of volatile fractions is likely to occur as a result of this latter step and this problem is mentioned in the paper. Another difficulty likely to be encountered with the use of support bonded coatings and solvent extraction techniques is the possible removal of very minute quantities of coating and, the degradation of labile components under warm solvent reflux conditions. Bellar et al [35] described an earlier sample trapping system using a combination of liquid phase coated firebrick and cryogenic condensation to identify more abundant atmospheric hydrocarbons at concentrations of 0.1

ppb in 300mL of air. A system of collecting and transferring amounts as small as 10mg of substances of varying volatilities utilising coated supports is discussed by Bierl et al [35a]. Percentage recoveries varied from seventy to one hundred. However, only single compounds are mentioned and the system described would not appear to have the versatility to trap and recover a wide range of compounds due to the selectivity of liquid phase on the packing material.

c) Porous Polymer Trapping

Microporous polyethylene was first used as a low temperature support in 1963 by Baum [39]. A number of reviews [40] and papers [41-47], have documented the more recent developments of this packing and trapping material. Various types of porous polymers are widely used for separating water, alcohols and aldehydes [48] as well as for the analysis of low molecular weight gases [49,50].

Authors differ in explanations as to the mechanism of adsorption and desorption of porous polymers when used for trapping and elution of organic compounds. Hollis [40] suggested that the solubility of the compound in the polymer is the most important factor in determining the order of elution, whereas Smith and Waddington [51] indicated that within a class of compounds there is a linear relationship between log retention time and boiling point of the eluent. However, pore size distribution, micropore volume, nature of the polymer and surface activity are all important features [52].

Dave [53] reviewed and summarised the information available on porous polymers up to 1969. (Table 1).

Porous Polymer	Surface Area m^2/g	Average Pore Dia. (Angstrom)	Water Affinity	Temperature Limit (Isothermal) °C	Chemical Composition
"Chromosorb" 101	30-40	3500	Hydrophobic	300	STY-DVB
"Chromosorb" 102	300-400	85	Hydrophobic	250	STY-DVB
"Chromosorb" 103	15-25	3500	Hydrophobic	250	STY-DVB
Porapak N	437	-	Hydrophobic	200	-
Porapak P	-	-	Hydrophobic	250	DVB-STY
Porapak Q	840	74.8	Hydrophobic	250	EVB-DVB
Porapak Q-S	-	-	Hydrophobic	250	?
Porapak R	780	75.6	Hydrophobic	250	NVP
Porapak S	670	76.0	Hydrophobic	300	?
Porapak T	450	91.4	Hydrophobic	200	EGMA
PAR 1	100	200	Hydrophobic	250	
PAR 2	300	90	Hydrophobic	250	
Tenax GC	19	720	Hydrophobic	375	DPPO
XAD-2	300	90	Moderate	200	DVB

DPPO = 2,6-diphenyl-p-phenylene oxide; STY = styrene; DVB = divinyl benzene; EVB = ethyl vinyl benzene; NVP = N-vinyl pyrrolidone; EGDMA = ethylene glycol dimethacrylate.

Table I. A Comparison of the Physical Properties of Some Porous Polymers [53].

The development in 1972 by Applied Science Laboratories of a new porous polymer, 2,6-diphenyl-p-phenylene oxide (Tenax GC) provided a versatile, efficient, thermally stable trapping medium that has been widely used for trapping volatiles from air [2,54,55,56], water [2,57], and biological samples [54,58].

A number of authors have compared the various types of porous polymers available for sample trapping and have reached different conclusions [59], Butler and Burke [60] after an investigation utilising test samples of t-butanol, methyl ethyl ketone, benzene and acetonitrile, concluded that Porapaks Q and R had the best overall sampling capacities. However, the statement was made that Tenax GC may be the absorbent of choice for samples consisting of high boiling components because of the high temperature limit and relatively low retention volumes. These characteristics allow sample components to be desorbed more rapidly from Tenax than from other adsorbents.

Zlatkis et al have used Tenax GC as a trapping system for volatiles from human breath [54], urine [54,61], and plasma [58], but do not appear to have critically evaluated the method for loss of volatile components. Pellizzari et al have conducted the most systematic comparison of collection efficiencies [62], and field sampling variables with Tenax GC [63]. The effects of humidity, background load levels, repeated re-use of sorbent, and transportation and storage of collected samples were investigated. Tenax GC was

superior to other sorbents in most cases, percentage recovery by thermal elution procedures being better than 90% at the 50 and 100 mg level [64].

Another porous polymer, XAD-2, has been widely evaluated [65] and used [66-68], for the trapping of trace amounts of organic materials mainly in water. Claims are made that the concentration range extends from 5 parts per trillion (10^{12}) to 50 ppm [65]. It should be noted that some of the claims made in this paper especially concerning recoveries of some higher molecular weight acids have not been verified in this laboratory [69]. Nevertheless, the method has found many applications in trace organic water analysis [70, 71] despite some of the limitations posed by the removal of water from the organic extract and the losses entailed.

Morrison et al [70] claimed that "thermal desorption makes quantitative analysis difficult". This view contrasts with the opinion of a number of other authors [72 - 74], who have successfully used Tenax GC and thermal desorption techniques. As a result of the improvement in sample collection efficiency and the coupling of powerful capillary GC mass spectrometer computer systems, over one hundred volatile components have been collected and identified from atmospheric sources [56] using Tenax GC. Ciccioli et at [75] compared the recoveries of Tenax GC and concluded that a mixture of 0.25g of Tenax GC and 0.45g of Carbopac B provided a good compromise for the trapping of most volatile organic compounds from open air and industrial sites. (Table II)

A cryogenic trapping procedure however, was advocated for low boiling point compounds up to the boiling point of pentane.

Dressler has published a review of applications of porous polymers for the extraction of trace organics from aqueous samples [76] and commented on aspects of method sensitivity and sample storage.

Compound	Carbopack B			Tenax GC		
	0.5 L sample	1.5 L sample	5.0 L sample	0.5 L sample	1.5 L sample	5.0 L sample
Methanol	3	0	0	1	0	0
Ethanol	3	0	0	1	0	0
Methyl chloride	1	0	0	3	1	0
Acetone	5	1	0	68	2	0
Chloroform	100	54	1	100	84	5
Diethylamine	100	80	50	80	50	1
Isobutanol	100	100	25	100	95	16
n-Pentane	100	100	100	100	50	9
Cyclohexane	100	100	100	100	50	9
n-Hexane	100	100	100	100	100	20
Ethyl acetate	100	100	100	100	100	35
n-Butanol	100	100	100	100	100	35
Benzene	100	100	100	100	100	35
Toluene	100	100	100	100	100	100
_*	-	-	-	-	-	-
n-C_{13}	65	65	65	100	100	100
n-C_{14}	46	46	46	100	100	100
n-C_{15}	25	25	25	100	100	100
n-C_{16}	8	8	8	100	100	100
n-C_{17}	1	1	1	100	100	100
n-C_{18}	0	0	0	100	100	100

*Styrene, ethylbenzene, xylene, pyridine, chlorophenol, alkanes, alkenes from C_7-C_{12} had 100%.

Table II. Recovery (percent) of Organic Compounds from Air Samples Using Carbopack B and Tenax-GC Traps.

d) Miscellaneous Adsorption Techniques

Activated alumina [77] and molecular sieve 5A [30] have also been used to trap volatile organic compounds from the atmosphere. However, both materials tend to irreversibly adsorb some of the higher molecular weight labile components and to show the same disadvangages as silica.

(iii) Solvent Trapping

Solvent scrubbing of organic components from air [74] has met with only limited success. The reduction of solvent volume in order to achieve the required final concentration may be accomplished with minimal losses of high boiling components but significant losses of volatile compounds do occur.

The design by Goldberg et al [78], of a closed loop solvent extraction system for trace organic compounds in water, has enbabled the concentration of components by a factor of 10,000. The system operates with any water-immiscible solvent, however, the selectivity of the solvent for particular compound classes and the high losses associated with concentration, as mentioned above, tend to limit the applicability of the method.

Grob [79] refined the solvent extraction procedure and extracted 1 litre of tap water with 200 microlitres of n-pentane and evaporated the solvent to 3 microlitres for one GC injection. (Figure II). Over fifty components were separated and identified by this method.

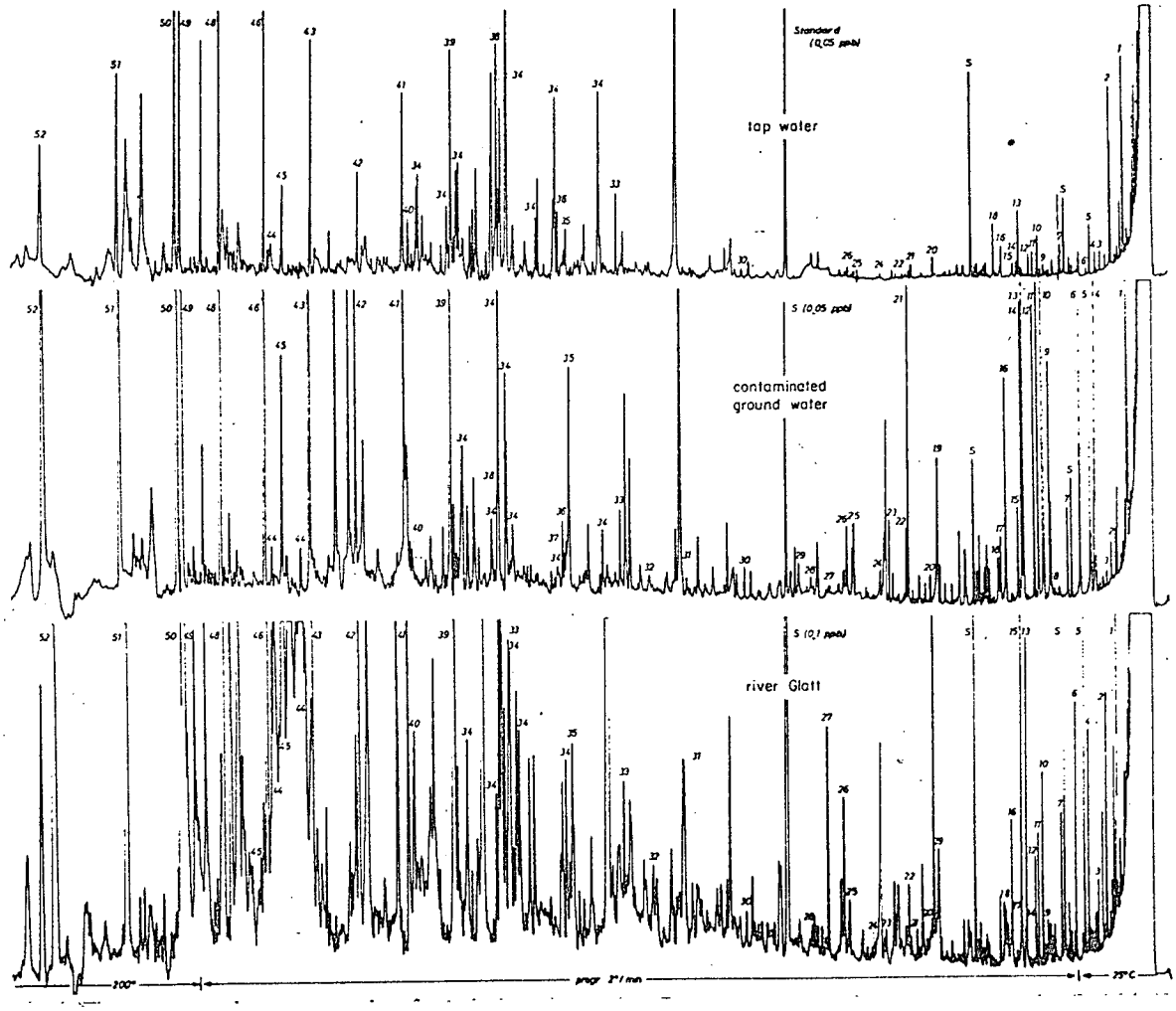

Figure II. GC Traces of Pentane Extracts of Water Samples [79].

B. Direct Headspace Collection.

Headspace collection and analysis of volatile organic compounds is applicable if the concentration of the components is sufficient for direct detection by the analysing system. Hence, for GC analysis, one of the previously mentioned concentration steps is often employed. Headspace sample collection is a simple, effective method of analysing volatile components in a closed vessel. A number of automatic and semi-automatic systems for syringe headspace GC analysis are now available commercially [80] following earlier work by Kolb, Novak and others [81-82]. Figure III illustrates applications of the technique to a number of different sample types.

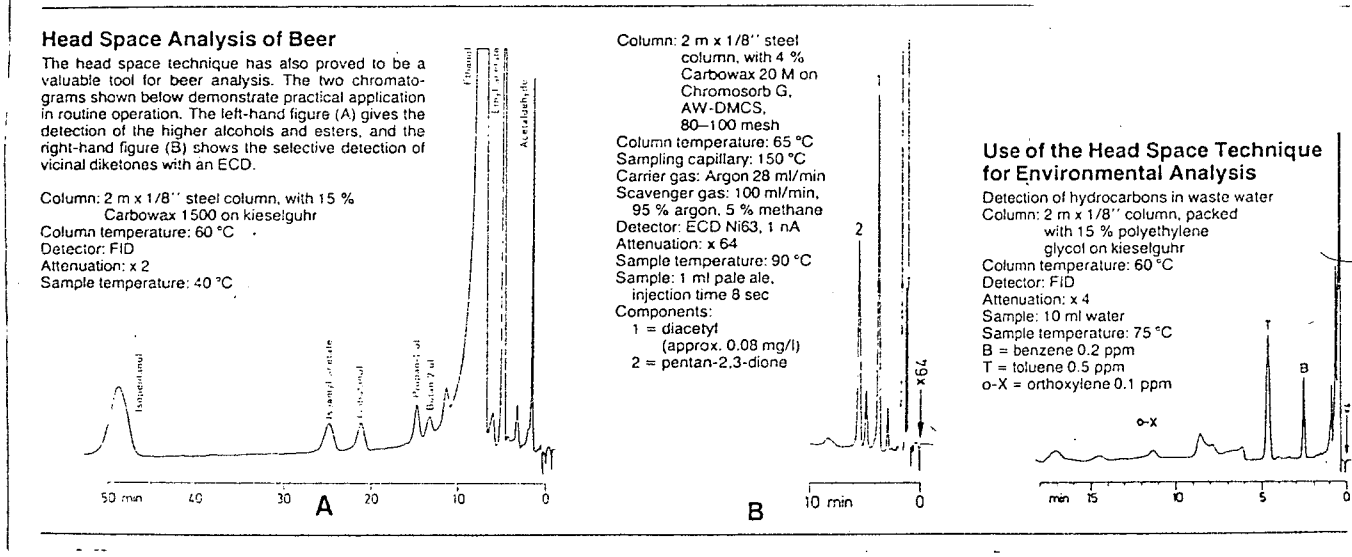

Figure III. Headspace Analysis of Volatile Components [80].

The headspace sample is drawn from a closed vessel by means of a gas tight syringe needle through a silicon rubber or PTFE seal [83,84]. Careful temperature and gas flow control is required in order to obtain reproducable results.

Problems with adsorption onto the septum may be encountered with some volatiles and solvents [85-87]. This effect may be minimised by use of the more expensive but inert PTFE seals.

Injection of total headspace volatiles was undertaken by Loper [88] utilising a heated gas tight syringe in his examination of alfalfa flowers. Many other applications of routine headspace analysis are being developed. The chief advantage being speed in a quality control situation where samples such as blood alcohol, plastic volatiles, obnoxious odours, plant ripening volatiles [80,89] are to be monitored.

C. Separation and Analytical Techniques.

The introduction of capillary GC separation techniques and mass spectrometer-computer data systems, has enabled the separation and identification of complex mixtures of volatile organic compounds that would previously have been very difficult. Examples include the separation of automobile exhaust and miscellaneous background volatiles from ambient air [2,75], and human expired air volatiles [73].

Development work is continuing on the coupling of liquid chromatographic systems to the mass spectrometer to extend the variety of sample types capable of being introduced to this sensitive identification equipment [90].

i) Separation Techniques

Efficient separation of closely related chemical compounds in complex mixtures is a necessary prerequisite to positive identification. Unfortunately it is not always possible to achieve this objective. In many instances therefore, only a probability of component identification can be assigned.

a) Gas Chromatography

Capillary GC columns, to date, have provided the most effective system for the separation of complex mixtures of volatile organic compounds [91,92]. The characteristics of small sample requirement, high resolution, lower temperature and speed make the use of capillary GC columns especially

useful. Opposed to this, glass capillary columns are relatively fragile, require special techniques for preparation that are normally outside the scope of the average laboratory, and require somewhat complicated plumbing arrangements within the GC. Glass capillary columns are usually drawn from borosilicate or soft glass that contain levels of metal oxides that may catalyse stationary phase decomposition at elevated temperatures, resulting in column bleed.

The use of vitreous silica instead of glass as a column material provides the efficiency and resolution characteristics of glass columns while offering improved inertness, thermal stability, flexibility and mechanical strength [93,94]. The flexibility allows the positioning of the end of the GC column through the GC-mass spectrometer interface to a point adjacent to the ion source [95] thus reducing the peak broadening effects associated with normal interface systems. Silica capillary columns are being used in diverse areas of medical [96], environmental [97] and flavour analysis [98] to provide resolution of complex mixtures of volatile components. The wide acceptance of silica columns is shown by the number of papers presented on this subject in the 1982 "Pittsburg" Conference held in the U.S.A. [99]. (Five papers from a total of twelve in the subject of Gas Chromatography).

The sharpness of peaks in capillary chromatograms often allows measurement of quantities of materials which would escape detection when eluted as broad bands of equal area

from packed columns [100].

Temperature programming is usually employed due to the wide range of boiling points represented in complex mixtures. Sub-ambient temperature programming has been used by a number of authors [101] for separation of low boiling compounds. The advantages of capacity of packed columns and the efficiency of capillary columns has been utilised by Blass et al [102] in a versatile combined configuration that allows repetitive trapping and a number of other operations within the one GC oven. Figure IV illustrates the connections required to perform packed column operation, capillary column operation, or combinations of the two. A relatively large quantity of a mixture may be injected onto the packed column and some components held by the trap TD for further separation on the capillary column.

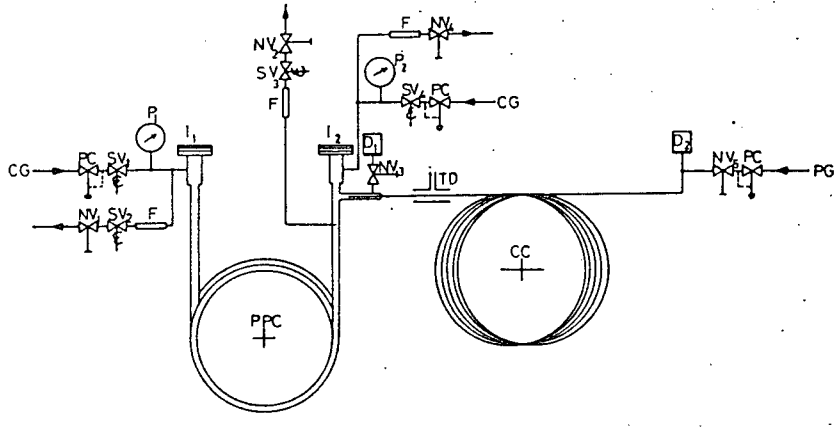

Figure IV. Two Column GC System - Packed and Capillary with Valve Switching [102].

PPC - Packed Column. CC - Capillary Column.
D 1/2 - Detectors. I - Injectors.
Switching Valves, Needle Valves, and Filters.

Development of sampling techniques for trace volatile organics from atmospheric sources [54,72,103] complements the recent advances in capillary gas chromatography. Due to the very fine detail discernible in complex mixtures, capillary columns find a number of applications in 'fingerprinting' or source tracing in forensic science and other fields. Examples include identification of oil spills [104], air pollution sources [105] and the origin of Cannabis plant material [106].

Capillary columns may be considered under two headings - SCOT columns are Support Coated Open Tubular columns with an internal diameter of 0.5mm, where fine solid particles of diatomaceous earth support, coated with a film of stationary phase, are distributed evenly over the wall of the column. They are suited to the analysis of volatile samples [107,108] and are capable of accepting a greater sample load than WCOT columns. Wall Coated Open Tubular columns have an internal diameter of approximately 0.25mm and are used where maximum resolution is required. A thin film of liquid phase of 0.2 to 0.7 micron thickness is deposited on the inner surface of the column. The inner wall is etched to provide the correct surface properties and good mechanical support for the liquid phase. Due to the thin film of liquid phase the loading of this column type is restricted in comparison to SCOT and packed columns. An inlet splitter is frequently used to deposit the optimum quantity of material onto the column - the remainder of the sample or solvent being vented.

b) Mass Spectrometry (MIKES)

The mass spectrometer may be used as an efficient separation/ identification tool when coupled to data reduction and library search computer facilities. The direct introduction of a complex mixture of volatile components into a MS, the use of computer controlled scanning and selected ion monitoring, has enabled the separation and identification of components [109], and the study of reactions and reaction mixtures [110,111]. The method is based on the mass-analysed ion kinetic energy spectrometer (MIKES) first described by Beynon et al in 1973 [112]. Sample preparation is minimal - in some cases none at all - and the technique is useful for structural elucidation. However, quantitation has been difficult to achieve [113] and further developments are required to make the technique amenable to routine work.

c) High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) has not been widely used in the past as a separating method for volatile organic mixtures. However, recent advances in HPLC technology have made the technique comparable to GC in speed, convenience and efficiency [114,115]. The chief advantage of HPLC is the fact that milder solvent and thermal conditions may be employed for the separation of labile components that may decompose under harsher GC temperatures. Precursers of many volatile components are labile and HPLC could prove to be of value in determining breakdown pathways. One of the

disadvantages of HPLC has been that the separation efficiency of HPLC columns (approximately) 7,000 theoretical plates) has been a lot lower than the 120,000 theoretical plates of silica capillary GC columns. Recycling of the column effluent and the use of microbore columns can improve the resolution [116]. However, peak capacity is reduced and complex mixtures with a wide range of boiling points cannot be effectively separated by this procedure.

HPLC has been widely used for the separation of polynuclear aromatic compounds in airborne particulate material [117], and to complement and extend the determination of this class of compounds in conjunction with GC techniques [118].

d) Miscellaneous Separation Techniques

Gel permeation chromatography [119] has been used for separation and molecular weight determination of labile substance of similar molecular size [120]. Hendrickson [121] referred to the method as "a new basic tool that could be called a liquid phase size spectrometer". However, this chromatography technique is applicable to compounds of high molecular weight and low volatility.

Liquid-liquid extraction systems are now available commercially as counter- current chromatography apparatus. Claims are made [127] that the method combines the benefits of countercurrent distribution apparatus and liquid chromatography, with minimium sample loss, no contamination from solid supports and no tailing of solute peaks due to

adsorption effects. Other liquid chromatography techniques such as droplet counter- current chromatography [122] have separation efficiencies close to that of GC, but also have limited applicability in trace volatile separations except where, as above, labile components are encountered.

Liquid-liquid fractionation techniques are frequently used as preliminary separation steps where complex mixtures of organic compounds are separated into various classes [123-125]. The combination of chemical information obtained by fractionation, GC and/or HPLC retention data coupled with spectroscopic information is usually sufficient to identify components of complex mixtures with reasonable certainty [126]. The disadvantages of fractionation methods of sample separation are twofold, involving the efficiency of separation under slightly differing conditions, and problems concerning the formation of artifacts or the introduction of impurities. Many authours fail to provide data on these aspects of the technique [126].

Programmed multiple development chromatography (PMD) is a method of processing thin layer chromatography plates[128-132] to improve resolution and sensitivity. A system of sequential solvent advance and evaporation ensures reconcentration of spot material along the axis of solvent motion, producing a thin band rather than a diffuse spot. Advantages claimed are:- shorter development times, improved resolution of up to 50 times compared with conventional TLC, sensitivity improvement of 5 to 10,and a greater tolerance

to overloading. Most of the above techniques have only limited applicability to volatile trace organic separation systems.

D. Detection and Analytical Techniques.

Trace volatile components eluted from a GC are usually identified according to the retention time compared to a standard under identical conditions. Incorrect identification may result if several compounds elute at the same time, or if a massive amount of solvent alters conditions in the column.

The flame ionisation detector combines sensitivity and versatility for trace compound detection. However a range of on-line spectroscopic detectors is available [133]; and the selectivity of the electron capture [134] and flame photometric [135] detector is widely utilised. Development of a helium microwave emission detector [136-138] has enabled the determination of trihalomethanes in 10 ml of drinking water to levels of 1 part per billion [139].

The most powerful combination for separation, structural determination and quantitation is the capillary GC/MS - computer system [21], [91-92], [140-144]. This combination is capable of the separation and identification of complex mixtures of volatile organic materials in a variety of matrices [145-146]. The data processing capability allows the storage, retrieval and tentative identification of several hundred component peaks of a complex mixture [147-148], [149-150].

Data processing systems coupled to GC/MS can be used to resolve overlapping GC peaks and to counteract unwanted

contributions from column and septum bleed that would otherwise distort the relative intensities of ions in the mass spectrum [151-153]. The resolving effect relies upon the distinction between the MS parent ion peaks, which may be detected even though the original GC peaks were overlapping (see Figure V). Usually 5-10 mass spectra can be collected per GC peak and this provides enough information for processing and reconstruction of a resolved mass chromatogram.

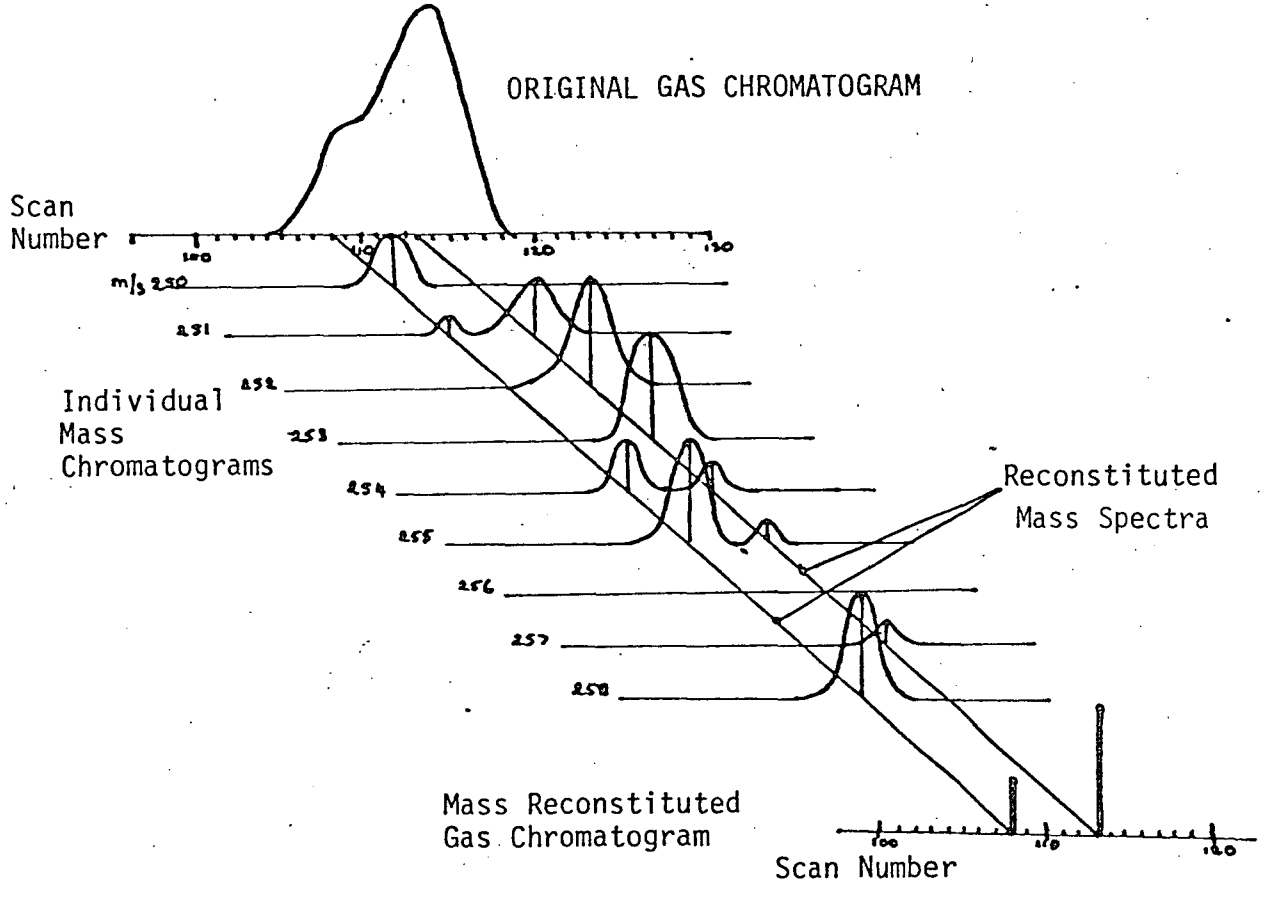

Figure V. Complex Peak Resolution by MS-Computer Techniques.

Sweeley and co-workers have developed methods for separating complex mixtures using computer programs to control repetitive scanning and selected ion monitoring [154]. They have developed a system that incorporates the use of retention indices with off-line reverse library searching of selected mass chromatograms from repetitive scanning of the GC/MS of complex mixtures. Observed precision of retention index was 0.2 percent and lower limit of detection 10ng. The GC/MS precision was 8 percent within duplicate detection of the same sample and the linear range for quantitative ananlyses was 1,000 fold [155].

The most significant advance in techniques in this field have been the combined utilisation of the developments of splitless sample injection, the preparation [156], and evaluation [157] of the operation and performance of WCOT columns, open split injection [158] and direct connection of the GC capillary to the ion source of the mass spectrometer.

Other detection and analysis techniques for monitoring volatile components include; Fourier transform spectroscopy [159-161] using folded path optics for the measurement of 10 ppb levels of hydrocarbon and other species; infrared spectrometry coupled with microprocessor control [162], chemiluminescence [163] as well as a variety of laser based systems [164-165].

Vapour phase infrared spectrophotometric detection of GC eluant peaks [166] using on line computer techniques has

recently shown to be effective in some applications where mass spectral techniques are inadequate [167].

Ancillary techniques, or modified computer search methods, need to be utilised if positive identification of some components is required. Comparison of published mass spectra of terpenes [168], for example, indicate that structurally different terpenes such as tricyclene, alpha-pinene, and 3-carene show differences only in ion intensities of the principle ion peaks with identical mass. These differences are often within the normal operational variables if there are other contributing factors such as GC column bleed or incomplete peak resolution and hence, unequivocal identification by mass spectral means alone is not possible [169].

So rapid are the changes in GC/MS - data system applications that the quantity of literature published in the field of trace organic analysis using this combination of techniques is extremely difficult to scan. The various reviews in Analytical Chemistry provide a useful method of gaining some overview of the topic. A summary of detection systems for trace organic volatiles may be found in the Application Reviews of Analytical Chemistry [170] and also under the specific headings of Mass Spectrometry [171] and Gas Chromatography [172] in the Fundamental Reviews.

E. Sources of Error in Trace Volatile Analysis.

Many organic compounds present in air and water are labile and the method of sampling will influence the qualitative and quantitative result of any analytical programme. The use of complementary techniques for sampling and analysis and the choice of conditions that tend to keep decomposition and rearrangements to a minimum should be utilised wherever possible. Contamination of a sample at any stage of the collection analysis chain may lead to false assumptions and costly errors. A well documented example was the contamination of lunar rock samples [173-175] and the difficulty in establishing if the substance measured was a contaminant or otherwise.

An accurate measurement has been defined [176] as a precise numerical value that is free of, or corrected for, all systematic errors. In order to attain such a result, all aspects of sample collection, storage, extraction, concentration, isolation, identification, and quantitation must be examined. Lewis [177] has discussed some of these problems with special emphasis on trace organic analysis.

The correct choice of sampling method to ensure a respresentative sample depends on factors such as representative volumes, times and avoidance of contamination by the sample collection and analysis method. Each succeeding step should be undertaken in the shortest practical time, however if storage is necessary a

temperature of 0 deg.C or less should be chosen to minimise effects of photo- decomposition, microbiological action, and chemical interaction between components and container [178].

During the extraction of volatile components from air and water, contamination and losses may occur from a number of sources; solvents and solid extraction systems contain impurities, and extraction efficiencies are often considerably less than and extraction efficiencies are often 100 percent, especially where a wide range of compound types are involved. If a solvent extraction procedure is employed the components in the solvent may require concentration prior to analysis. Loss of volatile components and reaction of labile compounds often occurs as a result of this step. The use of Kuderna-Danish concentrator [179] can help to minimise the loss of volatiles provided care is taken in heating and the choice of solvent. Concentration to approximately 50 microlitres is possible with a micro-Kuderna-Danish concentrator. XAD and Tenax resins are also used to concentrate components as outlined previously, however volatile losses may also be significant using this technique and should be monitored where possible.

Problems with isolation of individual components involving rearrangements, irreversible adsorption, decomposition and incomplete separation are common to chromatographic and MS methods. Optimisation of instrumental parameters and correct choice of technique for the sample type will help to minimise many of the effects mentioned.

Identification of a component by comparison with properties of a previously measured known compound may be extremely difficult where complex mixtures of trace organic materials are to be analysed e.g. drug, food and plant and pesticide breakdown products. Pure standards for these compounds are often not available to allow addition techniques to be employed for positive identification.

Combined GC/MS systems employing internal standards incorporating carbon 14 have been extensively utilised [180] as an internal quality control system. Addition of an isotope labelled labelled compound is an effective method for the determination of losses of components during subsequent extraction, concentration and isolation steps. Isotope labelling cannot, however, be undertaken for each component in a complex mixture and differences in chemical nature between compounds can cause variations in recoveries. One compound of each class likely to be present should be selected to check on recoveries through the system.

A variety of methods have been employed to assess accuracy in trace organic analysis [178]. These include collaborative laboratory studies, analysis of spiked samples and inter-laboratory comparisons [181]. Many of these studies have shown the need for more extensive in-laboratory quality control checks, and the necessity for the development of a wide range of appropriate Standard Reference Materials [182].

CHAPTER III

DEVELOPMENT OF A SAMPLING SYSTEM FOR VOLATILE ORGANIC MIXTURES.

Introduction.

A simple method of sampling volatile compounds from a variety of sources is required in many applied areas of chemistry. The detection and analysis for example, of volatile solvents in paint spraying industries, odour tracing in environmental problem areas, and plant volatiles for the perfume and flavour indistries are some typical examples where the use of a rapid routine method of collection and analysis of volatile compounds would be of advantage.

Ideally a sampling system should be capable of trapping quantitatively and reproducably a wide range of chemical compounds in sufficient quantity to give an accurate analytical assessment. The trapping method should not degrade or alter the collected components on collection, storage or elution. The above properties of a trapping system are often difficult to effectively check, particularly in the case of complex mixture trapping. Upon adsorption, there is a possibility of chemical reaction between the components trapped, due to the higher concentration in the medium, with other species and also with the trapping medium.

investigation of the available information in the literature was made in order to select the adsorbants with the most favourable characteristics. An outline of this literature search is provided in the previous chapter. A number of different sample collection and elution methods were selected, tried and some rejected, as described in the following pages.

A. Selection of a Sample Adsorption Medium.

(i) Carbon.

The efficiency of carbon as a trapping material in the form of 25mg charcoal disks, as demonstrated by Grob [21], prompted the investigation of this material as a trapping medium for the collection of organics from ambient and contaminated air. Difficulties encountered involved the manufacture of a consistant porous charcoal filter that was mechanically rigid enough to withstand the force of the air passing through the structure. The original commercial disks as described by Grob were not readily available. Various modifications of a dye press were tried and varying amounts of heat were applied to the carbon in order to obtain a consistant useable product - without a great deal of success.

Crushed granular carbon (activated charcoal) from B.D.H. Ltd. U.K., "Special for Gas Adsorption", of two screen sizes was cleaned by Soxhlet extraction with methanol and dichloromethane as solvents. Each size fraction was packed into 9mm diameter by 95mm long glass tubes with a B10 cone at one end and held in position by glass wool plugs at the ends. Material similar to this is extensively utilised for removing organics from air in gas masks[190].

Recovery checks on a range of compounds yielded the information in Table III. The test compounds were introduced into a flowing nitrogen carrier gas stream by

controlled addition using a Waters HPLC pump feeding into a mixing vessel. The liquid sample flow rate in conjunction with the gas flow rate was adjusted to give a concentration of 100 ppm (Figure VI).

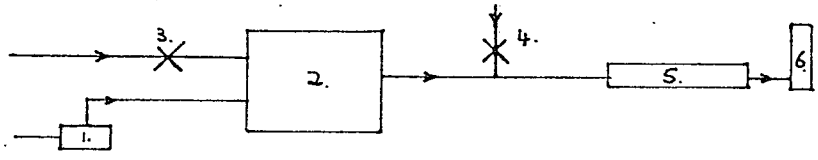

Figure VI. Flow Diagram of Recovery Test Apparatus.

1. HPLC pump.
2. Thermostated mixing vessel.
3. Carrier gas inlet valve and flowmeter.
4. Bleed valve and flowmeter.
5. Sample trap.
6. F.I. detector.

	Size Fraction	
	-10+20 Mesh	-200+250 Mesh
Pentane	95	98
Hexane	96	96
Acetone	85	92
Methanol	92	93
Ethanol	83	87
Benzene	82	86
Ethyl acetate	78	68
Carbon tetrachloride	83	86
Diethylamine	64	58

Table III. Percentage Recovery Test Activated Charcoal Adsorbent. Test Compounds at a Concentration of 100ppm.

The flame ionisation detector of the GC was used to determine the breakthrough of the test compound and the sample tube was then removed for solvent extraction and recovery. A second recovery check was made by adding one microliter of the steam distillate of Pinus radiata to the top of the column and washing in with 500 microliters of

carbon disulphide. Extraction from the activated charcoal was accomplished by refluxing 5mL of carbon disulphide using a cold finger apparatus as shown in Figure VI. The small volume refluxing through the trap reduced the concentration of the impurities upon solvent reduction in the micro Snyder distillation (Figure VII). An internal standard of n-decane was added to the carbon disulphide at the completion of the extraction to enable allowances for some of the losses likely to take place during the solvent reduction step in the concentration apparatus.

Recovery of the lower molecular weight components of the test compounds was quite acceptable but losses of higher molecular weight components, especially oxygenated terpenes of the radiata pine oil, was unacceptable. For this reason the use of activated charcoal was not continued.

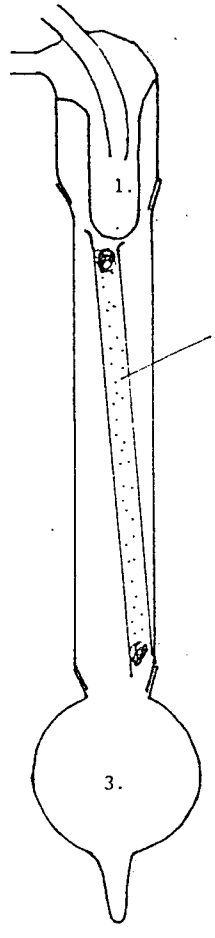

Figure VIIa. Micro Reflux Apparatus.

1. Cold Finger.
2. Sample Tube.
3. Solvent Flask (10mL).

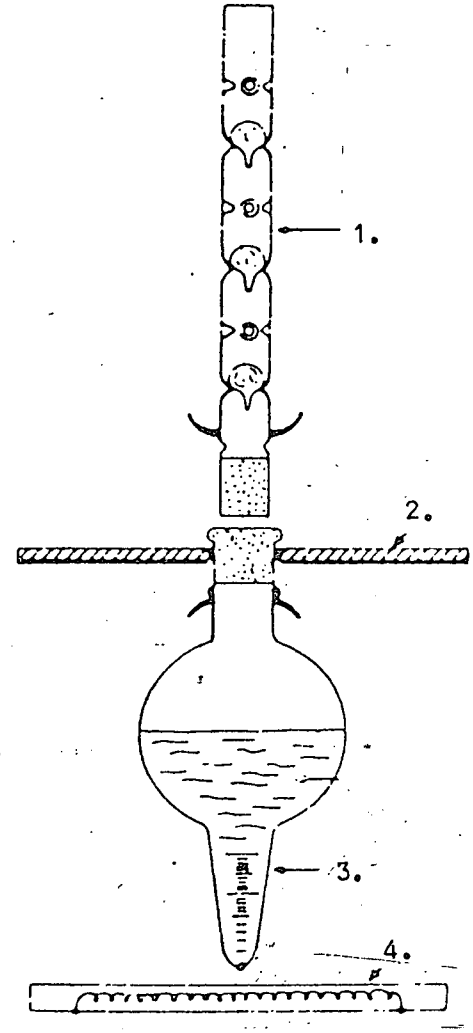

Figure VIIb. Snyder Concentration Apparatus.

1. Snyder Distillation Column.
2. Heat Shield Covered With Al Foil.
3. Graduated and Calibrated Taper.
4. Hot Plate.

ii) Tenax GC

Tenax-GC has been widely utilised for the concentration of trace organic compounds in air as described in the previous chapter. Tenax (poly-p-2,4-diphenylphenylenoxide) has the structure shown in Figure VIII and the manufacturers claim it is stable up to temperatures of 350 deg.C.

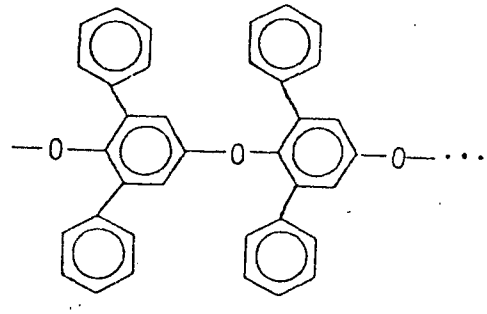

Figure VIII. Chemical Structure of Tenax GC.

The thermal stability and hydrophobic nature of the material coupled with the ability to trap a wide range of organic compounds would appear to make Tenax a favourable choice as an adsorbant.

Tenax was prepared by conditioning overnight at 325 deg.C in a wide bore glass tube in a stream of high purity nitrogen. The packing was stored in capped glass containers prior to packing in sample tubes and then reconditioned at 275 deg.C before use.

Recovery Checks. Pellizzari et al [63], have recorded the breakthrough volumes of a number of volatile organic compounds. Checks were made on many of the figures presented using a 4mm internal diameter by 170mm long glass tube packed with Tenax (Table IV). The results shown were

calculated back to 2.15g of Tenax for comparison [187]. There was substantial agreement for all compounds except acrolein. Apparatus used for the test was similar to that of Figure V.

Compound	Breakthrough Volume (L)* 2.15g Tenax	2.87g Tenax	Lab. Comparison
Acrolein	9	13	3
Propylene oxide	15	20	15
Diethyl sulfate	19	25	18
Trichloroethylene	50	-	52
Nitromethane	86	114	87
Glycidaldehyde	147	195	-
Chlorobenzene	300	-	310
B-propiolactone	330	440	-
Bis-(chloromethyl)ether	400	530	-
Butadiene diepoxide	646	860	-
Cyclohexene oxide	1,040	1,380	1,100
N-nitrosodiethylamine	1,220	1,620	1,200
Aniline	2,100	2,800	2,250
Ethyl methanesulfonate	2,420	3,220	-
Styrene oxide	7,550	10,000	7,600
Acetophenone	2,880	3,380	2,850

*Volume required to elute one-half of adsorbed vapour at 25 deg.C.

Table IV. Breakthrough Volumes for Several Highly Volatile Compounds on Tenax GC (40/60 Mesh) Cartridges

Janak [188] and other authors, have confirmed the negligible influence of water vapour on the trapping and elution efficiency of Tenax. Tests conducted in this laboratory at 50% and 70% humidity levels, using steam distillate of Pinus radiata bark oil, showed no alteration of trapping and recovery efficiency.

B. Development of Sample Collection and Desorption Equipment.

i) Sample Collection

Optimum sample collection efficiency is dependent on factors such as gas flow rate, rate of diffusion of sorbate into the pores, particle size and shape, bed geometry, porosity and temperature [187]. The geometry of the sample collection tube was limited by mechanical aspects of the desorption apparatus as well as theoretical considerations.

The equipment used to collect volatile organics from air samples consisted of:- 1. a Pyrex glass or metal tube packed centrally with 40-60 mesh Tenax held in position with silanised glass wool. The weight of Tenax per sample tube was 0.40g. 2. A calibrated flowmeter measured the rate of gas passing through the sample tube. 3. An electrically driven diaphragm pump was used to draw the gas through the system (Figure IX).

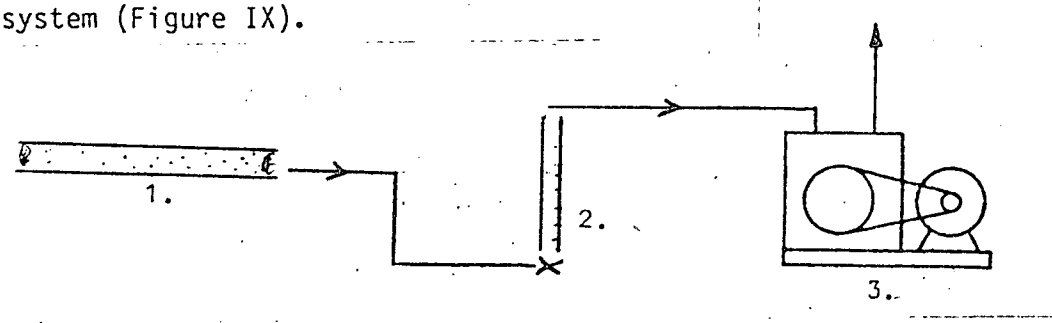

Figure IX. Flow Diagram of Apparatus for Sampling of Volatile Organic Compounds.
1. Glass Tenax trap. 2. Calibrated Flowmeter.
3. Diaphragm pump.

Flow rate for sample collection was 30-50 mL per minute and the temperature of the sample tube was maintained at or below 20 deg.C (by a water cooled jacket if required).

ii) Sample Desorption

The requirements for thermal desorption and injection of the sample into a GC include quantitative removal of the sample from the collection medium, and rapid injection of the vapour into the inlet of the GC without bleed during secondary trapping.

A trapping system described by Houghton [189] and illustrated in Figure X, was constructed with some modifications. A luer adapter was silver soldered onto a 6mm Swagelock fitting to allow the connection of a syringe needle to the metal sample tube using a compression Graphlok seal. The equipment consists of a heating coil mounted on two metal formers with a gap between to allow the insertion of hot or cold metal probes [190].

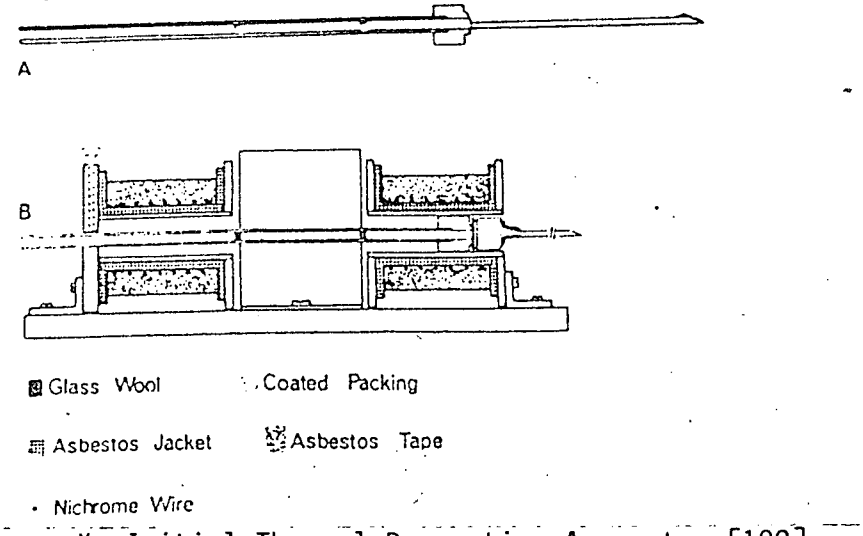

Figure X. Initial Thermal Desorption Apparatus [190]. (A) Stainless-steel collection tube; (B) cross section of the collection-tube heater with tube in position.

The sample tube was partially inserted into the apparatus and a syringe needle attached and inserted into

the septum of the GC. The carrier gas line was attached by a second Swagelok fitting to the other end of the sample trap. Heat was applied to the tube by the passage of an electric current through the heater windings and the application of a liquid nitrogen cooled trap prevented the passage of the components into the GC. When the system reached a steady temperature of 200 deg.C the cold probe was removed and a hot probe placed in the same position. The carrier gas from the GC at the same time being diverted through the sample tube to flush the components into the GC.

The system was found to function efficiently for a single component in air samples and was very good for isolating single peaks from a GC run. (This was accomplished using a heated column switching valve to divert the carrier gas flow from the FID to the trap at the expected elution time of the peak. A component collected in this manner could be reinjected into the GC onto a different column to check for purity.) Problems were encountered however, with complex mixtures of components with similar boiling points giving rise to overlapping peaks and poor recoveries (Figure XI). The trace is of a sample taken from an organic teaching store exhaust air stream.

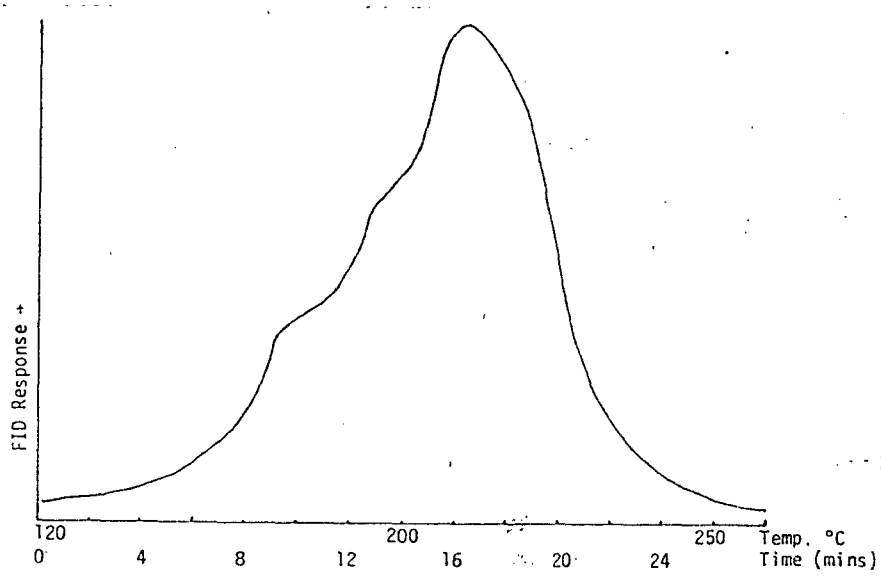

Figure XI. GC Trace of Trapped and Injected Volatile Organic Compounds in Air (2m OV101 GC Column, 120-260 deg. C at 5 deg./min. Air Sampled 1.96L 20 deg. C)

The problem with the technique appeared to be the inefficient transfer of heat to the sample tube resulting in lack of resolution on the analytical column. A variety of columns, including capillary columns, were used but with no major improvement in resolving power.

Redesign of the system to give better heat transfer and improved cold trapping appeared to be necessary. The heating block was constructed to enable continuous desorption of the organic compounds as heat was applied, and flushing of the components by the carrier gas stream to a cold trap directly immersed in liquid nitrogen.

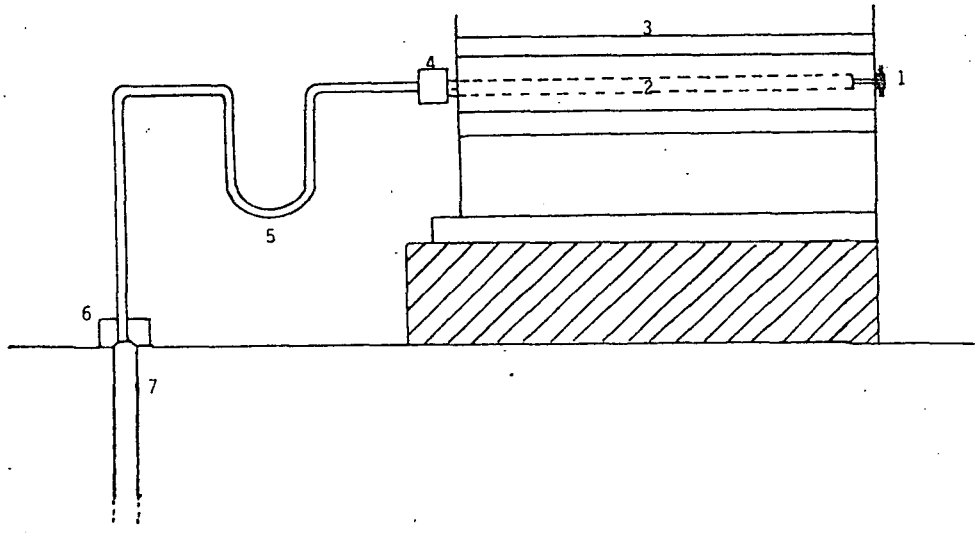

Figure XII. Thermal Desorption and Injection Apparatus.

1. 2mm Swagelock Fitting - carrier gas inlet.
2. Tenax Sample Tube.
3. Resistance Wire Round S. Steel Heating Block.
4. 6mm Swagelock Coupling and Electrical Connector.
5. 3mm GLT.
6. Electrical Connector and Coupling to GC inlet.
7. GC Column.

A diagram of the equipment is shown in Figure XII. The apparatus consists of a 25mm diameter stainless steel cylinder (2), drilled through the centre to accept a 170mm by 6mm sample collection tube, and off-center to accept a thermocouple probe. The metal cylinder was covered with a heating element consisting of 7.2m of 1.779 ohm/m in a single layer of No. 20 gauge B. and S. resistance wire wound over mica. Carrier gas tubing was connected to the 2mm coupling at one end of the heater block (1), and the Tenax sample tube was inserted into the other end of the block through a drilled out 6mm Swagelock fitting silver soldered

to the stainless steel. Gas sealing by a Graphlok ferrule (4), also prevented the tube from being ejected as did the coupling of the 3mm diamter glass lined metal U tube (5). At each end of the U tube brass lugs were attached to provide electrical connections for coupling to a welding transformer. A number of different configurations of glass lined metal U tube were manufactured, the use depending upon the configuration of the inlet system of the GC or GC/MS unit. A horizontal version with a luer fitting and a 20 guage needle was frequently used. The system illustrated shows the 3mm glass lined tubing (GLT) coupled directly to a piece of 6mm GLT inserted into the inlet heater of the GC/MS.

Cooling of the U tube involved placement of a small insulated vessel filled with liquid nitrogen under the U section of the tube. The apparatus was then coupled to the carrier gas flow and the system purged of air for a few minutes at a low flow rate. Optimum carrier gas flow adjustments could be undertaken when the system was connected to the GC inlet and then heating of the block could commence. A power supply of 50V from a variable voltage transformer enabled the heating block to reach a temperature of 200 deg.C within 6 minutes. A chromel-alumel thermocouple inserted into the stainless steel block was used to monitor the desorption temperature. Thermal elution times of 6 to 10 minutes proved to be adequate for most of the volatile air samples trapped using Tenax. The carrier gas transported the desorbed organics to the U tube section

of GLT where secondary trapping (condensation) concentrated the material.

Rapid injection of the organic mixture onto the GC column involved resistance heating of the 3mm GLT by connecting the secondary output from a welding transformer across the two lugs, at points 5 and 6, immediately after the removal of the liquid nitrogen bath. A current setting of 40A applied for 30 seconds rapidly heated the GLT to a maximum temperature of 300 deg.C, at a rate that ensured breakage of the tubing did not occur.

Following a number of field trials, where mechanical breakage of glass sample trap tubes had occured, the decision was made to replace the glass with glass lined stainless steel tubing of the same dimensions. The added mechanical strength of the GLT also was an advantage in the desorption apparatus where coupling of the 3mm U tube to the desorption system had often placed an unacceptable degree of strain on the glass tube. Heat transfer to the packing from the heating block was also improved.

The redesign of the thermal desorption equipment, as outlined above, improved the quality of the traces obtained from the GC and GC/MS runs and enabled use of the method for routine sampling of volatile mixtures in a number of areas that would not have been possible using previously available techniques.

C. Blank Determinations and Sample Trap Storage.

Introduction.

An important aspect of the sampling of trace volatile organic compounds is the requirement to reduce the risk of contamination of the collected sample. Contamination may occur in a number of ways; from degradation of the collecting material, from breakdown of the collected components so that there is no resemblance to the original sample; or, the ingress of chemicals, such as solvent vapours, from the handling or laboratory.

A number of instances occurred, in the course of the investigations that are documented in the following pages, where solvents such as chloroform and 'Freon' were detected in collected air samples that should have been free of such components. The steps that were followed to reduce the contamination that tended to result from working in a general purpose organic laboratory are described.

Experimental.

Tests were conducted on the desorption efficiency at 250 deg.C and 300 deg.C on portions of Tenax that had been previously used for trapping terpene volatiles. One tube was initially conditioned at 250 deg.C for 60 minutes in a stream of high purity nitrogen, and the other was conditioned at 300 deg.C under similar conditions. Each sample tube was then placed in the stainless steel desorption block at 250 deg.C and 300 deg.C respectively for

ten minutes and the eluted 'blank' run through the GC/MS system. An OV101 WCOT 50m silica column was used to separate the components prior to entry into the MS system. The GC/MS conditions are set out below:

Figure numbers XIII, XIV.

Carrier gas - hydrogen at 1.5 mL/min
Temperature range 50-220 deg.C
4 deg./min to scan 350 then 8 deg/min
Vacuum 10^{-6} Torr.

The mass spectrometer system was adjusted to a relatively high sensitivity range and calibrated to scan from 0-350 mass units. The total ion current traces are shown in Figures XIII, XIV. The components are listed in Tables V and VI, the corresponding total ion current traces are shown in Figures XIII and XIV.

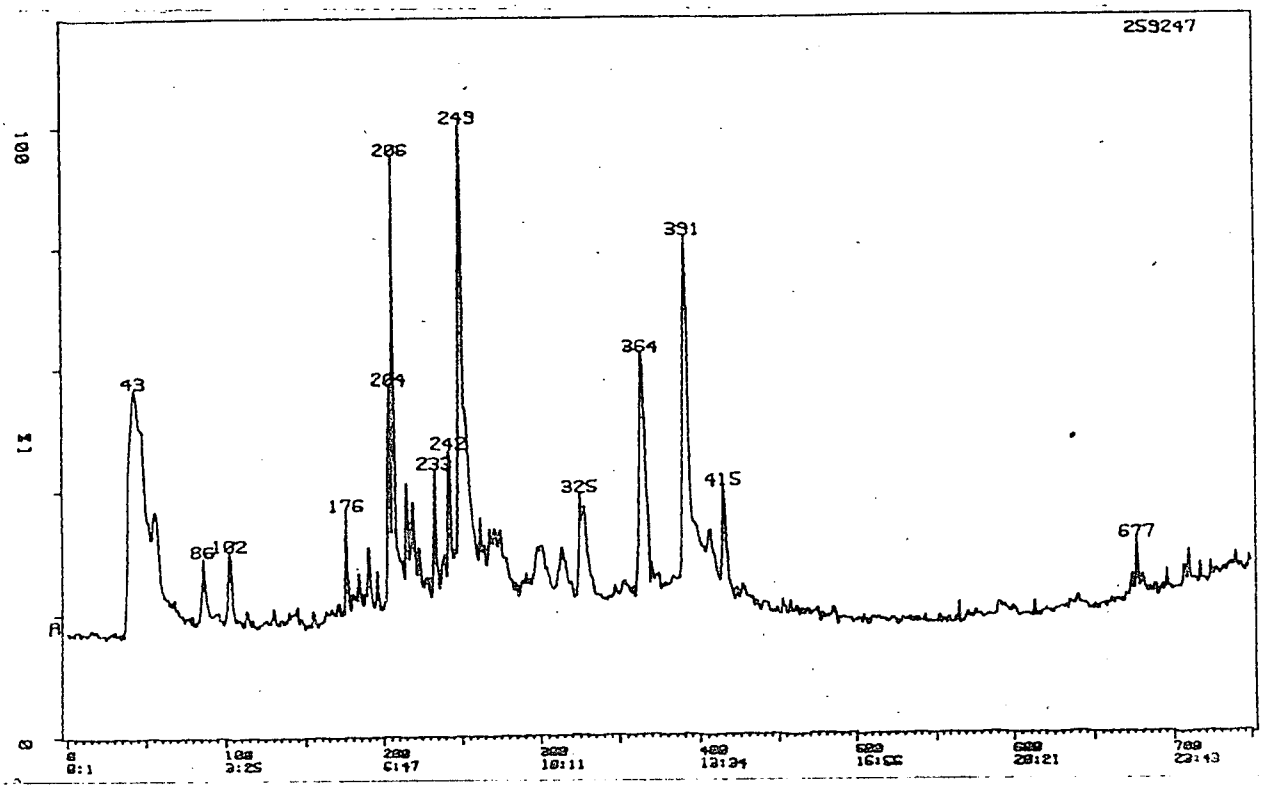

Figure XIII. Total Ion Current Trace Tenax Sample Tube Conditioned at 250 deg. C.

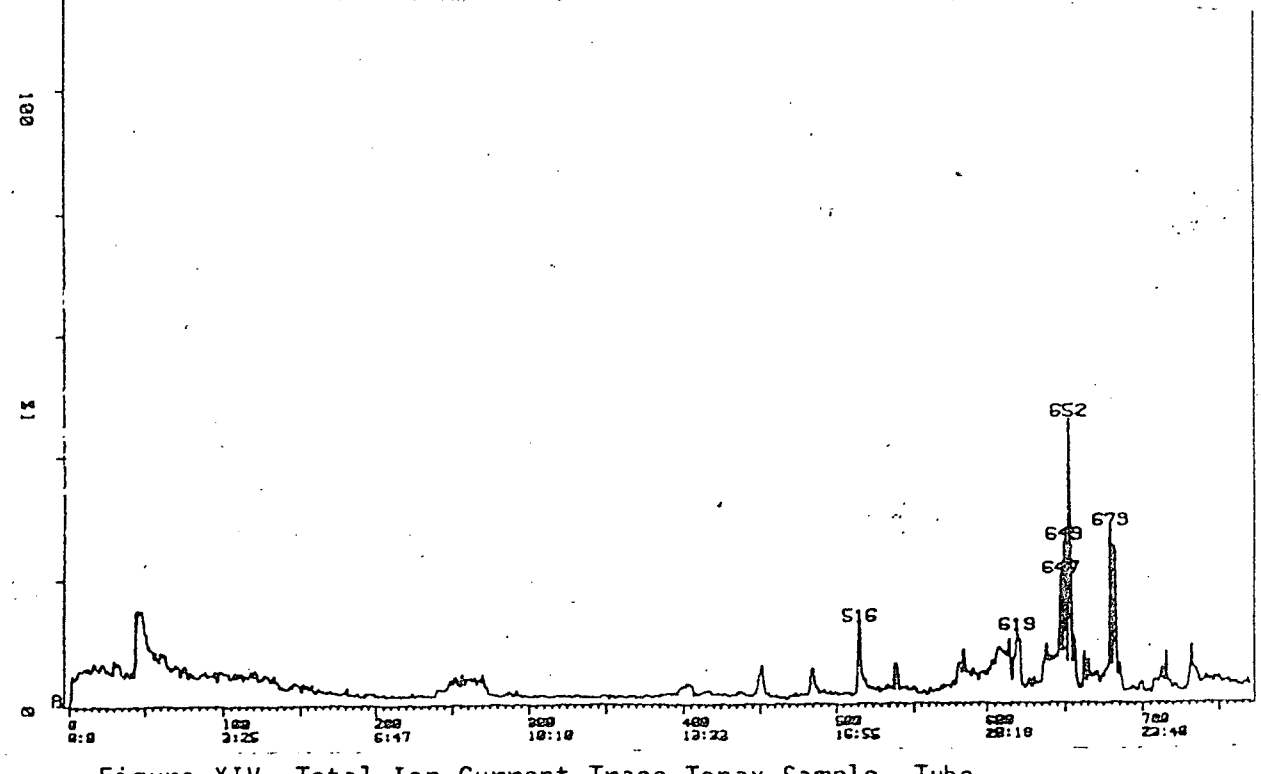

Figure XIV. Total Ion Current Trace Tenax Sample Tube Conditioned at 300 deg. C.

Scan No.	Component
43	carbon dioxide
44	carbon dioxide plus unknown HC M. Wt 96
86	toluene
102	chloroethylene
176	monoterpene
204	monoterpene
206	monoterpene
215	trimethyl benzene isomer
229	monoterpene
242	monoterpene M. Wt 134
249	monoterpene M. Wt 136
253	monoterpene
272	monoterpene
301	unknown
314	hydrocarbon
327	undecane - C11 hydrocarbon
364	menthofuran M. Wt 150
391	myrtenal
406	unknown - possibly a terpene
415	dodecane M. Wt 170

Table V. Compounds Eluted from Tenax Sample Tube Conditioned at 250 deg.C.

Scan No.	Component
44	carbon dioxide
249-270	unresolved mixture of trace quantities of unknown mixture
451	unsaturated C10 aldehyde
516	decenal
539-585	unknown mixture
598	trimethyl naphthalene
619	unknown mixture containing one branched HC
647	unknown ketone
649	heptadecene M. Wt 238
652	heptadecane M. Wt 240
655	branched HC - weak parent ion
679	octadecene M. Wt 252
682	octadecane M. Wt 254
712	nonadecane? or ecosane?
732	palmitic acid (carboxylid acid peaks 60 & 73)

Table VI. Compounds Eluted from Tenax Sample Tube Conditioned at 300 deg.C.

Discussion.

The results indicate that quantitative desorption does not occur when the Tenax sample tube is heated to 250 deg.C for trapped terpene components. The traces obtained indicate that either a higher conditioning temperature, or, a longer conditioning time is required to reduce the blank contamination carry over level. Higher desorption temperatures should improve the initial recovery percentage, simultaneously reducing the conditioning required provided that unacceptable levels of thermal breakdown products are not generated. Desorption temperatures of 270 deg.C and 290 deg.C were used by Pellizzari [56] and Bertsch [19] for recovery of components adsorbed onto Tenax.

A paper by a research group of the U.S. Air Force [192] lists benzene as a major thermal breakdown product of Tenax and as a result use a conditioning and desorption temperature of 240 deg.C. The trace at 300 deg.C (Figure XIV) did not show any measurable quantity of benzene, this would appear to contradict the work of the above authors who claimed that the quantity of benzene trapped was directly related to the conditioning temperature in excess of 250 deg.C. Tenax used in all the traps packed had previously been conditioned in this laboratory at 325 deg.C under a stream of high purity nitrogen for twelve hours. Treatment at this temperature removed any loosely bound or unreacted solvents and decreased the tendency to form voids in the sample tubes. Glass Tenax analytical GC columns showed a

tendency to form large visible voids unless the packing was preconditioned in the above manner. Presumably the above authors did not precondition at a temperature higher than 240 deg.C and this may account for the continual loss of benzene. At a desorption temperature of 240 deg.C quantitation of components would also be somewhat difficult, unless, a range of internal standards was added to the original sample to enable collection efficiencies to be calculated.

Conclusions.

Air sampling of volatile organic compounds by the use of a Tenax sample tube should be undertaken with due regard to the possible effects of conditioning temperature and time. Care should be exercised in the initial preconditioning of the packing material. A blank run should be conducted on the tube prior to dispatch to the sampling area and a similar blank tube should accompany the sample tubes. Sample tubes should be stored individually in glass stoppered carrying containers with a small quantity of dried silica gel. Where possible Tenax sample tubes should be allocated to one particular sample type; i.e. one set of tubes for ambient air monitoring, one set for volatile terpenes etc.

The use of glass lined metal tubing for Tenax sample tubes provides the mechanical strength of steel with the inert properties of glass and has proved most satisfactory

for field sampling. The procedure adopted to reduce cross contamination of sample collection tubes involved the following: the GLT was baked in a furnace at 600 deg.C, packed with the preconditioned Tenax, and reconditioned at 300 deg.C immediately before despatch to the sampling point in glass stoppered tubes. The sample trap could be stored for up to two weeks in a cool room without loss of sample, however processing was generally undertaken as soon as possible following collection of the sample.

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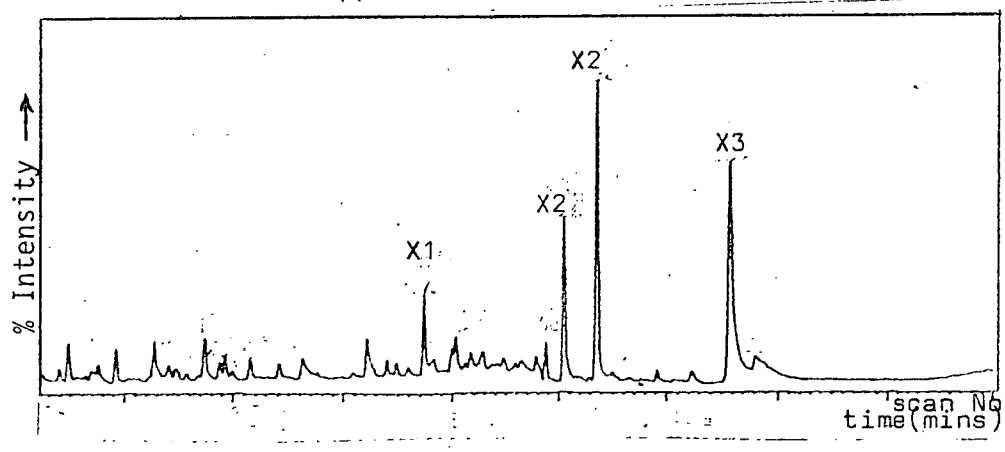
Note. Interpretation of MS total ion current trace. The information from the ion current scans is stored in the data system and the output intensity is calculated relative to 100 percent of the highest peak - unless overloading occurs. The output trace is percentage intensity (vertical axis) vs scan number with time in decimal minutes printed below (horizontal axis). Prominant peaks are labelled with the respective scan numbers (X1,X2,etc). Details of the MS equipment used are provided in Table VII, and in the appendix.



Explanatory Diagram of MS Total Ion Current Trace.

CHAPTER IV

AN EXPERIMENTAL COMPARISON OF VOLATILE ORGANIC SAMPLING TECHNIQUES.

Introduction.

Exposure to mixtures of volatile organic components has become an accepted part of normal living experiences and little attention is paid to various odours unless they are particularly obnoxious or dangerous. Irritant effects at low concentration in the air of working environments can be tolerated with some compounds but not with others.

Assistance with the qualitative determination of an irritant that was present in the atmosphere surrounding a furnace was requested from industry. The persistant, mildly lachrimatory, eye irritant nature of the substance made working conditions in the vicinity of the furnace particularly unpleasant. Conventional methods of detecting the compound type, i.e. by use of commercially available gas detection equipment (Draager Tubes etc.) had failed.

This request provided an ideal case study to compare four different sampling and concentration techniques:-

a) Direct gas sample collection in a Teflon bag

b) Solvent adsorption

c) Cryogenic trapping

d) Tenax sample tube adsorption.

A. Experimental

The furnace consisted of a rotating steel drum heated to 180 deg.C by a liquified petroleum gas flame. Modifications had been made to the burner upon the recent installation of the unit. Heat loss from the gas flame was minimised by three different types of thermal insulation that were placed on the inside of the support structure adjacent to the flame area. Hot air from the flame jet rose around the outside of the rotating furnace and was conveyed by a duct to the outside of the building. Round the front of the rotating drum of the furnace was a rubber flap to minimise heat loss, however, a certain amount of hot gas escaped at this point and thus carried quantities of the irritating component into the atmosphere of the room. (Figure XVa) Considerable discomfort caused by irritation of the face skin, and lachimatory action to the eyes, occured whilst sampling the hot gas stream. The effect was somewhat similar to that of low concentrations of acetyl chloride.

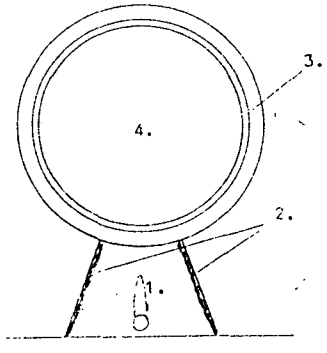


Figure XVa. Front Elevation of Furnace.

1.Gas Flame 2.Glass Fiber Insulation
3.Rubber Seal 4.Rotating Cylinder

i) Sampling

All glassware used was cleaned by washing with detergent, rinsed with distilled water and then heated to 600 deg.C in a furnace. The solvent used was redistilled AR dichloromethane, and where direct adsorption was not possible Teflon tubing was used to convey the gases.

a) Direct Gas Sampling

Gases escaping through the top of the rubber seal round the drum of the furnace were sampled directly into a 300 x 300 mm Teflon gas ample bag and the bag sealed with a Teflon faced septum. This was accomplished by placing the empty Teflon bag into a 20L plastic barrel with the inlet of the bag projecting through the lid of the barrel. Air was withdrawn from the barrel. The resulting decrease in pressure expanded the bag inside the barrel and allowed the collection of several litres of sample.

b) Solvent Adsorption

A Venturi water pump was used to draw the sample gases through two Dreschel bottles in series containing a total of 200mL of the dichloromethane solvent. The Dreschel bottles were immersed in a water-ice mixture to prevent rapid loss of the solvent due to evaporation, and gases were ducted to the system via Teflon tubing. The flow rate was 30L per hour and sampling continued for two hours.

c) Cryogenic Trapping

A sample of the gas mixture was drawn through a glass U tube immersed in liquid nitrogen within a Dewar flask to condense volatile material. The U tube was washed out with dichloromethane at frequent intervals to ensure that as much as possible of the condensed organic material was retained. The volume of gas mixture sampled was 20L. Problems encountered included frequent ice buildup in the U tube resulting in blockage of the flow line, and the difficulty of disconnecting and reconnecting tubing that was rigid at the low temperature.

d) Tenax Sample Tube

Gases emanating from the furnace were at a temperature in excess of one hundred degrees, therefore, in order to retain volatile components on the Tenax sample tube, a method of cooling was required. This was accomplished by inserting the sample collecting tube into a water jacketed length of 8mm diamter copper tube surrounded by a cooling water jacket (Figure XVb). The temperature of the glass Tenax tube was therefore maintained at less than twenty degrees enabling the adsorption of low boiling point components. The sample tube was held in position by a 6mm Swagelok fitting silver soldered onto the end of the copper tube.

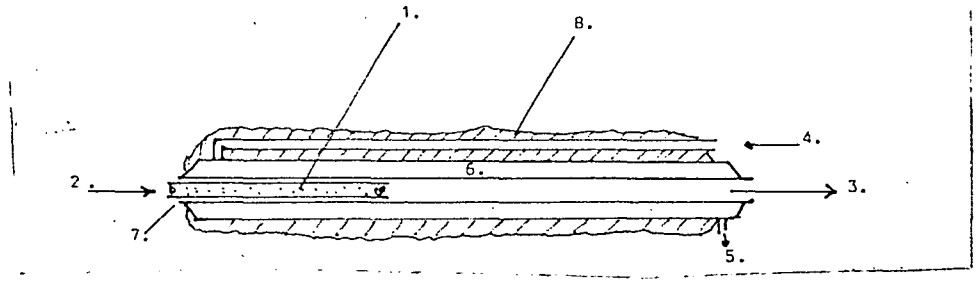


Figure XVb. Water Cooled Sample Collection Probe (Cross-section).

1. Tenax sample tube.
2. Hot gaseous sample in.
3. Cooled gas out.
4. Cooling water inlet.
5. Cooling water outlet.
6. Cooling water jacket.
7. 6mm Swagelok coupling.
8. Aluminium foil wrapped over fiber glass insulation.

The inlet of the Tenax sample tube, in the water cooled jacket, was suspended above the furnace adjacent to the rubber seal. A flow rate of 50mL per minute was maintained through the sample tube for two hours.

ii) Analytical results

Analytical work on the collected samples was undertaken using packed columns on the GC and capillary columns on the GC/MS runs. Sample pretreatment of the solvent collected samples consisted of careful evaporation under a controlled stream of high purity nitrogen gas at 30 deg.C.

a) Direct Gas Sampling

A 2.0mL portion of the gas sample was injected onto a packed GC column (3 percent Dexil 300 on 100-120 mesh Chromosorb W HP). A gas tight syringe was used to transfer the sample to the 2m column maintained isothermally at 50 deg.C. On maximum sensitivity only one minor multiple peak of retention time 0.50 seconds was noted. This was identified by GC/MS as air with a trace amount of propane.

b) Solvent Adsorption Sample

The 200mL volume of dichloromethane solvent was reduced to 100 microlitres by careful evaporation under a stream of dry nitrogen. Water traces were removed by passing the liquid through a small column of anhydrous sodium sulphate, and samples were stored in small volume glass vials with Teflon seals. An equivalent volume of the distilled dichloromethane was treated in a similar manner to provide a blank. Injection of 1.0 microlitre portions of sample onto the Dexil 300 packed column, described above, gave a GC trace with a large solvent peak with a number of shoulder peaks. Trace amounts of other compounds were observed, however the blank solvent run provided a very similar trace, indicating the presence of solvent impurities. A high resolution 55m OV101 SCOT column was installed in the GC mass spectrometer system to enable separation and, where possible, identification of the components. 0.5 microlitre of sample was injected onto the column in a Grob type injection at ambient temperature. Temperature programming was commenced at 50 deg.C. Details of operating conditions are set out in Table VII.

Gas chromatograph:	Pye series 204
Column:	OV101 SCOT 55m glass 0.5mm dia
Carried gas:	He at 1.0 mL/min.
Temperatures(deg.C):	Inlet 225, outlet 250, interface 250
Oven programme:	Ambient, then 50 deg. to 200 deg, 2 deg/min to scan 375 then 8 deg/min.
Mass Spectrometer:	VG Micromass 7070F Scan rate 1 per 2.5 seconds. Energy 70Ev.
Data System:	VG 2235 using a PDP 8/A620 minicomputer.

Table VII. GC/MS Operating Conditions

Identification was made by comparison of mass spectral data in the literature [193], and the library of authentic samples stored in the data system, and also on the basis of retention time data. Additional information was gained from the fact that OV101 is a relatively non-polar phase and separates most components on a boiling point basis. The trace obtained from the solvent run is shown in Figure XVI and the component identities in Table VIII.

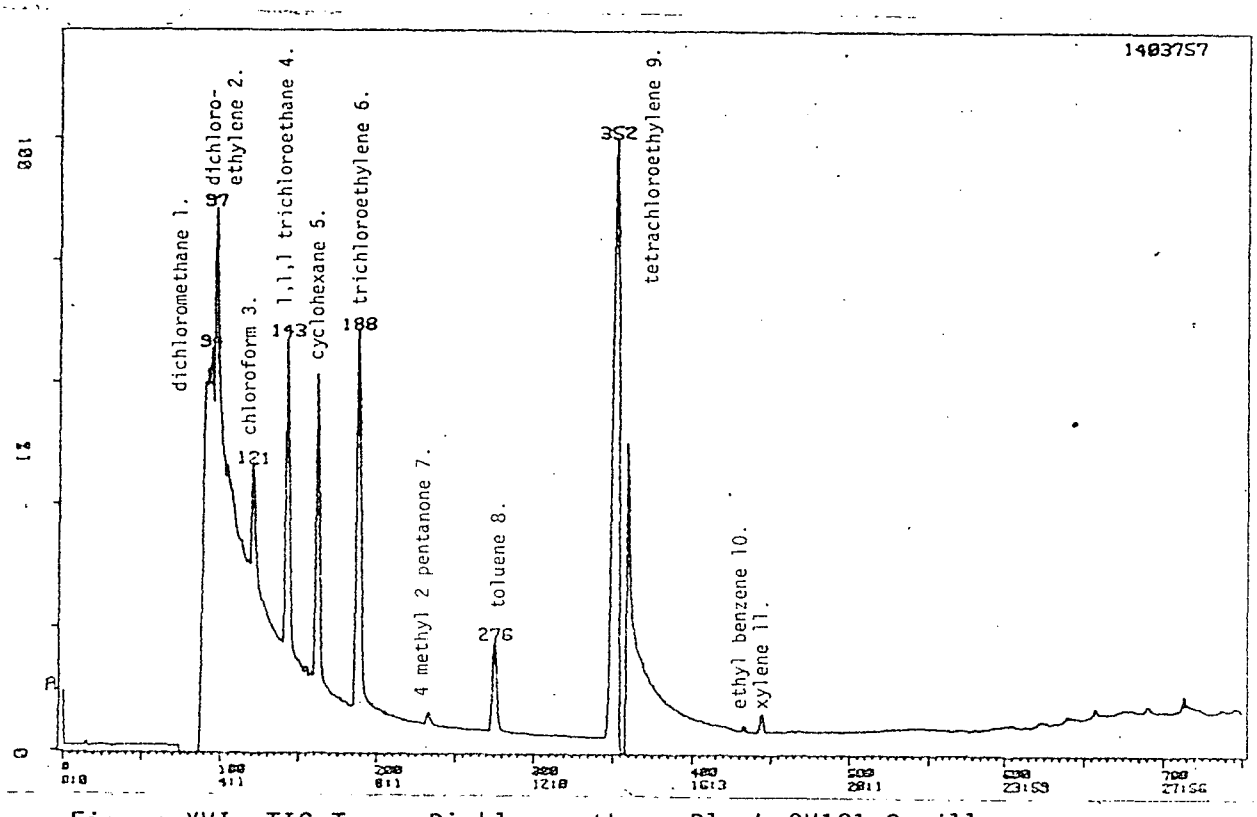


Figure XVI. TIC Trace Dichloromethane Blank OV101 Capillary Col. 50-200 deg. C. (Conditions as per Table VII.)

Peak No.	Scan No.	Identity
1	75-90	dichloromethane
2	97	dichloroethylene
3	121	chloroform
4	143	1,1,1 trichloroethane
5	162	cyclohexane
6	188	trichloroethylene
7	234	4 methyl 2 pentanone
8	276	toluene
9	352	tetrachloroethylene
10	432	ethyl benzene
11	444	xylene

Table VIII. Components Identified in Dichloromethane Solvent Blank

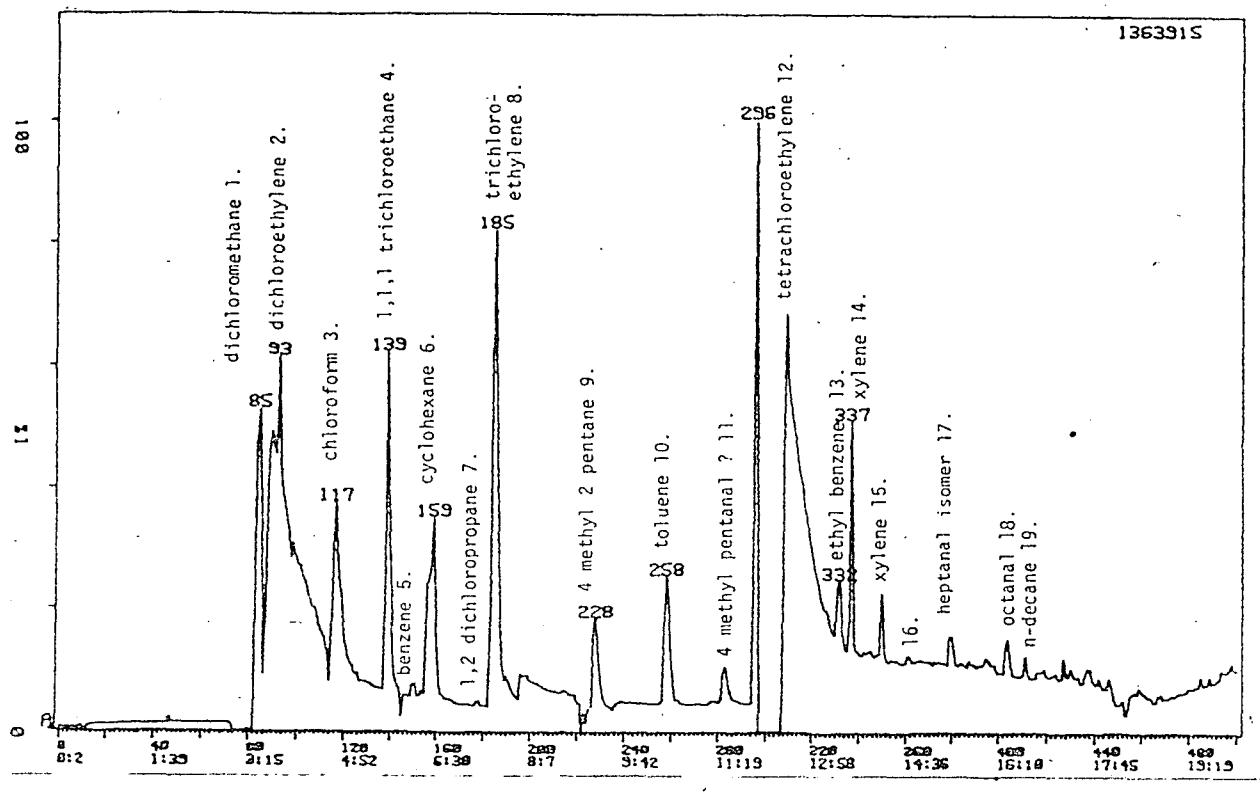


Figure XVII. TIC Trace of Solvent Trap Volatiles OV101
Capillary Col. Conditions as per Table VII.

Peak No.	Scan No.	Identity
1	74-88	dichloromethane*
2	93	dichloroethylene*
3	117	chloroform*
4	139	1,1,1 trichloroethane*
5	150	benzene
6	159	cyclohexane*
7	177	1,2 dichloropropane
8	185	trichloroethylene*
9	228	4 methyl 2 pentanone*
10	258	toluene*
11	284	4 methyl pentanal (?)
12	296	tetrachloroethylene*
13	332	ethyl benzene*
14	337	)
15	350	) O,m and p xylene*
16	362	)
17	378	heptanal isomer
18	404	octanal
19	411	n-decane

Table IX. Components Identified in Solvent Trap Concentrate.

Injection of the same quantity of sample from the

solvent trap under similar conditions gave the total ion current trace shown in Figure XVII. Initial oven temperature conditions caused a shortening of retention times and hence the peak scan numbers are not identical to those in Figure XVI. Components identified are shown in Table IX with peaks also found in the solvent marked with an asterisk *. High concentrations of dichloromethane and tetrachloroethylene caused overloading of the MS system and temporary shutdown of the beam as shown by the return of the trace to baseline.

c) Cryogenic Trap Sample

The dichloromethane washing from the cryogenic trap sample also contained a considerable amount of water, was passed through an anhydrous sodium sulphate column and then evaporated to 200 microlitres, as described above. The GC and total ion current traces were virtually identical to the dichloromethane solvent blank traces. No other compounds were detected.

d) Tenax Trap

The Tenax sample trap was removed from the stoppered glass carrying tube and placed into the thermal desorption apparatus, flushed with carrier gas and the system coupled to the GC/MS. A 10 minute thermal desorption time at 300 deg.C was used. The total ion current trace is shown in Figure XVIII the components are identified in Table X, and the mass spectra are listed in the appendix.

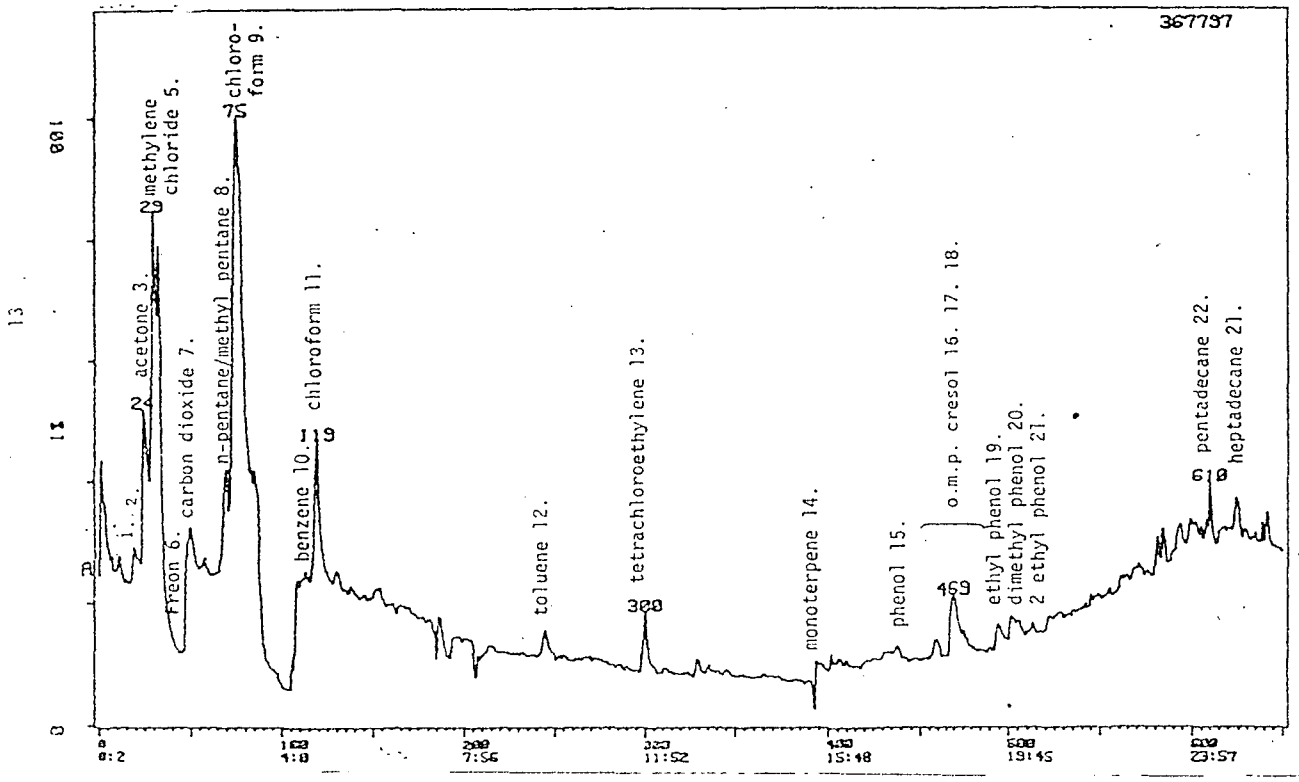


Figure XVIII. TIC Trace of Tenax Trap Volatiles .
Conditions as per Table VII.

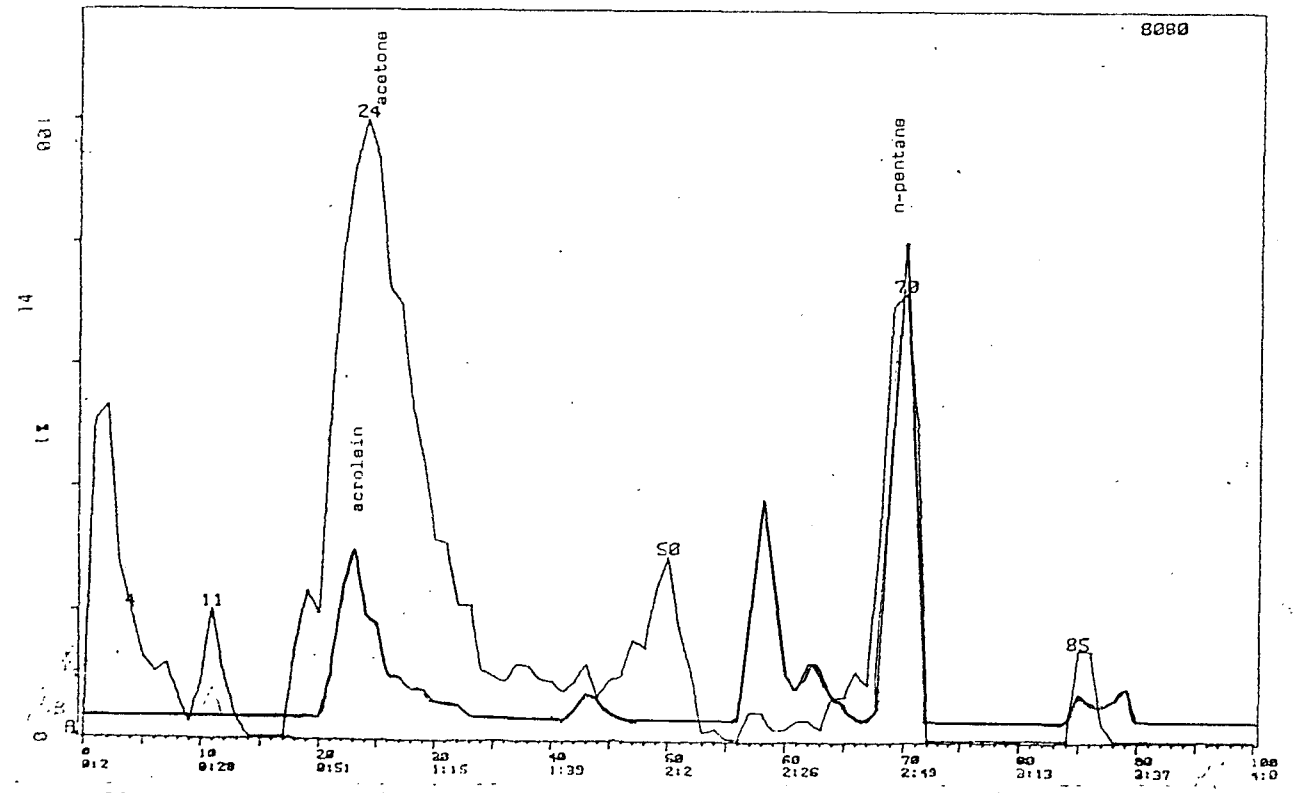


Figure XIXa. Specific Ion Traces of Tenax Trap Volatiles.
Scan Nos. 1-100 vs Intensity.
— Ion Intensity of Mass = 27
— Ion Intensity of Mass = 56

Peak No.	Scan No.	Identity
1	20	Hydrocarbon (pentadiene)
2	23	acrolein + pentadiene isomer + acetone
3	24	acetone
4	28	methylene chloride + acetone + unknown
5	29	methylene chloride
6	32	Freon
7	50	carbon dioxide
8	70	n-pentane + methyl pentane
9	75	chloroform
10	114	benzene
11	119	chloroform
12	245	toluene
13	302	tetrachloroethylene
14	402	unknown monoterpene
15	438	phenol
16	460	)
17	469	) o,m and p cresol
18	476	)
19	490	ethyl phenol
20	495	dimethyl phenol
21	502	2 ethyl phenol
22	610	pentadecane
23	642	unknown

Table X. Components Identified in Tenax Trap.

High concentrations of contamination adsorbed from the solvent traps tended to mask some of the earlier peaks, however, acrolein, acetone , a number of phenols and cresols were detected. A plot of the 27 and 56 mass ions in the first 100 scans shows the presence of a suspected acrolein peak in the early section of the trace - Figure XIXa. The characteristic ions 27 and 56 maximise at scan number 23 under the leading edge of the acetone peak, this information coupled with the coincident retention time of acrolein confirmed the presence of the substance.

B.Discussion.

The problems associated with the various trapping methods, as outlined in the literature sources, were shown to be considerable in this attempt at collecting a trace component in an industrial process. Solvent contamination and escape proved to influence each determination. Trapping efficiency of the unknown component in the direct headspace collection, the solvent trap, and the cryogenic trap, proved to be too low, or the losses during concentration too high, that instrumental methods failed to detect the substance. This was in spite of the fact that the substance was painfully obvious to the eyes and nose.

Components detected in the solvent trap extract could not account for the observed effects in the concentrations measured. The components present could be explained as either solvent impurities, products from the furnace or breakdown products of the insulation.

Acrolein (propenal), detected in the Tenax trap at a concentration of approximately 1 part per million, has a toxic dose level (TDL) OF 0.1 PPM [194], and the boiling point of 52.7 deg.C correlates with the elution from the GC column just prior to acetone (bp 56.2 deg.C). A small quantity of acrolein was manufactured synthetically and collected along with some of the industrially generated material. The two substances co-eluted from the GC column and gave identical mass spectra. (Figure XIXb.) The physiological effects of the synthetically produced acrolein

were identical to the gaseous product from the furnace; to this point some difficulty was experienced in convincing the industrial operators that the active constituent was present in relatively low concentrations.

A search was conducted of the stored spectra from the solvent and cryogenic trap runs but acrolein and several of the other low boiling components could not be detected. Apparently the evaporation of the solvent and the drying step has removed the lower boiling point components.

Literature sources describe a number of ways in which acrolein may be produced, from oxidation of petroleum gas [195], as a by-product from pyrolysis of paints and degreasing solutions and from the heating of plastic tubing, insulation and metal foil tape [196]. Two main sources of the acrolein would therefore appear possible.

i. from oxidation of the L.P. fuel gas
ii. from pyrolysis of the furnace construction/insulation material.

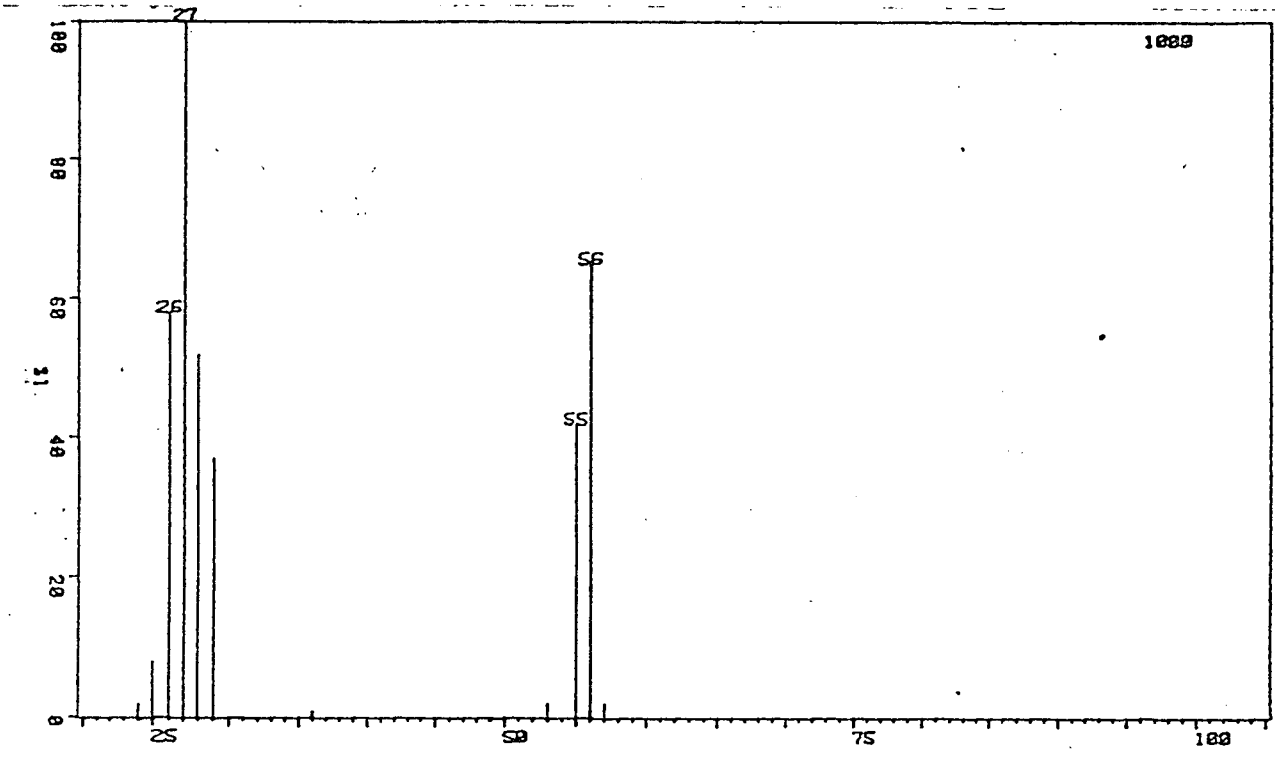


Figure XIXb. Mass Spectrum of Acrolein (propenal).

C.Summary and Conclusions.

Four trapping techniques were used in order to determine the nature of an air contaminant in the vicinity of an industrial furnace. Direct headspace injection provided little useful information as the ambient concentration of the contaminant was below the instrument detection level. Solvent trapping and cryogenic concentration did not provide sufficient quantity of the unknown contaminant, free from solvent interferences, to give positive identification. Major losses of the highly volatile unknown compound occurred during the removal of solvent and/or water, and this problem coupled with the low concentration present, made identification difficult with the more classical techniques.

Tenax trapping of the component from the air allowed qualitative and approximate quantitative determination of acrolein in the hot gas stream from the furnace. Acrolein was confirmed using a synthetically produced compound as a comparison. Follow-up work using the more polar Chromosorb 104 as a trapping medium also confirmed the presence of acrolein at the 1ppm level.

The source of the acrolein was either:

i) incorrect combustion conditions of the L.P. flame.
ii) a pyrolysis by-product of the furnace construction/ insulation material.

CHAPTER V.

VOLATILE COMPONENTS OF SOME NATIVE PLANTS.

Introduction.

A need exists to examine systematically the chemical composition of the essential oils of Australian native plants. Work on the Eucalyptus genus has been conducted by Penfold and Morrison [197], Hellyer and McKern [198] and others at the Museum of Applied Arts and Sciences in New South Wales. McKern [202] has reviewed some of the history of essential oil studies in Australia, and has also reviewed [203] the problems associated with attempts to utilize chemical compositions of volatile oils in taxonomy. General reviews of work on alkaloids and terpenes are published by the Royal Society of Chemistry [204,205]. Investigations of the alkaloids of native plants has been conducted by Bick et al [206], and of terpene composition by Ayling [207].

A number of Tasmanian plants have volatile components that impart attractive odour or taste properties. Two of these, Drimys lanceolata and Prostanthera lasianthos, are examined in this work, with the object of documenting the steam distillate oil and of developing techniques for the characterisation of small quantities of volatile organic compounds. The third section examines the relationship between the volatile components of Boronia megastigma, a native plant of Western Australia.

A. Components of the Steam Volatile Oil of *Drimys lanceolata*.

Introduction.

Drimys lanceolata occurs in the Tasmanian highlands and also in Victoria and New South Wales. Commonly called 'Mountain Pepper' due to the very 'hot' peppery taste of the leaves, the plant is widely distributed in Tasmania. Plants on high windswept plateaus and exposted ridges tend to be short and flattened in appearance, whereas, in gullies the growth tends to resemble small trees or tall shrubs. The height varies from 0.2m to 5.0m and the young stems are crimson in colour [208].

Previous experimental work on extracts from the plant were conducted by Stevens [209], and Loder [210], and work on the related New Zealand plant, *Pseudowintera colorata*, was performed by Corbett and Grant [211].

A preliminary investigation of the steam distillate of Tasmanian samples of *Drimys lanceolata* by Stevens indicated that there existed considerable variations in physical and chemical properties of oils derived from plants found in separated areas of the state. The sesquiterpene alcohol guaiol was found to crystallize from two of the oils.

Loder [206] used a hexane extraction method to isolate two crystalline components from the leaves, polygodial (0.26%) and guaiol (0.035%). Polygodial was described as

partly responsible for the pungent taste of the leaf. Corbett and Grant listed a number of components derived from column distillation of the volatile oil from Pseudowintera colorata (Maori Pepper). The fractions and percentage composition are listed in the discussion section.

The composition of the volatile leaf oil components of Drimys lanceolata has apparently not been reported in the literature. Samples of the plant were collected from a number of areas of Tasmania to determine whether significant compositional variations occured.

1) Experimental

a) Sample Collection

Small branches and leaves were collected from five scattered areas of Tasmania. Samples of the plant collected adjacent to the Mt. Wellington park differed from the others in that the height of plant was relatively small (0.25m). The other samples were collected from small trees or shrubs growing in sheltered valley situations in deeper soil.

b) Distillation

The leaves were stripped from the branches and the steam volatile components were passed through a vertical glass column packed with 5mm lengths of glass tube and condensed before collection in a saturated aqueous sodium chloride solution. The oil was separated from the aqueous solution by decantation and triple extraction with diethyl ether. Ether

was removed by low temperature evaporation using a dry nitrogen gas stream. Residual water was removed by passing the oil through a small column of granular anhydrous sodium sulphate. Percentage yield and some physical properties of the volatile oil are recorded in Table XI.

Sample Area	Plant Height(m)	Oil Yield (%)	Density(g/mL)
Mt. Wellington	0.25	0.37	0.901
Parrawe	2.5	0.70	0.910
Mt. Field	2.5	0.43	0.917
Moogara	1.5	0.50	0.920
Wtern Tiers	2.0	0.35	0.928

Table XI. Average Percentage Yield and Physical Properties of the Steam Distillate of Drimys lanceolata.

c) Analytical Results

Identification of components in the steam distillate was carried out by comparison of GC retention times on two columns and mass spectral data. The result for each district is derived from a composite of the oil from three trees.

The GC traces are shown in Figures XX - XXIV. Relative retention indices were caculated from separate and coinjected mixtures of C10 to C22 n-alkane hydrocarbon standards at a concentration of 0.040 percent each in chloroform. Reproducability of the coinjected mixture was generally excellent on the OV101 capillary GC column; however, some variations occured on the Carbowax 20M column compared with the literature values [212]. Retention times and peak areas were recorded on a Shimadzu Chromatopac-E1A

and the percentage composition of each component calculated on the basis of the peak areas.

The GC/MS total ion current traces (Figures XXVI,XXVII) were obtained on the VG instrument previously described, using a 50m CW20M silica capillary GC column (Figure XXVII), and a similar OV101 column (Figure XXVI); temperature programmed at 4 deg.C/min. from 80 to 200 deg. C. Individual component mass spectra are listed in the appendix at the end of the thesis.

The peak scan numbers and component identities of the more complex Moogara sample are listed in Table XII.

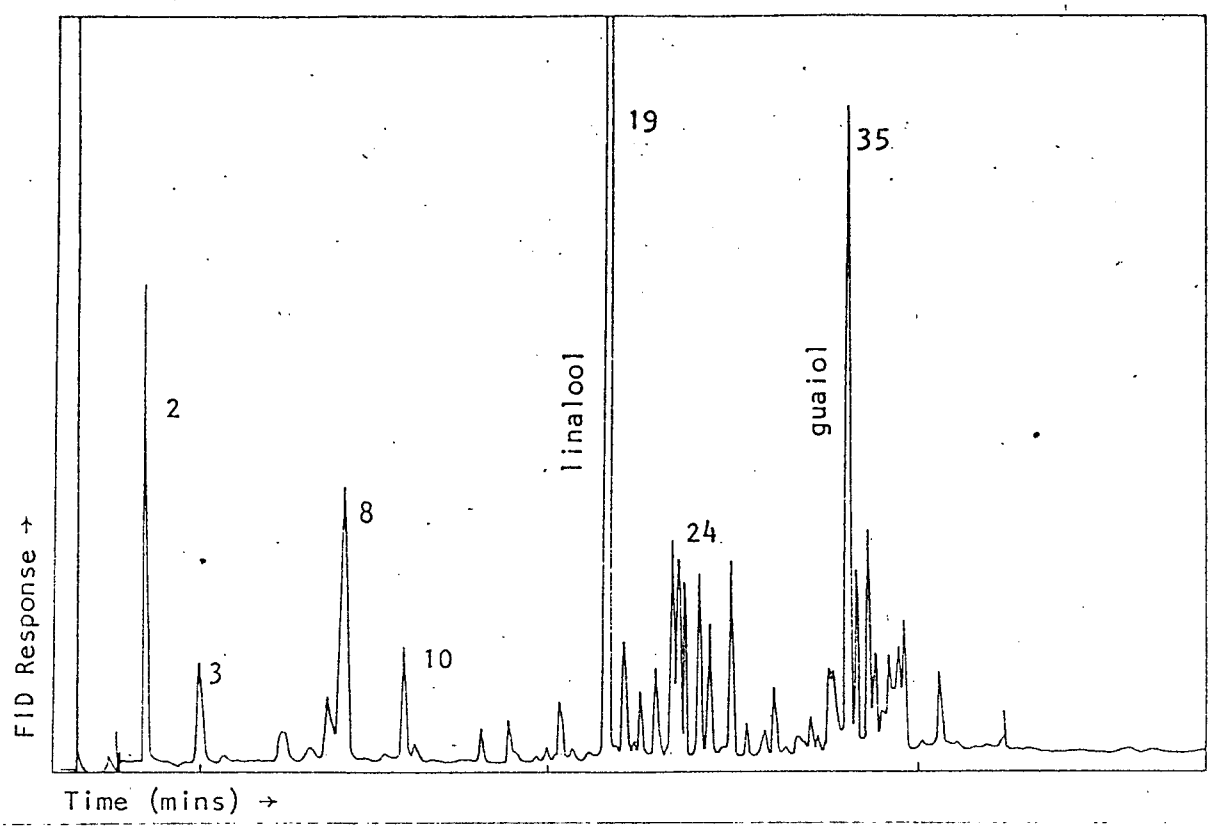


Figure XX. GC Trace D. lanceolata on CW20M Capillary Col. 50-200 deg. C at 2 deg./min. Sample ex Moogara. Component Identification Table XII.

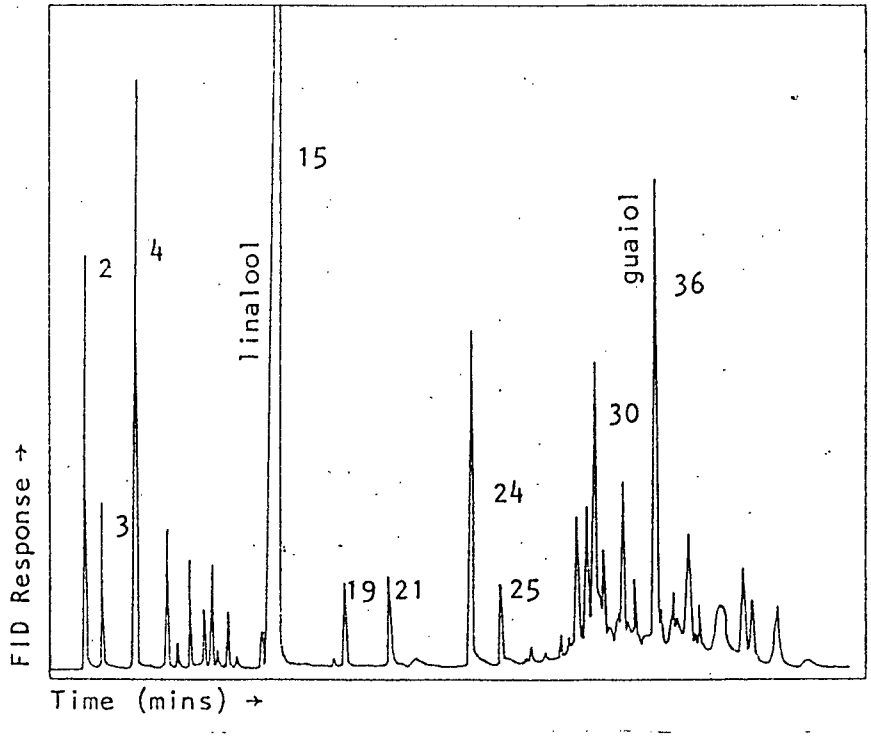


Figure XXI. GC Trace D. lanceolata on CW20M Capillary Col. 50-200 deg. C at 4 deg./min. Sample ex Parrawe. Component Identification Table XIII.

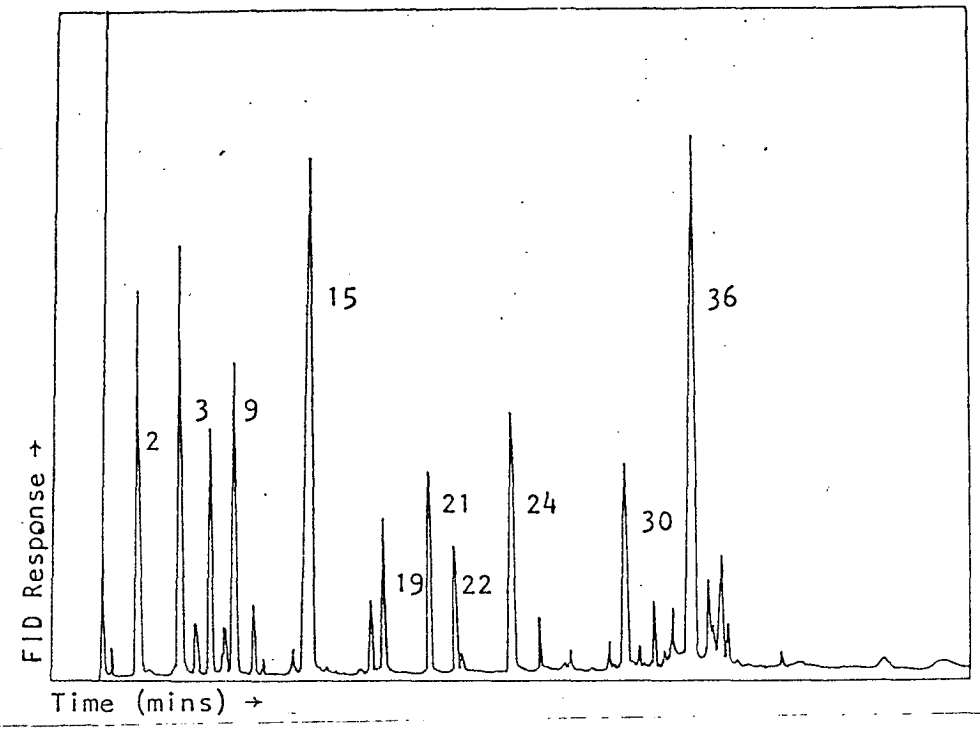


Figure XXII. GC Trace D. lanceolata on OV101 Capillary Col. 50-200 deg. C at 4 deg./min. Sample ex Wtern Tiers. Component Identification Table XIII.

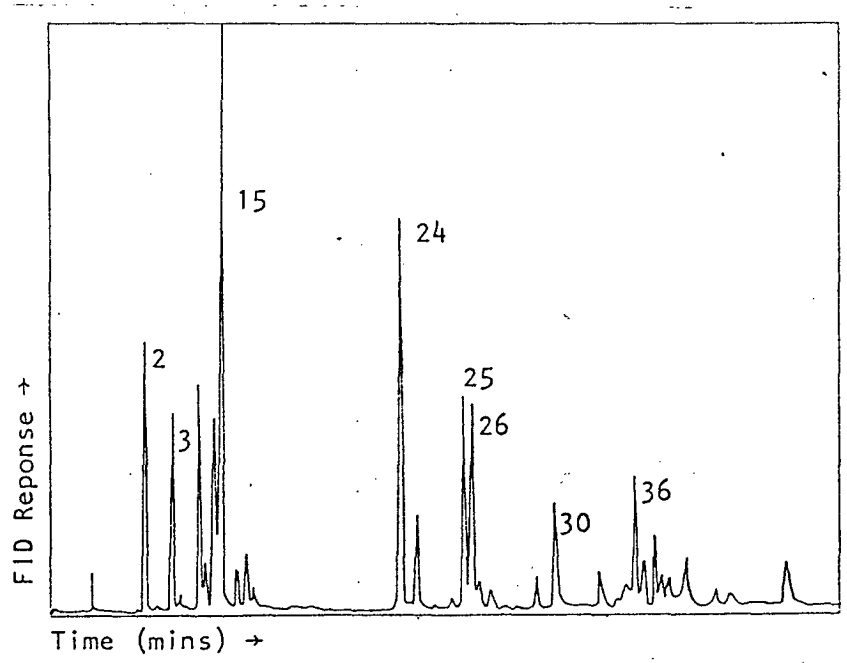


Figure XXIII. GC Trace D. lanceolata on CW20M Capillary Col. 50-200 deg. C at 4 deg./min. Sample ex Mt Field. Component Identification Table XIII.

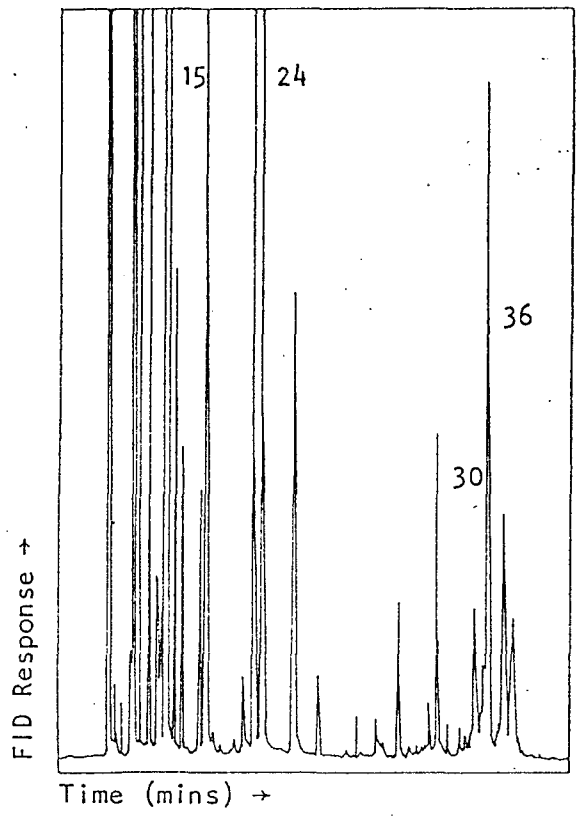


Figure XXIV. GC Trace D. lanceolata OV101 Capillary Col. 50-200 deg. C at 4 deg./min. Sample ex Mt Wellington. Component Identification Table XIII.

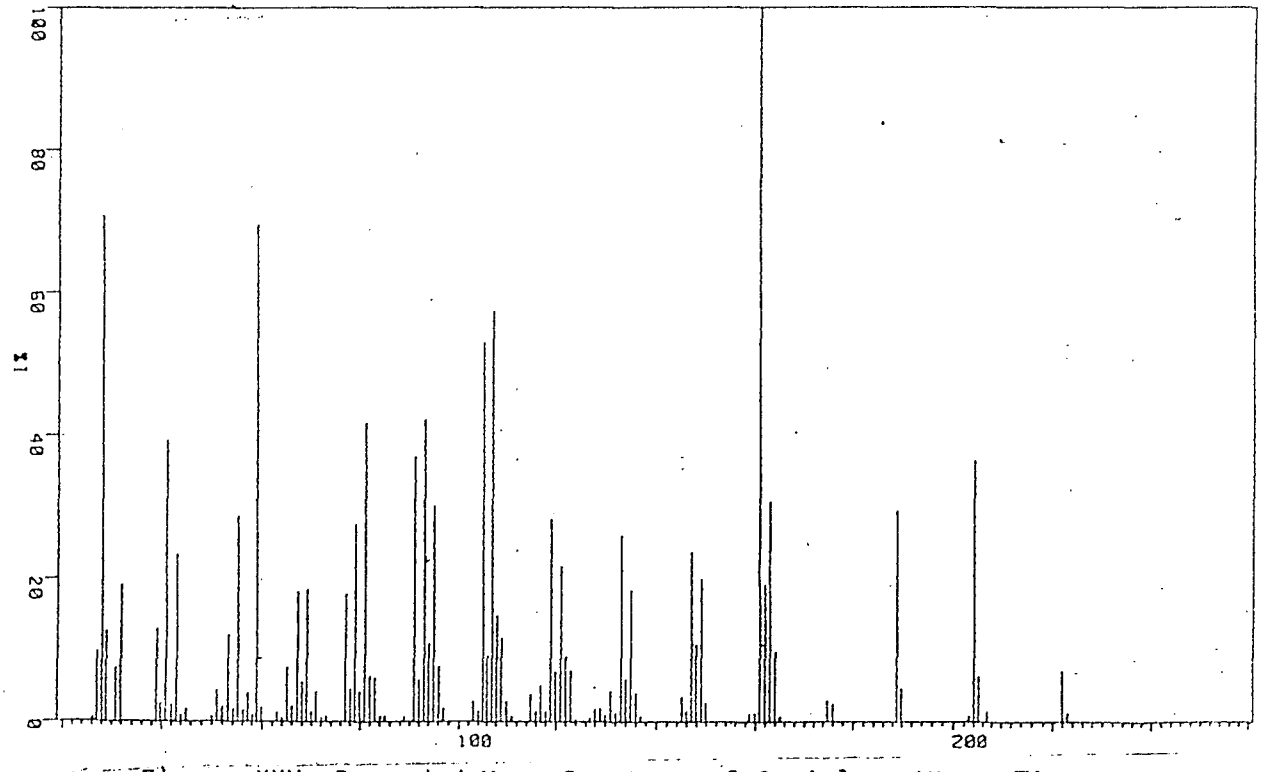


Figure XXV. Recorded Mass Spectrum of Guaiol ex Wtern Tiers.

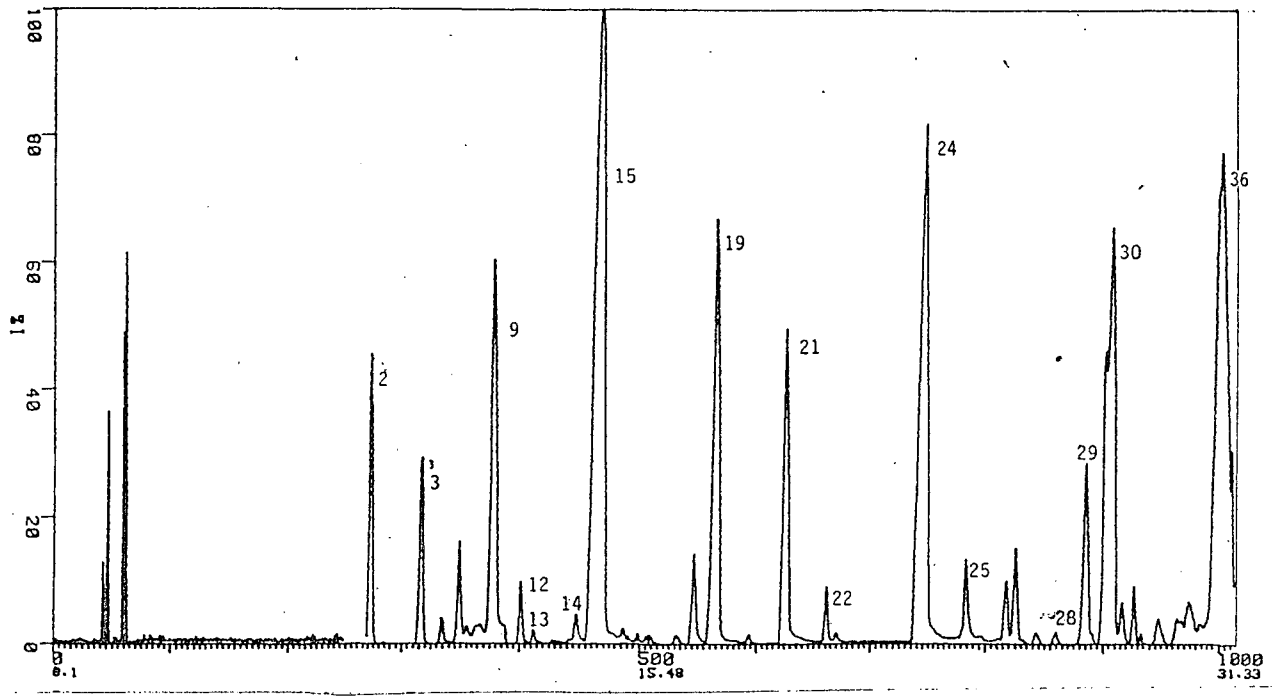


Figure XXVI. TIC Trace D. lanceolata ex Wtern Tiers.
OV101 Capillary Col. 80-200 deg. C; 4 deg./min.
Component Identification Table XIII.

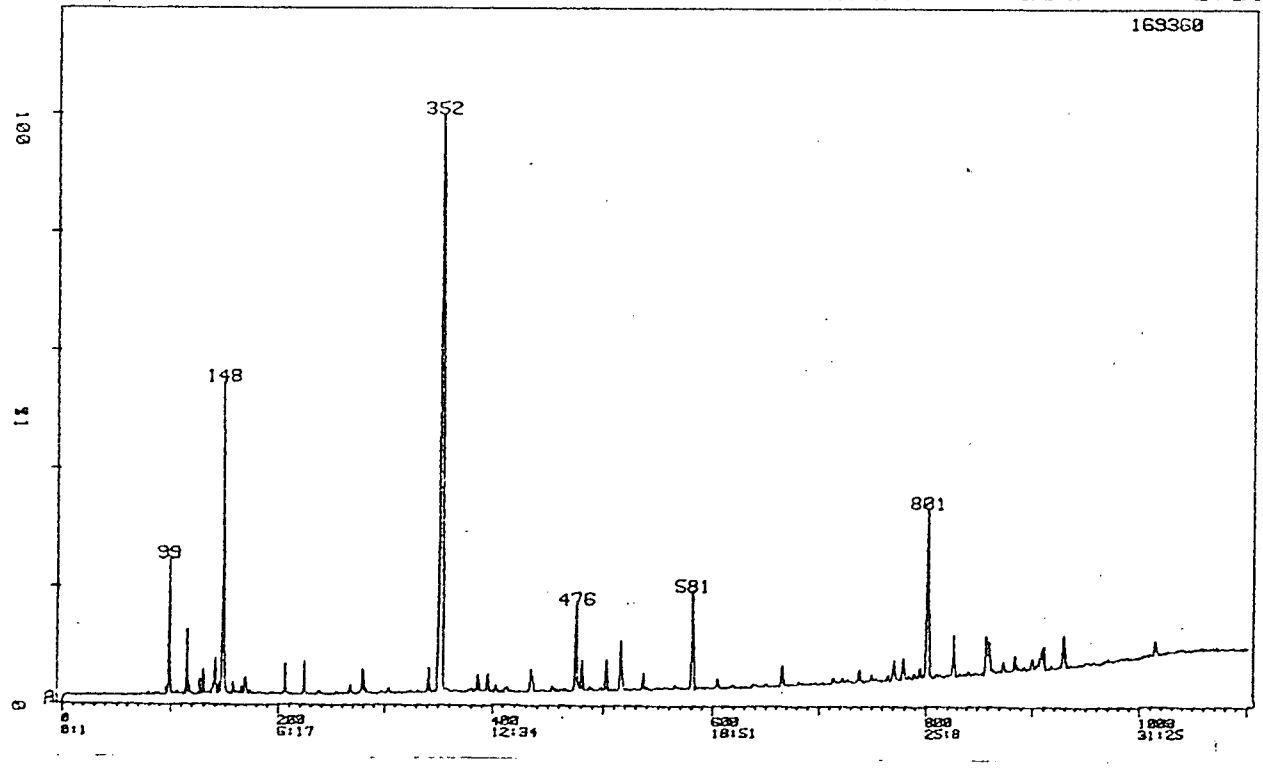


Figure XXVII. TIC Trace D. lanceolata ex Moogara.
CW20M Capillary Col. 80-200 deg. C; 4 deg./min.
Component Identification Table XII.

Peak No.	Scan No.	Retention Index	Percent Composition	Identity
1	96	-	-	solvent (chloroform)
2	98	1039	7.8	α-pinene
3	116	1124	3.6	β-pinene
4	127	1156	1.5	myrcene
5	130	1177	0.3	α-phellandrene
6	141	1206	1.9	limonene
7	145	1218	0.1	β- phellandrene
8	148	1228	18.8	1,8 cineole
9	158	1246	0.1	monoterpene (?)
10	170	1272	0.4	p cymene
11	206	1328	0.3	unknown X (base 68)
12	224	1351	0.4	isomer of X
13	268	1402	0.1	isomer of X
14	279	1420	0.3	cubene
15	304	1448	0.1	unknown
16	325	1482	0.1	bourbonene
17	332	1494	0.1	unknown
18	342	1501	0.3	unknown (X + CH2)
19	353	1506	38.8	linalool
20	386	1617	0.4	caryophyllene
21	395	1628	0.4	terpinene-4-ol
22	435	1648	0.4	sesquiterpene
23	455	1655	0.1	monoterpene alcohol
24	476	1661	3.4	α-terpineol
25	481	1702	0.2	sesquiterpene
26	503	1739	0.3	piperitone
27	516	1758	0.8	cadinene (?)
28	537	1782	0.1	cadina 1,4 diene
29	581	1842	3.6	calamanine
30	605	1875	0.1	farnesol
31	666	1938	0.2	unknown
32	738	2044	0.1	methyl eugenol (type)
33	771	2046	0.2	sesquiterpene alcohol
34	779	2049	0.2	sesquiterpene alcohol
35	801	2058	8.8	guaiol
36	826	2078	0.4	oxygenated sesquiterp.
37	858	2103	0.4	eugenol
38	861	2112	0.3	isomeric guaiol (?)
39	874	2122	0.1	unknown
40	885	2132	0.3	methyl eugenol + CH2
41	905	2154	0.1	unknown
42	910	2158	0.3	unknown
43	929	2172	0.5	myristicine (?)
44	1015	2208	0.1	unknown
			3.2	others

Table XII. Identification Details of Steam Volatile Oil of Drimys lanceolata ex Moogara.

Peak No	Component	Mt. Wellington	Parrawe	Mt. Field	Western Tiers
2	α-pinene	10.2	5.4	5.1	6.5
3	β-pinene	11.2	1.3	4.6	8.1
4	α-phellandrene	3.1	3.9	5.8	0.7
5	myrcene	0.6	0.2	1.6	3.7
6	β-phellandrene	0.4	0.1	0.1	)
7	heptanone	0.1	0.1	0.1	) 1.0
8	limonene	0.1	0.7	5.7	0.6
9	1,8 cineole	2.6	0.5	11.2	7.6
10	monoterpene	0.1	0.1	1.1	0.1
11	p-cymene	0.2	1.1	1.9	0.3
12	β-ocimene or, Δ-3 carene	0.1	0.1	0.1	0.8
13	terpinolene	0.6	0.3	0.7	0.2
14	unknown	0.4	0.1	0.1	0.3
15	linalool	31.8	40.7	18.8	17.2
16	monoterp. acetate	1.2	0.3	0.1	0.1
17	caryophyllene	0.1	)	0.1	0.1
18	terpinen-4-ol	0.7	) 2.9	0.4	0.9
19	α-terpineol	4.1	0.9	0.8	2.3
20	sesquiterpene	0.3	0.1	-	-
21	piperitone	0.1	0.9	7.0	3.4
22	safrole	0.1	0.2	1.1	1.7
23	unknown	2.7	0.1	0.8	0.3
24	eugenol	8.6	5.7	10.0	5.5
25	methyl eugenol	1.6	0.9	1.3	0.7
26	unknown	0.3	0.2	1.1	0.1
27	unknown	0.2	0.6	0.1	0.3
28	geranial	0.5	0.4	0.4	0.1
29	unknown	0.2	2.4	1.1	0.5
30	myristicine	1.2	5.7	5.0	5.1
31	β-cedrene(?)	0.1	0.1	0.1	0.1
32	γ-murolene(?)	0.1	1.4	1.7	0.3
33	mycenol or elemol	0.2	0.9	2.2	1.1
34	β-farnesene(?)	0.1	3.1	0.9	0.3
35	dihydrocarvyl acetate(?)	0.9	1.8	0.6	1.3
36	guaiol	4.3	8.0	1.6	16.5
	Others	10.8	13.0	6.7	12.2

Table XIII. Percentage Composition Drimys lanceolata From Various Areas of Tasmania.

The percentage composition of the oil samples from the other areas of the state are shown in Table XIII.

A number of components were not identified due to the

lack of comparative data in the literature, and the lack of time available to prepare pure standard samples from the crude oil on a preparative scale.Characterisation of minor components would require the collection of large quantities of leaf material as the percentage of oil present is relatively low.

ii) Discussion

Variation in the percentage composition of the main components: linalool, α-pinene, β-pinene, 1,8 cineole, guaiol, was considerable (up to three times for each component) between areas. The sample taken from Moogara varied in composition from the other sites in that the oil contained a number of components that were not present in significant concentrations in samples collected in the other areas. The presence of a component with a similar mass spectrum to guaiol was of particular interest (mass spectra from Scan No. 861 compared with Figure XXV). Unfortunately there was insufficient material to isolate and confirm the structure of this component.

The similarity in composition of the Tasmanian plant to that of New Zealand Pseudowintera colorata is shown by the components from this plant listed in Table XIV.

Fraction	% Composition	Components
1	1.0	α-pinene, α-thujene
2	1.0	β-pinene
3	0.5	myrcene
4	0.5	carbonyl cpd
5	2.25	limonene, dipentene, α-terpinene
6	2.25	β-phellandrene mixture
7	1.0	terpene alcohol ($C_{10}H_{18}O$)
8	-	carbonyl cpd ($C_{10}H_{14}O$)
9	1.0	α-terpinene
10	1.0	terpinolene, ρ-cymene
11	0.5	ester
12	0.5	alcohol ($C_8H_{14}O$)
13	1.0	alcohol ($C_{10}H_{20}O$)
14	0.5	hexenyl valerate
15	1.0	eugenol
16	16.5	bicyclic sesquiterpene
17	1.0	bicyclic sesquiterpene
18	1.0	aromadendren
19	1.0	humulene
20,21	4.5	alcohol unknowns
22	3.0	aromatic hydrocarbon
23	4.5	alcohol
24	2.0	sesquiterpene ketone ($C_{15}H_{22}O$)
Residue	52.0	tricosane, pentacosane and sesquiterpene ketone

Table XIV. Percentage Composition of Steam Distillate of Pseudowintera colorata [211].

A considerable amount of additional experimental work is required to enable a final characterisation and confirmation of the identity of the remaining components of the steam distillate of the oil of Drimys lanceolata. Techniques such as GC Fourier transform infrared analysis, as well as laser-Raman and UV methods, for determining functional groups and molecular structure would assist in the complete characterisation of the oil.

B. Components of the Steam Volatile Oil of *Prostanthera lasianthos*.

Introduction.

Prostanthera lasianthos occurs in Tasmania, Victoria and New South Wales on the margins of wet eucalypt forests. The shrub or small tree grows to a height of from 2 to 6m [208]. The strong-smelling flowers are formed in December to January, hence the common names of Christmas Bush (or Mint Tree).

The terpene composition of the steam volatile oil of the related *Prostanthera rotundifolia* has been reported by Ayling [207] but there was no indication in the literature of previous experimental work being performed on P. lasianthos.

1) Experimental

(a) Sample Collection

Leaves were collected in April from four trees growing in small valleys draining to Pirates Bay on Tasman Peninsula. The leaves were concentrated on the extreme outer ends of the branches and were somewhat low in numbers due to heavy growth of surrounding plants. Height of the trees were 3 to 4m.

(b) Distillation

The procedure followed for distillation of the leaf oil was as described in Section A for D. lanceolata. Percentage yield (by weight) of the steam distilled oil derived from a composite of the leaves from the four trees was 0.12.

(c) Analytical Results

50m silica capillary GC columns were used to separate components in the oil and their mass spectra recorded. The total ion current trace (Figure XXVII) was obtained by injecting 0.4 microliters of the oil (with a 10:1 split), into the GC/MS using a CW20M GC column temperature programmed from 50 to 210 deg.C at 4 deg./min. to separate and characterise the peaks. Component identification was based on relative retention index and mass spectral data. The component mass spectra from two GC/MS runs are shown in detail in the appendix. DE1036 (Figure XXVIII) shows the total ion current trace from the OV101 silica capillary GC column with a similar loading to the CW20M column but temperature programmed from 50 to 240 deg.C at 4 deg./min. Scan numbers and tentative MS identification data are recorded in Table XV, and the component mass spectra are listed in the appendix.

The n-hydrocarbon standards peaks are shown in the temperature programmed GC trace of Figure XXIX. Table XVI lists the standards and the temperature programmed retention times used to calculate the retention indices obtained on a

50m OV101 glass SCOT capillary column. The same column under identical programming conditions was used to obtain the GC trace of Figure XXX. The retention indices of the recorded peaks, the literature values and the percentage composition are tabulated in Table XVII.

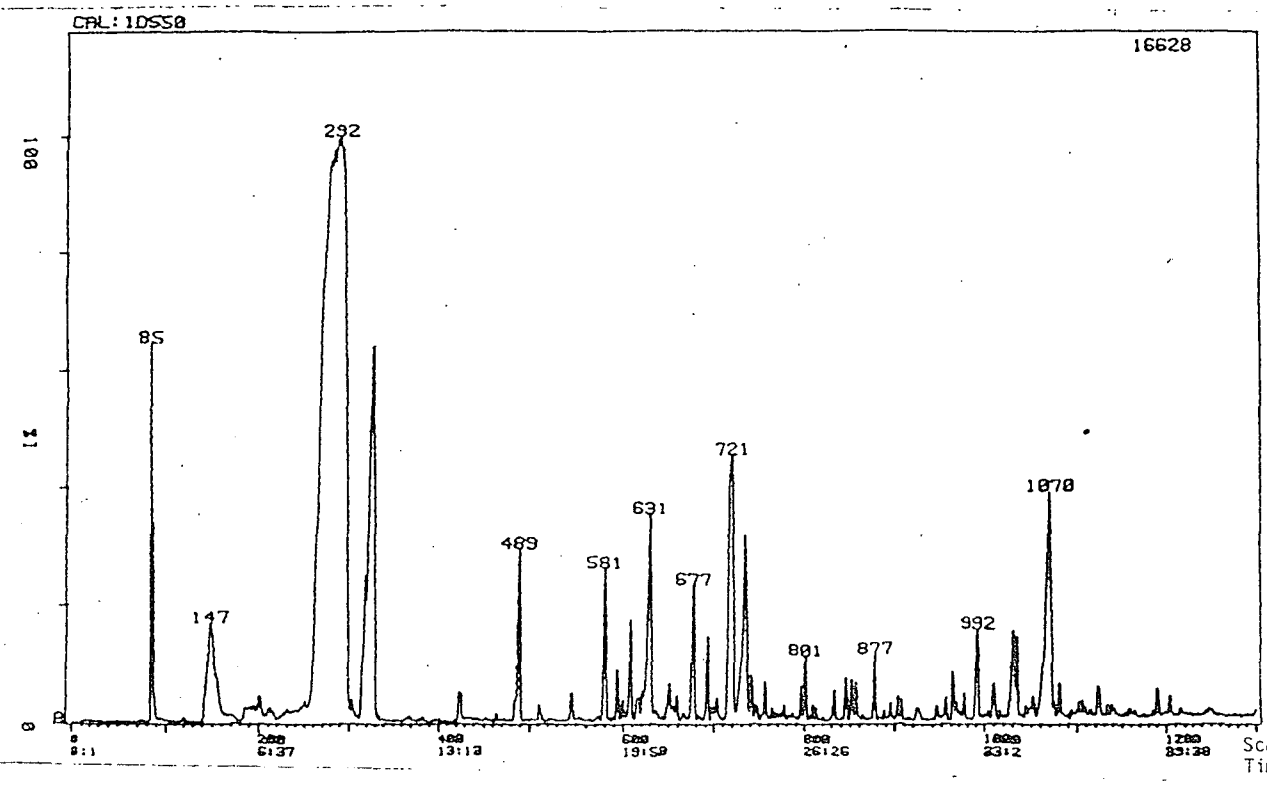


Figure XVII. TIC Trace P. lasianthos CW20M Capillary Col.
50-210 deg. C at 4 deg./min.
Component Identification Table XV.

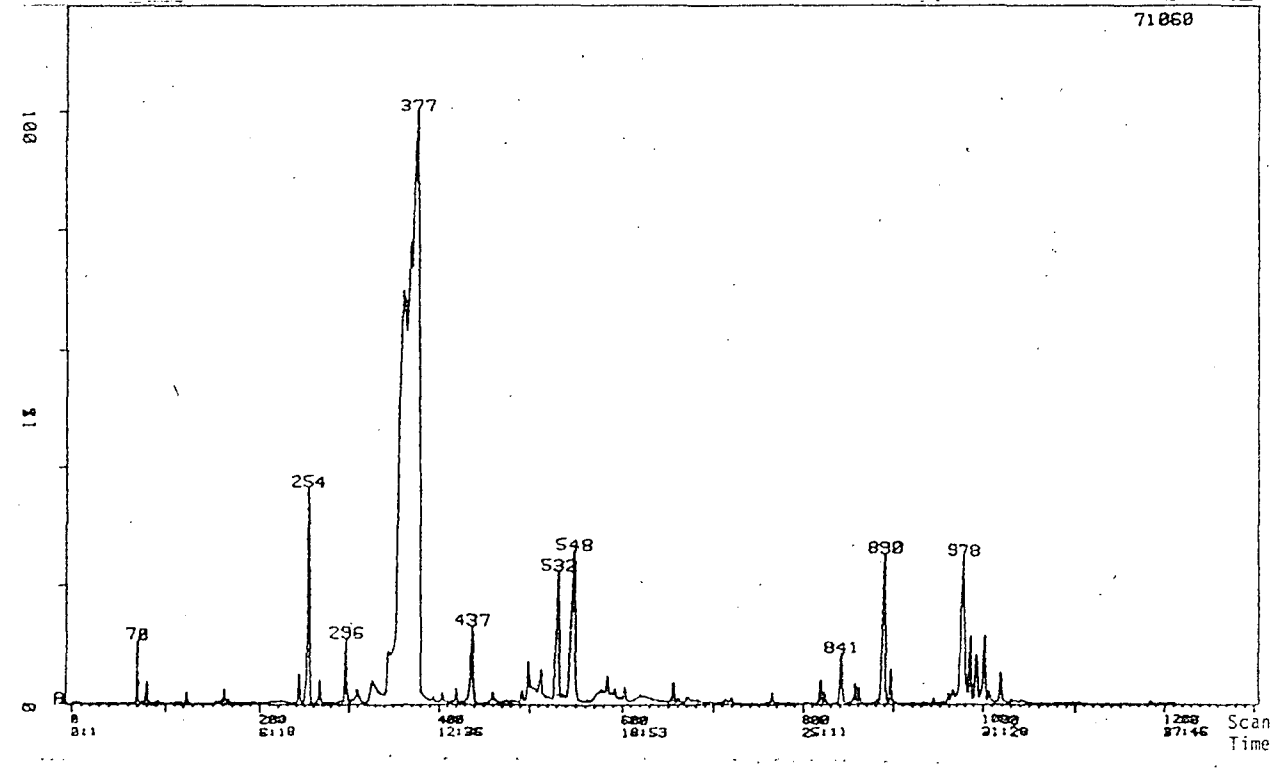


Figure XVIII. TIC Trace P. lasianthos OV101 Capillary Col.
50-240 deg. C at 4 deg./min.
Component Identification Table XV.

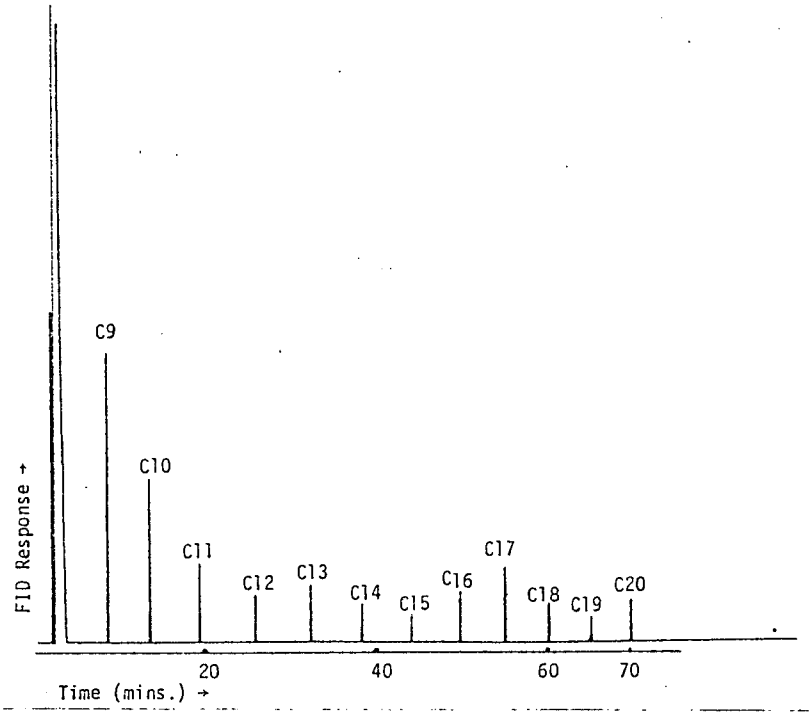


Figure XXIX. GC Trace n-hydrocarbon Standards. Conditions as Shown Below.

Standard	Retention Time (minutes)	Retention Index
n-C9	8.55	900
n-C10	13.50	1,000
n-C11	19.53	1,100
n-C12	25.95	1,200
n-C13	32.36	1,300
n-C14	38.56	1,400
n-C15	44.51	1,500
n-C16	50.20	1,600
n-C17	55.61	1,700
n-C18	60.81	1,800
n-C19	65.78	1,900
n-C20	70.58	2,000
n-C21	75.69	2,100

Table XVI. Retention Times and Indices for n-hydrocarbon Standards on OV101 Glass Capillary Column 50-220 deg.C at 2 deg./min.

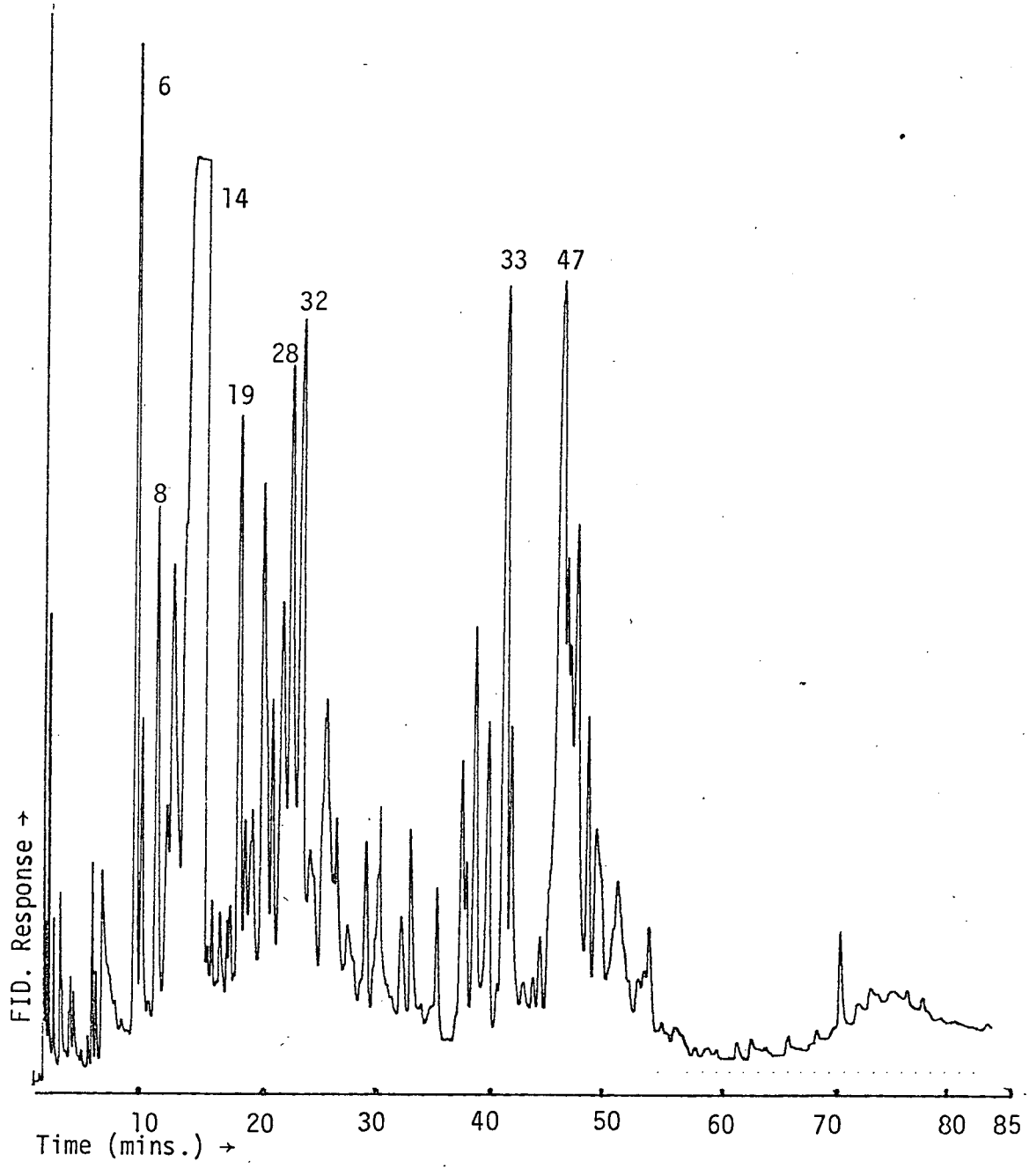


Figure XXX. GC Trace P. lasianthos OV101 Capillary Col.
50-220 deg. C at 2 deg./min.
Component Identification Table XV.

Scan No. CW20M	Scan No. OV101	Peak No.	Tentative Identification
85	78	1	solvent
	123	2	4 methyl-pent-1-en-3-one
	153-189	3	unknown
	243	4	pentyl ester
	250	5	benzaldehyde
	(254	6	α -pinene
146-180	(267	7	camphene
	(296	8	β -pinene
	(309	9	myrcene
	327	10	α -phellandrene
304,319	331	11	cymene mixture
258		12	limonene
	344	13	1,8 cineole + cymene
292	377	14	1,8 cineole
	394	15	unknown momoterpene
423		16	trans hex-3-enol
484	404	17	cis linalool epoxide
511	420	18	trans linalool epoxide
581	437	19	linalool
	458	20	unknown
	460	21	unknown
	492	22	camphene hydrate
594	499	23	pinocarvone
	505	24	unknown
693	514	25	archillinol (?)
608		26	fenchone (?)
617		27	caryophyllene
631	532	28	terpinene-4-ol
658		29	sesquiterpene (farnesene?)
677		30	unknown
691		31	unknown mixture
721	548	32	α-terpineol
735	890	33	β-selinene
852		34	4 phenyl butan-2-one
	584	35	carvone
	593-603	36	unknowns
741		37	unknown
742		38	γ elemene
796		39	myrtenol
801-832		40	unknown
833		41	carveol
	655	42	iso-bornyl acetate
1123	670	43	thymol
	714-765	44	unknowns
845		45	ρ-cymene-8-ol
857-976		46	unknowns
	978	47	unknown
992	1002	48	ledol
1052	1019	49	β-eudesmol

Table XV. Component Scan Numbers and Tentative MS Identification of Prostanthera lasianthos Oil Components.

Peak No.	Rel.Ret. Index (Lit.)	Rel.Ret. Index (Calc.)	Percent Composition	Component Identity
1				solvent
2			0.1	4 methyl-pent-1-en-3-one
3			1.3	unknowns
4			0.1	pentyl ester
5	947		0.2	benzaldehyde
6	942	930	3.2	α-pinene
7	954	941	0.8	camphene
8	981	968	1.8	β- pinene
9	986	987	0.5	myrcene
10	1002	996	0.7	α-phellandrene
11	1020)			cymeme mixture
12	1030)	1024	22.6	limonene
13	)			1,8 cineole + cymene
14	1027)			1,8 cineole
15			0.1	unknown
16			0.1	trans hex-3-enol
17	1068		0.1	cis linalool epoxide
18	1082	1080	0.2	trans linalool epoxide
19	1092	1093	2.1	linalool
20		1101	0.1	unknown
21		1107	0.1	unknown
22		1111	0.2	camphene hydrate
23		1125	2.4	pinocarvone
24		1138	1.1	unknown
25		1152	1.6	archillinol
26	1080		0.3	fenchone ?
27	1428?	1351	0.2	caryophyllene ?
28	1175	1165	3.2	terpinene-4-ol
29		1447	0.2	sesquiterpene (farnesene?)
30		1467	0.1	unknown
31			0.3	unknown mixture
32	1185	1180	3.8	α-terpineol
33		1494	3.9	β-selinene
34		1502	1.8	4 phenyl butan-2-one
35	1228		0.4	carvone
36			1.7	unknowns
37			0.2	unknown
38			0.8	γ-elemene
39			0.4	myrtenol
40			0.4	unknowns
41			0.7	carveol
42	1279	1275	0.2	iso-bornyl acetate
43	1287		1.3	thymol
44			0.3	unknowns
45			1.1	ρ-cymene-8-ol
46			3.7	unknowns
47		1581	3.4	unknown
48		1623	1.4	ledol
49		1728	1.9	β-eudesmol
			28.9	other

Table XVII. Component Identification by Retention Index (on OV101) and Approximate Percentage Composition Prostanthera lasianthos.

ii) Discussion

The use of retention indices to assist in the identification of components in complex mixtures has been widely reported in the literature [213, 214]. Identification of a well resolved component in a GC run is relatively straight forward if the component retention time has been accurately measured previously and the run is reproduceable. Problems are encountered when the peak is not well resolved or, if the component has not been previously measured. Tables provided in the literature [212] are often of assistance but must be used with caution. Polar phases, such as Carbowax, can readily alter in characteristics as the column ages. Components that eluted in the order a,b,c,d,e can alter and elute a,b,d,e after a certain amount of the liquid phase has been stripped from the column with either repeated injections of solvent, or high temperatures.

The presence of a large number of components with similar boiling points made baseline separation and quantitation difficult. Hence, quantitation of components by area integration proved to be somewhat inexact. Main components were 1,8 cineole and a mixture of cymenes, α-pinene, α-terpineol, terpinene-4-ol, βselinene and an unknown compound with a molecular weight of 220. A relatively high proportion of the unknowns were oxygenated sesquiterpene compounds that would contribute to the aroma characteristics of the oil. Preliminary separation of the compounds into

terpene hydrocarbons and oxygenated classes would assist in clarifying the GC trace and allow greater accuracy in quantitation of components.

Ayling [207] examined the steam volatile oil of the related Prostanthera rotundifolia. A comparison of the composition of the main components of this oil with Prostanthera lasianthos is given in the following table.

Component	P. lasianthos	P. rotundifolia [207]
α-pinene	3.2	1.4
camphene	0.8	0.1
β-pinene	1.8	2.3
myrcene	0.5)	
α-phellandrene	0.7)	3.7
limonene	)	1.1
1,8 cineole	) 22.6	47.0
ρ-cymene	-	23.2
terpinen-4-ol	3.2	1.5
α-terpineol	3.8	4.1
terpene alcohol	1.1	6.9
other	62.3	8.7

Table XVIII. Comparison of the Percentage Composition of Prostanthera lasianthos and P. rotundifolia.

1,8 cineole is the major component in both oils and many of the minor components are present in somewhat similar concentrations. Large differences are however apparent in the higher boiling components of the oils.

iii) Conclusions.

Examination of the steam volatile oils of D. lanceolata and P. lasianthos provided the opportunity to develop retention index and mass spectral techniques applicable to volatile components. The advantages of fine bore silica capillary columns and the introduction of the end of the

column through to the ion source of the mass spectrometer were proved using the steam volatile oils.

C. Volatile Components of Boronia megastigma.

Introduction.

The essential oil industry in Tasmania has developed gradually over the last few decades into a relatively small but viable agricultural/processing industry. Recent research within the Agricultural Science Faculty of the University has indicated that a number of groups of plants produce high quality essential oils when grown in selected areas of Tasmania [215].

The determination of the optimum time for picking the leaves or flowers of a crop is an important factor in the production of a high quality oil. Collection of the volatile compounds from the surrounding air and rapid analysis for critical components may provide a viable alternative to the normal steam distillation procedure. The collection of headspace air samples has a number of advantages in that it provides a non-destructive collection method and under most conditions an inbuilt averaging system as the sample collection tube can be moved from one area of a field or glasshouse to another. An automated variation of this collection-analysis system would provide rapid analytical results for the harvester.

Commercial processing of Boronia megastigma involves extraction of the soluble components by solvent and the production of a 'concrete' consisting of volatiles and higher molecular weight substances [216]. The objective of

the work described below was to compare the headspace components trapped from the flowers, the headspace above the concrete and the components present in the concrete.

i) Experimental

a) Sample Collection

Boronia flowers (Boronia megastigma) were provided by Mr. G. Leggett from the Agricultural Science Faculty. Samples of the headspace above the flowers were obtained by placing the flowers (163), in a clean glass jar (previously baked at 500 deg.C) and drawing the volatiles into a Tenax sample collection tube at 40 mL per minute for 15 minutes.

The flowers were then extracted with petroleum ether and the solvent was evaporated by warming the solution and blowing a stream of dry nitrogen over the surface. The larger portion of the resulting waxy residue - concrete - was then heated to its softening temperature (45 deg.C) by immersing the glass container in a water-bath. Headspace from the concrete was collected using a second Tenax tube under similar conditions to the first sample. A portion of the concrete was directly injected into the GC/MS system for comparison with the headspace volatiles.

b) Analytical Results

Separation of components was achieved using a 50m glass OV101 SCOT capillary GC column. Components were identified by mass spectral information verified by comparison with

library spectra of authentic compounds from previous work [215], and by retention times. Individual mass spectra are presented in the appendix.

Gas chromatographic conditions are described in Table XIX, and component identification in Table XX.

	Concrete	Concrete Headspace	Flower Headspace
Designation	AG110-AG113	DEBR04	DEBR00
Collection Temp.(deg.C)	-	45	20
Injection	In Solvent	Splitless	Splitless
Initial GC Temp.	80	30	30
Final GC Temp.	250	200	200
Carrier Gas	He	He	He
Flow Rate (mL/min)	1.0	1.5	1.5
Inlet Temp.	200	200	200
Outlet Temp.	250	250	250
Temp.Prog.Rate (deg.C/min)	4	3	3

Table XIX. Gas Chromatography Conditions for Boronia megastigma.

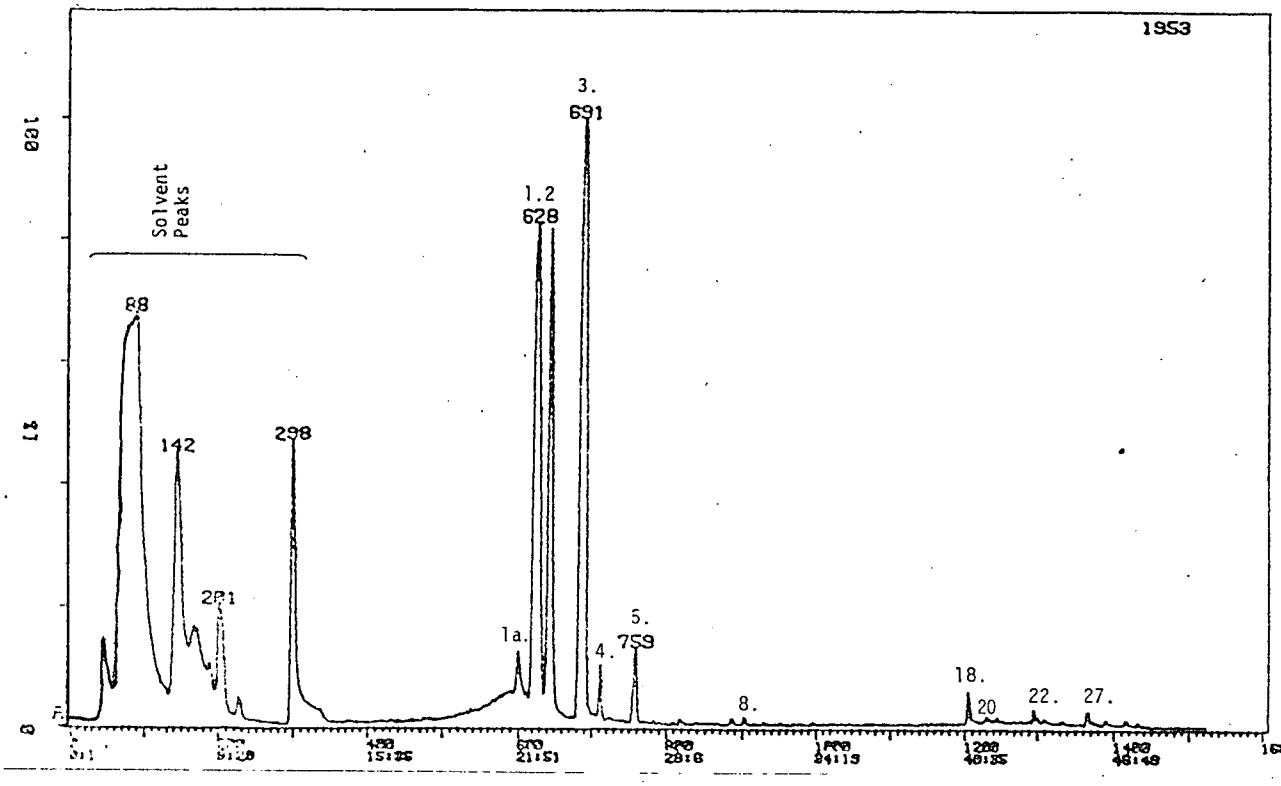


Figure XXXI. TIC Trace Headspace of Boronia megastigma Flowers.
OV101 Capillary Col. Peak Identification Table XX.

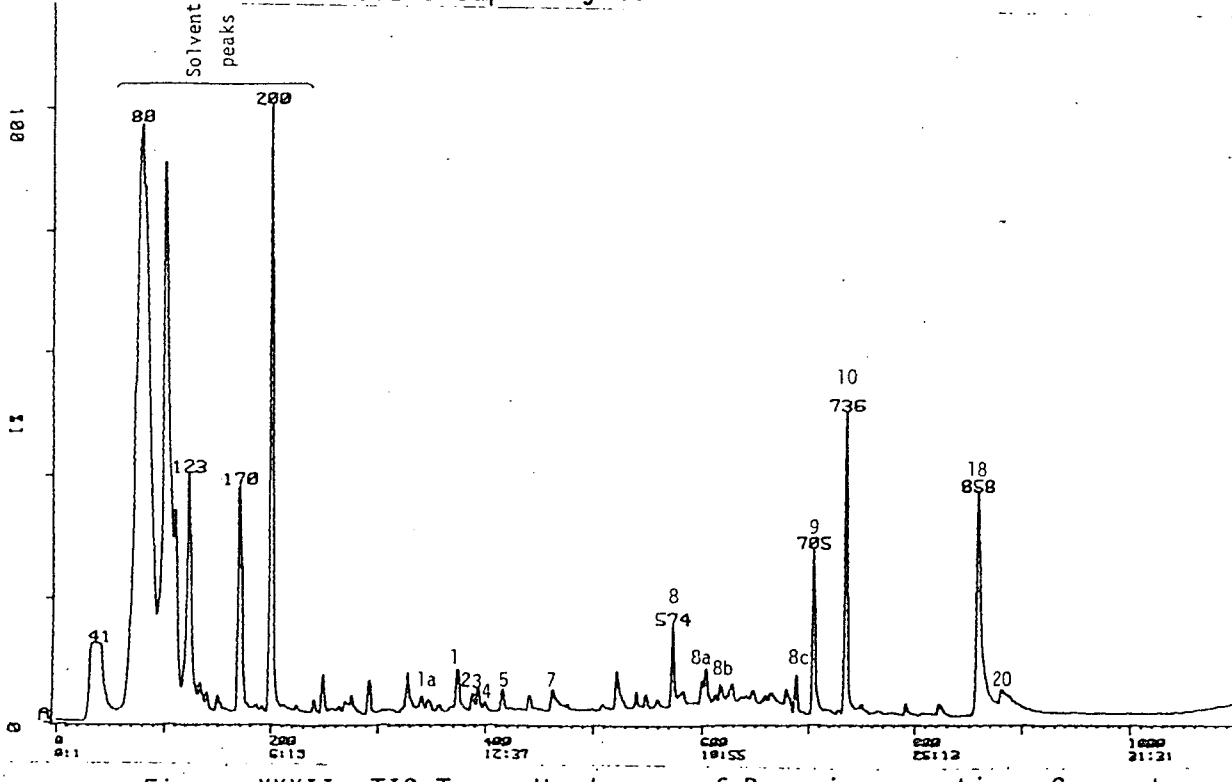


Figure XXXII. TIC Trace Headspace of Boronia megastigma Concrete.
Collected by Tenax Sample Tube.
OV101 Capillary Col. Peak Identification Table XX.

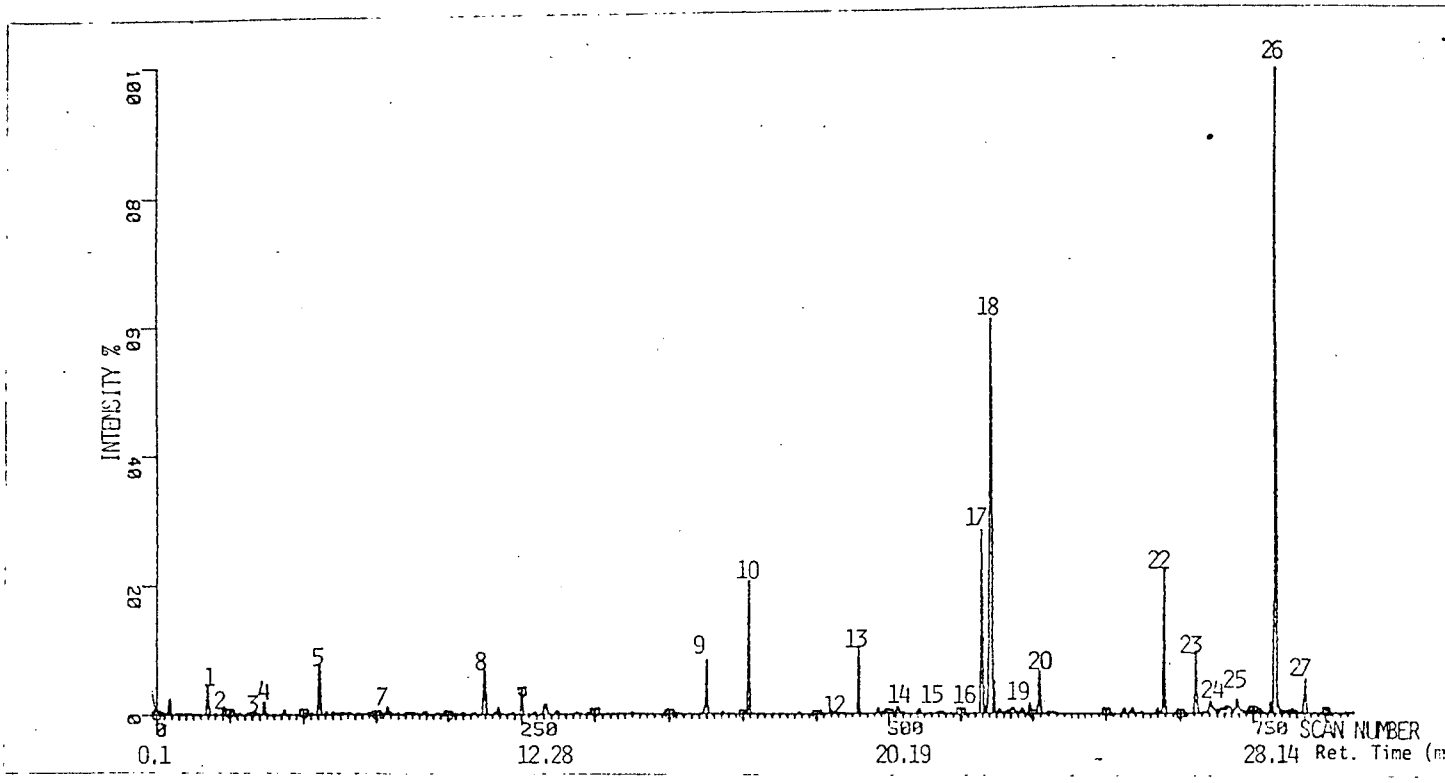


Figure XXXIII. TIC Trace of Concrete of Boronia megastigma [215].
OV101 Capillary Col. Peak Identification Table XX.

Peak No.	Component	Concrete	Scan Number Concrete Headspace	Flower Headspace
	Code:	Ag	DEBR04	DEBR00
1a.	Unknown monoterpene	8	340	-
1.	∝-pinene	34	372	628
2.	camphene	46	387	642
3.	β-pinene	-	392	691
4.	mycrene	72	399	710
5.	limonene	112	418	759
7.	linalool	151	462	nd
8.	methone	224	574	802
8a.	naphthalene	-	600	-
8b.	Unknown aromatic cpd.	-	604	-
8c.	Unknown C12H16 (?)	-	688	-
9.	methyl naphthalene	375	705	-
10.	methyl N decanoate	404	736	-
13.	ethyl decanoate	478	nd	-
17.	dodecanol	564	nd	-
18.	β-ionone	572	858	1024
20.	dihydroactinidiolide	-	883	1260
22.	dodecyl acetate	698	-	1296
26,27.	heptadecane	765	-	1366

Table XX. Peak Identification and Mass Spectra Scan Numbers for Boronia megastigma.

nd = not detected

The total ion current traces of the three samples of volatiles are shown in Figures XXXI to XXXIII.

A comparison of the relative proportions of the components is given in Table XXI.

Peak No.	Component	Concrete	Concrete Headspace	Flower Headspace
1a.	Unknown monoterpene	0.8	0.9	3.5
1.	α-pinene	1.6	3.1	26
2.	camphene	0.5	0.9	26
3.	β-pinene	0.3	0.9	32
4.	myrcene	0.5	0.4	3.1
5.	limonene	2.6	1.8	3.8
7.	linalool	0.3	1.8	-
8.	methone	2.4	6.8	0.3
8a.	naphthalane	-	3.1	-
8b.	Unknown aromatic cpd.	-	1.3	-
8c.	Unknown C12H16 (?)	-	3.1	-
9.	methyl naphthalene	2.6	15	-
10.	methyl N decanoate	6.8	26	-
13.	ethyl decanoate	3.4	-	-
17.	dodecanol	9.5	-	-
18.	β-ionone	21	19	1.8
20.	dihydroactinidiolide	2.1	0.9	0.3
22.	dodecyl acetate	7.6	-	0.5
26,27.	heptadecane	35	-	0.5
	Unknowns	3.0	15	2.2

Table XXI. Relative Percentage Composition of the Volatile Components of Boronia megastigma.

ii) Discussion

The relatively high proportion of monoterpene components in the headspace from the flowers was of considerable interest, as the aroma from the flowers was considerably "cleaner" than that of the solvent extracted material. Leggett [215] reported the presence of a number of components not normally found in natural Boronia extracts when he examined a sample of commercial Boronia absolute. The addition of the compounds, menthol, piperitone, β-ionone, menthyl propionate and elemol; may be an attempt by commercial interests to correct this difference in odour between the extract and the flowers.

Leggett has divided the volatile oils from Boronia megastigma into a number of different chemotypes on the basis of the presence, or absence, of certain components. The headspace from the flowers provided sufficient evidence to identify the plant as belonging to a particular class on the basis of the presence of menthone, methyl decanoate, ethyl decanoate, methyl naphthalene, although the concentration was low.

A Tenax sample collection tube in conjunction with an efficient separation and identification system, such as a GC/MS system has been shown to be an effective method for the collection and analysis of Boronia volatiles. The system as outlined could, with a few modifications, be utilised to determine rapidly the optimum time for harvesting flowers for commercial purposes. Monitoring the relative concentrations of the physiochemically active components over a period of time would provide valuable information for the commercial grower as to the optimum harvest time under a variety of weather conditions, without having to harvest selected areas of a field. The technique should also be applicable to other essential oil crops, as the steps of comminution, extraction, and evaporation would not be required.

CHAPTER VI

COMPOSITION CHANGES OF VOLATILE COMPONENTS OF PINUS RADIATA.

Introduction

The volatile components of Pinus radiata have been reported by a number of authors in the past decade generally using one specific method of sample collection and analysis. This chapter outlines a number of complementary techniques that have been used to document the changes in the volatile components occurring upon injury of a tree. Wide variations in the composition of the major volatile monoterpenes between individual trees made comparisons difficult. Trees were selected that appeared to be similar in initial volatile composition so that changes occurring could be documented on two individual trees using the techniques available.

Bannister [217] compared the volatile components of 189 trees of Pinus radiata in several locations in New Zealand and California and found a wide variation in the percentage composition. The percentage of α-pinene varied from 12.6 to 58 percent. The total of α plus β-pinene was of the order of 98 percent. Other indentified components were camphene, limonene and β-phellandrene. Previous work by Mirov [218] had identified many of the other major constituents of various pines including radiata.

Damage to Pinus radiata by the introduced Sirex noctilio wasp prompted investigations into the volatiles of damaged trees by Simpson and McQuilkin [219] who noted only minor changes in composition with time after felling of the tree, even though the attractiveness changed markedly over the first three weeks. The authors of this paper trapped the volatiles from sawn logs, with ends sealed, by cryogenic traps, and noted the change in response of components by the antenna of S. noctilio. The individual volatile components identified were α -pinene, camphene, β-pinene, sabinene, mycrene, 3-carene, limonene ,β-phellandrene, γ-terpinene, ρ-cymene, terpinolene as well as camphor, pinocamphone, isopinocamphone and trans pinocarveol. Tentatively identified were fenchone, terpinen-4-ol, thymol methyl ether, borneol and citronellol.

Work done by Madden [220] showed that the timing and duration of attack of S. noctilio correlated with the degree of stress undergone by the host tree. Felling of a tree induced immediate attack with susceptibility for approximately 14 days. Girdling was correlated with attack 9 to 12 days later, but susceptibility remained for an extended period i.e. over one season. It was thought that debilitation of the tree and the reduction of soluble solids caused the release of the attractant from the cambiumphloem region. Injection of mucosecretion by the female wasp appeared to worsen the initial stress condition and result in attacks by more females. Stress induced changes altered the tissue permeability and increased the rates of

monoterpene and water vapour loss through the bark [221]. Additional work has been undertaken in this project to confirm this finding and to identify and quantify some of the terpenes.

Alterations in tree chemistry of attacked and unattacked P. radiata are also given by Hillis and Inove [222] who observed changes in the composition of polyphenols in sapwood, knotwood and heartwood. Ethylene has been reported to be released in larger quantities and to correlate with polyphenol production of an injured tree [223].

Sampling and Analytical Methods

The Pinus radiata trees used for the experimental work were situated in a forest at Pittwater, Tasmania. The group of trees selected was a closely planted (1-1.5m) trial plot 15 years old.

Mass spectral information, together with relative retention times on two different capillary gas chromatography columns, was used to identify most of the components in the volatile oil and headspace gas samples. Comparison of the information with literature values and with authentic standards served to confirm the identity of all but a few of the components isolated. OV101 and Carbowax 20M were the two liquid phases used in the 50M silica GC capillary columns. Conditions of operation are set out in Table XXII.

Gas Chromotography

Column	OV101	CW20M
Type	Scot (silica)	Scot (glass)
carrier flow (ml/min)	1.0	1.5
carrier gas	hydrogen	hydrogen
Initial Temp. (deg.C)	50	50
Final Temp. (deg.C)	200	200
Temp. Prog. Rate (deg.C/min)	4	4
Injector Temp. (deg.C)	240	240
Detector Temp. (deg.C)	250	250
Inj. Vol. (microliters)	0.05	0.05
Detector	FID	FID

Gas Chromatography/Mass Spectrometry

GC Column	OV101 (silica)
Interface Temp. (deg.C)	250
Mode	Electron Impact 70 Ev
Scan Rate	1 second per decade
Mass Range	20-350

Table XXII. GC and GC/MS Operating Conditions.

A. The Composition of the Steam Volatile Components From the Bark Oil of P. radiata.

Earlier work by Simpson and McQuilkin [224] had established the occurrence of fifty components in the steam distillate of the bark oil. However, it was felt necessary to document these components using the GC and GC/MS facilities presently available. A section of the bark-phloem was carefully removed from a number of trees and 500g was broken up into small pieces and steam distilled. The yield was 0.3 percent.

High resolution gas chromatography using the OV101 and CW20M silica capillary columns indicated the presence of the two major peaks, α and β pinene, and a number of smaller component peaks.

The flame ionisation detector trace for OV101 is shown in Figure XXXIV. The GC/MS total ion current trace for the equivalent CW20M trace is shown in Figure XXXV. Scan numbers and peak identity information is shown in Table XXIII. A number of minor components were not identified but mass spectral information and the relative retention index was determined for each component. Elution order of some components did not always agree with the literature values [212] but a slightly higher programming rate and changes in the retention properties, (especially of the CW20M), could account for the discrepancies.

Identity	% Composition	Scan No.	Ret. Index	Base Peak	Parent Peak
α-pinene	32.8	154	1023	93	136
camphene	0.5	176	1075	93	136
β-pinene	55.2	205	1120	93	136
pinane ?	0.1	226	1140	95	138
Δ_3 carene	0.9	231	1145	93	136
myrcene	1.8	240	1150	93	136
cymene (type)	0.1	249	1175	119	
limonene	2.4	257	1195	68	136
dodecane	0.1	271	1200	57	170
β phellandrene	0.4	273	1215	93	136
unknown	0.1	278	1220	71	154
m cymene	<0.1	313	1265	119	134
ρ cymene	0.2	321	1270	119	134
α terpinolene	0.1	329	1285	121	136
C_{13} hydrocarbon + unknown	<0.1	349	1300	57	184
myrtenol	<0.1	371	1335	79	152
unknown mixt	0.1	396	1365	97	154
cymene (type)	<0.1	403	1375	119	134
unknown	0.2	416	1390	67	152
bornyl acetate	0.1	430	1405	95	158
fenchone	0.1	438	1410	81	152
α-dimethylstyrene	0.1	466	1450 *1278	132	132
unknown sesquiterpene	<0.1	495	1485	119	204
α copaene	<0.1	518	1520	161	204
dimethylstyrene plus unknown	<0.1	523	1525	117	204
iso pinocamphone	0.2	549	1545	83	152
pinocamphone	0.1	575	1580	83	152
linalool	0.1	579	1585 *1506	71	154
unknown sesquiterpene	<0.1	588	1595	161	204
iso borneol	<0.1	601	1605 *1660	95	-
fenchol	0.4	608	1015 *1575	81	204
6 tert. butyl cresol	<0.1	614	1620	149	164
terpinene-4-ol	0.1	628	1630	71	154

cont...

myrtenal	→0.1	651	1660	79	150
transpinocarveol	0.8	678	1690	no spectra printed	
borneal plus unknown	0.1	683	1700	95	-
			1728		
α terpineol	0.6	714	*1661	59	not present
muurolene	<0.1	728	1730	105	204
Δ cadinene	<0.1	755	1760	161	204
unknown	0.3	795	1810	79	152
calamenene	<0.1	819	1840	159	204
ρ cymene-8-ol	0.1	840	1850	135	150

* represents literature values.

Table XXIII. Mass Spectral and Retention Index Identification Data for Whole Bark Oil Distillate P. radiata. CW20M Capillary Col. 50-200 deg. C. 4 deg./min.

Table XIII lists over forty components in the steam distillate of the bark oil from P. radiata. Twenty or so other components were noted in varying trace concentrations. Many of these were not adequately resolved on either the OV101 or CW20M columns, and rearrangements to isomers would probably occur on separation. This work has substantially confirmed the results of Simpson and McQuilkin [224].

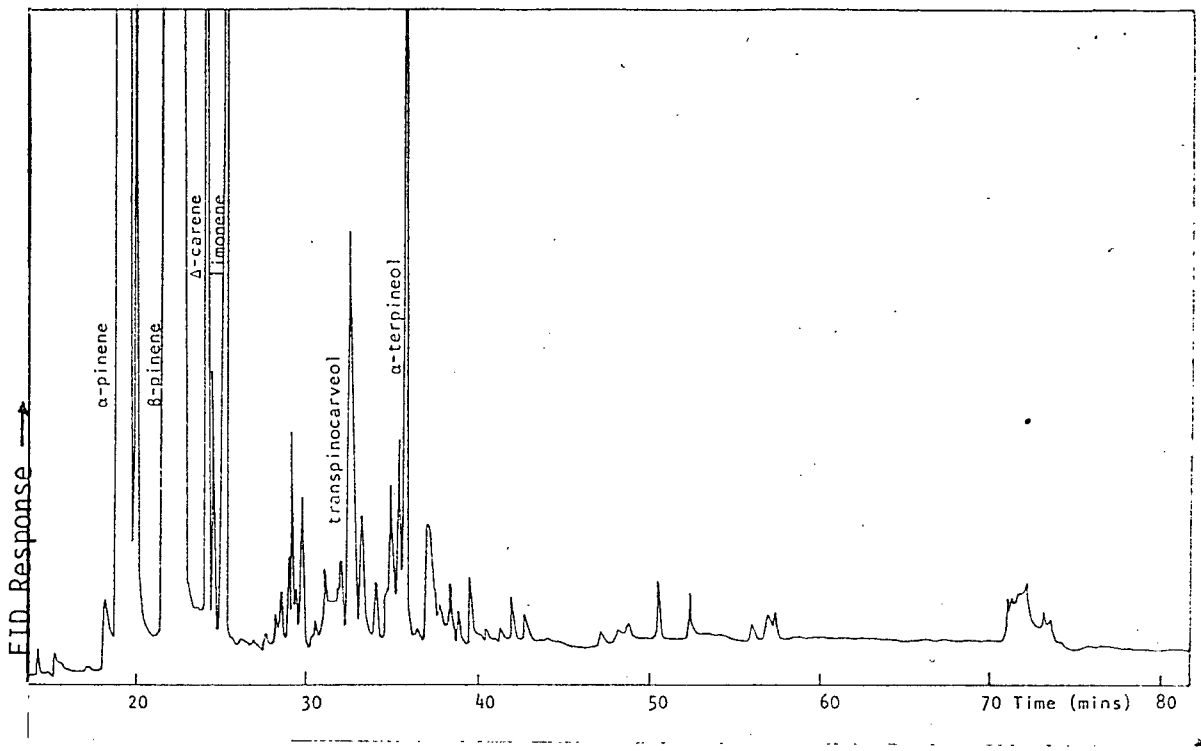


Figure XXXIV. GC Trace Bark Oil P. radiata OV101 Capillary Col. 50-200 deg. C at 2 deg./min.

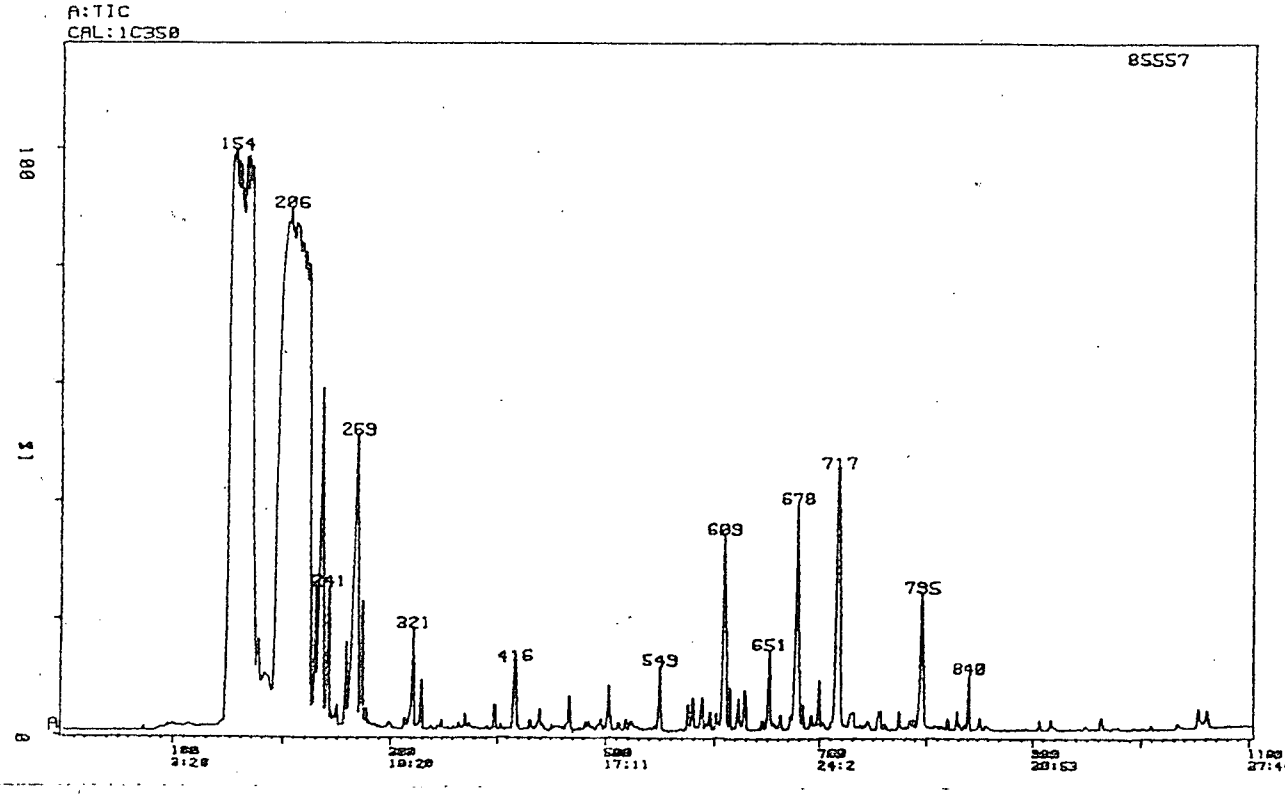


Figure XXXV. TIC Trace Bark Oil P. radiata CW20M Capillary Col. 50-200 deg. C at 4 deg./min. Peak Identification Table XXII.

B. Collection of Headspace Samples From The Bark of *P. radiata*.

Collection and trapping of the volatile components emitted from the bark were undertaken by placing a Polythene sheet collection bag round the tree and drawing the headspace through a Tenax sample tube to collect the components.

Each trap consisted of three pieces of 40mm wide aluminium strip bent so that the upper and lower ends rested against the trunk and the centre section stood away 100mm thus providing an annular space to collect the volatiles.

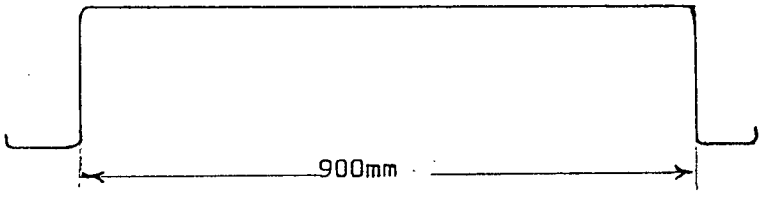


Figure XXXVI. Aluminium Framework for Headspace Trap.

The three aluminium strips were placed round the tree at 120 degree intervals and polythene film was wrapped round the outside and held in position by rubber straps and a bolted cover strip over one of the aluminium supports. Large 16mm dia. bolts with 4mm centre tapped holes, held the cover strip in position and at the same time allowed access to the headspace inside the polythene. The centre hole was plugged by a small threaded brass bolt before and after sampling.

Placement of the traps round the tree was undertaken 24 hours before sampling of the headspace commenced. Headspace

sampling was undertaken by attaching a 170mm long glass tube filled with previously conditioned Tenax GC to the 16mm dia. bolt with a suitable length of Teflon tubing. The centre 4mm bolt was removed and the glass tube butted up to the hole through to the airspace between the polythene sheet and the trunk. Air was drawn through the Tenax at a constant flow rate by regulating a needle valve in the gas stream before the air pump.

Prior to the placement of polythene sheet headspace traps round the tree, a sample of headspace from the sheet was taken by placing it in a previously cleaned large glass vessel and trapping the components given off when the vessel was warmed. The glass vessel was cleaned by heating to 600 deg.C and then allowed to cool. Polythene sheeting was placed loosely in the vessel and the volatiles adsorbed by withdrawing air from the vessel through a Tenax trap. Dry high purity nitrogen was admitted to the vessel via another Tenax tube. This blank run was made in order to characterise any components that may have resulted in using polythene as a containing medium for plant volatile headspace traps.

Considerable quantities of volatile material were emitted by the polythene sheet (Figure XXXVII) and the mass spectra and retention times for the major peaks were recorded for future reference.

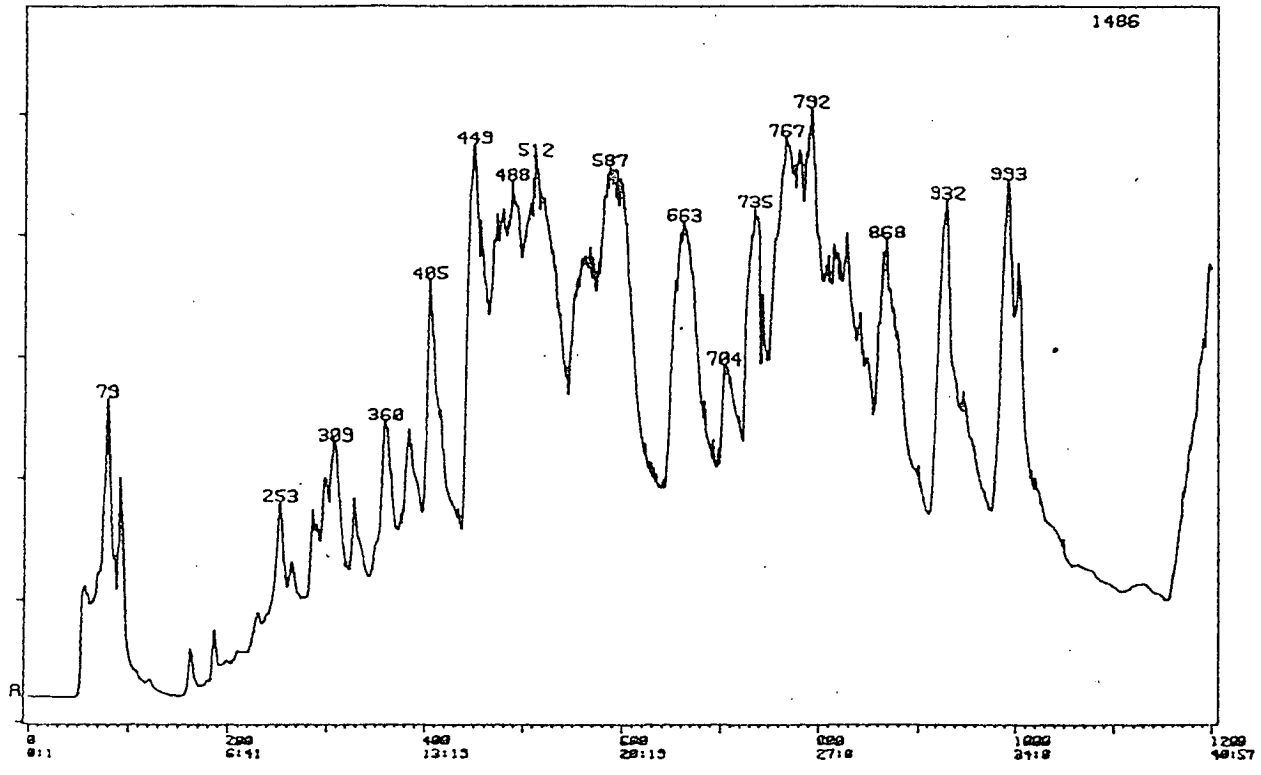


Figure XXXVII. TIC Trace of Sheet Polyethylene Volatiles.
OV101 Capillary Col. 50-200 deg. C at 4 deg./min.

C. A Comparison of Bark Volatiles From a Girdled P. radiata.

Examination of the volatiles emitted from the bark above and below the girdle of a standing Pinus radiata were made to document the changes that occurred when the tree was placed under stress. Samples of the headspace and bark oil were collected and a moisture trap was used to determine the transpiration difference between the bark above and below the girdled section of the trunk.

The tree selected was 15 years old and 160mm in diameter at the girdling point. A 50mm wide ring of bark was removed from the trunk 2m from the ground and the headspace traps were placed round the trunk immediately above and below. A 14 day time interval was allowed between girdling the tree and the sampling of the headspace as this marks the initial stage of attractiveness for S. noctilio.

Headspace from the trunk above and below the girdle of a Pinus radiata tree was examined by adsorbing the volatiles on a Tenax sample tube and GC and GC/MS techniques were used to identify the components.
The samples were collected in early March 1981 just before the end of a relatively dry summer period. A previously dried and weighed copper sulphate tube placed in series with the Tenax trap allowed the water transpiration of the two sections of the trunk to be calculated. Air was withdrawn at a rate of 41mL/min for two hours i.e. a total volume of 4.92L.

The volume of headspace round the trunk enclosed by the polythene sheet was calculated to be 9.99L. The copper sulphate tube was in series for 1 hour and therefore the volume of moist air was 2.46L in each case. Moisture adsorption above girdle was 0.0096g and below girdle was 0.0137g, or expressed in terms of area of bark 12.5 and 21.6 mg. m^{-3}. h^{-1}. These figures are in agreement with the findings of Madden [221] although a slightly different technique was used to measure the rate of water loss.

Following the removal of the headspace trapping framework from the tree, sections of bark from above and below the girdle were removed for distillation of the steam volatile oil. A comparison of the composition of the two oils may provide an indication of changes that occur in conjunction with the volatiles released through the bark.

Traces of the GC run on the two samples of distilled bark oil are shown in Figures XXXVIII and XXXIX. The runs were conducted at relatively high sensitivity (full scale deflection representing 0.2 percent of the mixture), to highlight the differences in the oil. Identification of a number of the peaks was not possible due to very small quantities present and the inability to separate sufficient quantities for confirmatory MS or infrared spectra. Peak numbers and where possible identification information are set out in the following table (Table XXIV).

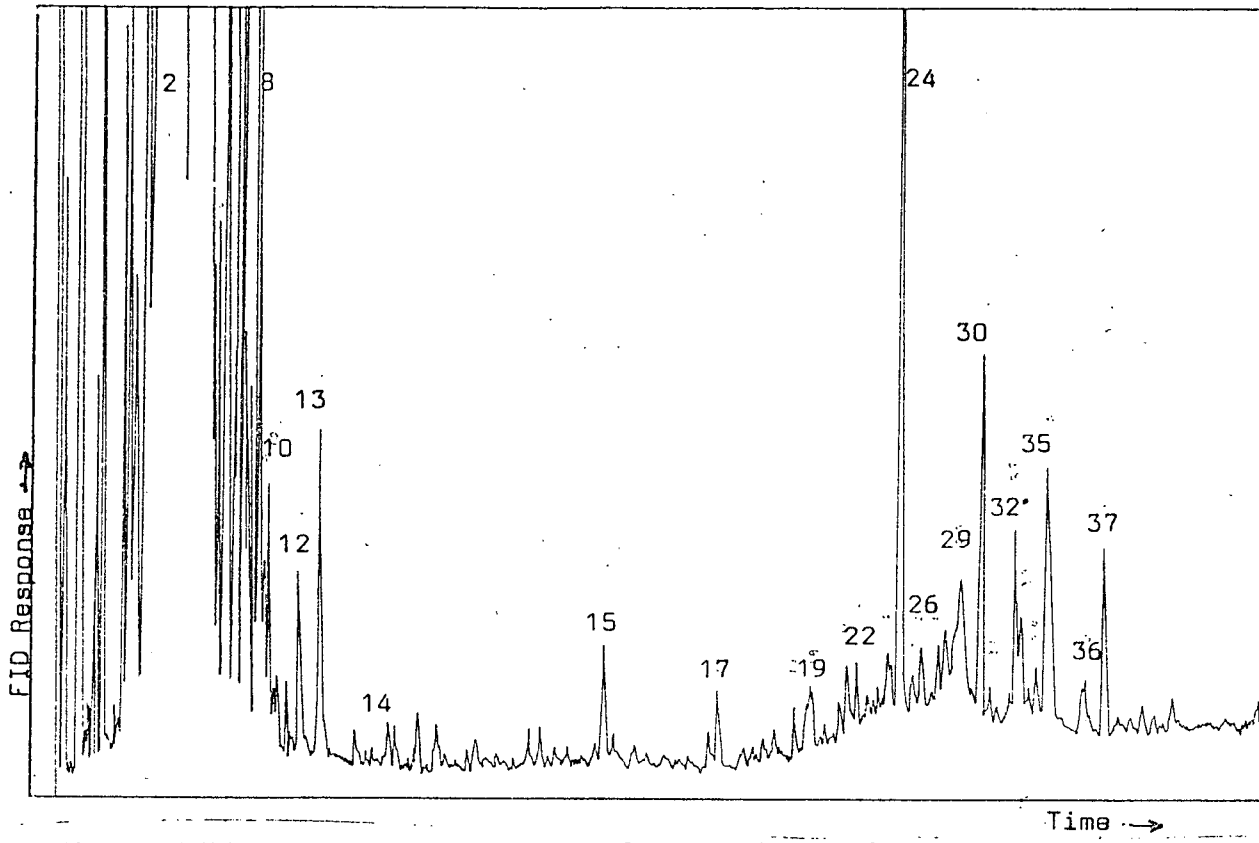


Figure XXXVIII. GC Trace of Bark Oil P. radiata Below Girdle.
OV101 Capillary Col. 50-200 deg. C. at 2 deg./min.

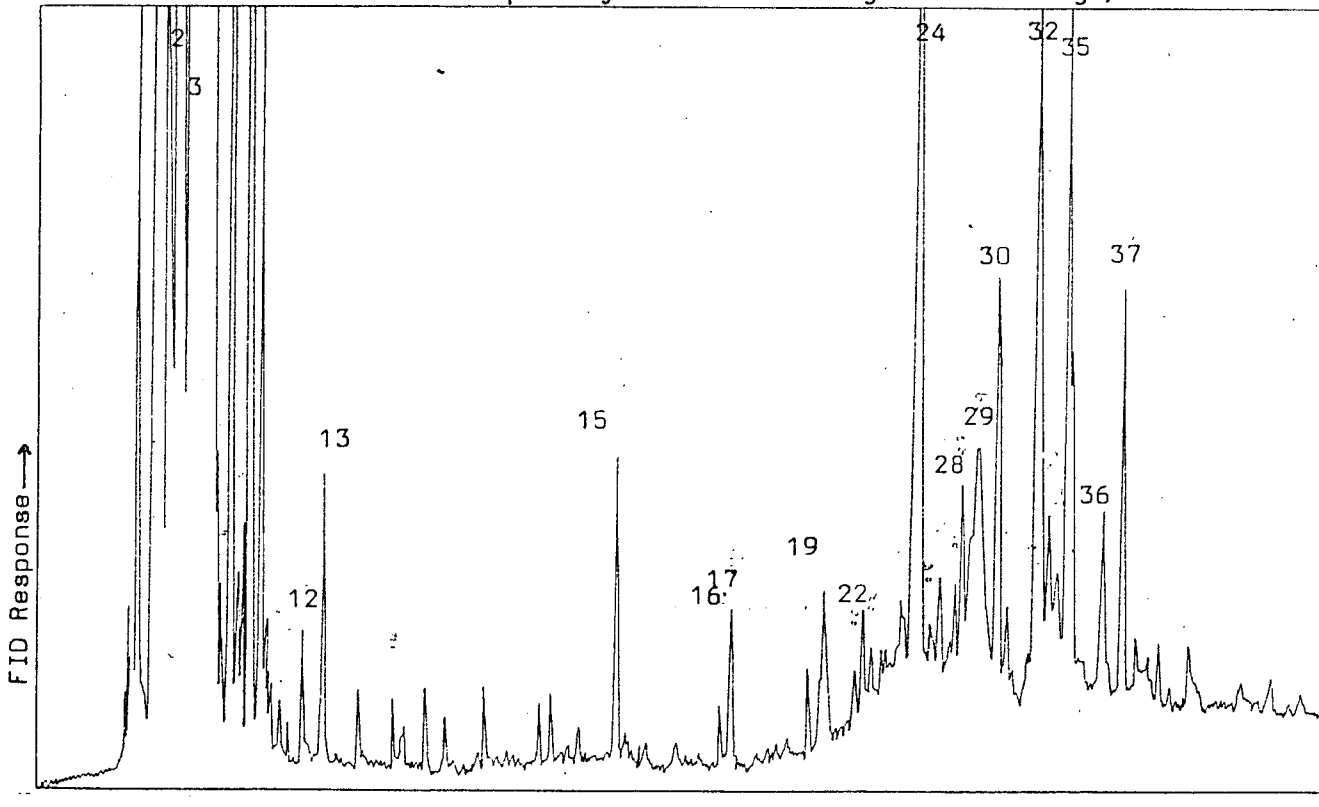


Figure XXXIX. GC Trace of Bark Oil P. radiata Above Girdle.
OV101 Capillary Col. 50-200 deg. C. at 2 deg./min.

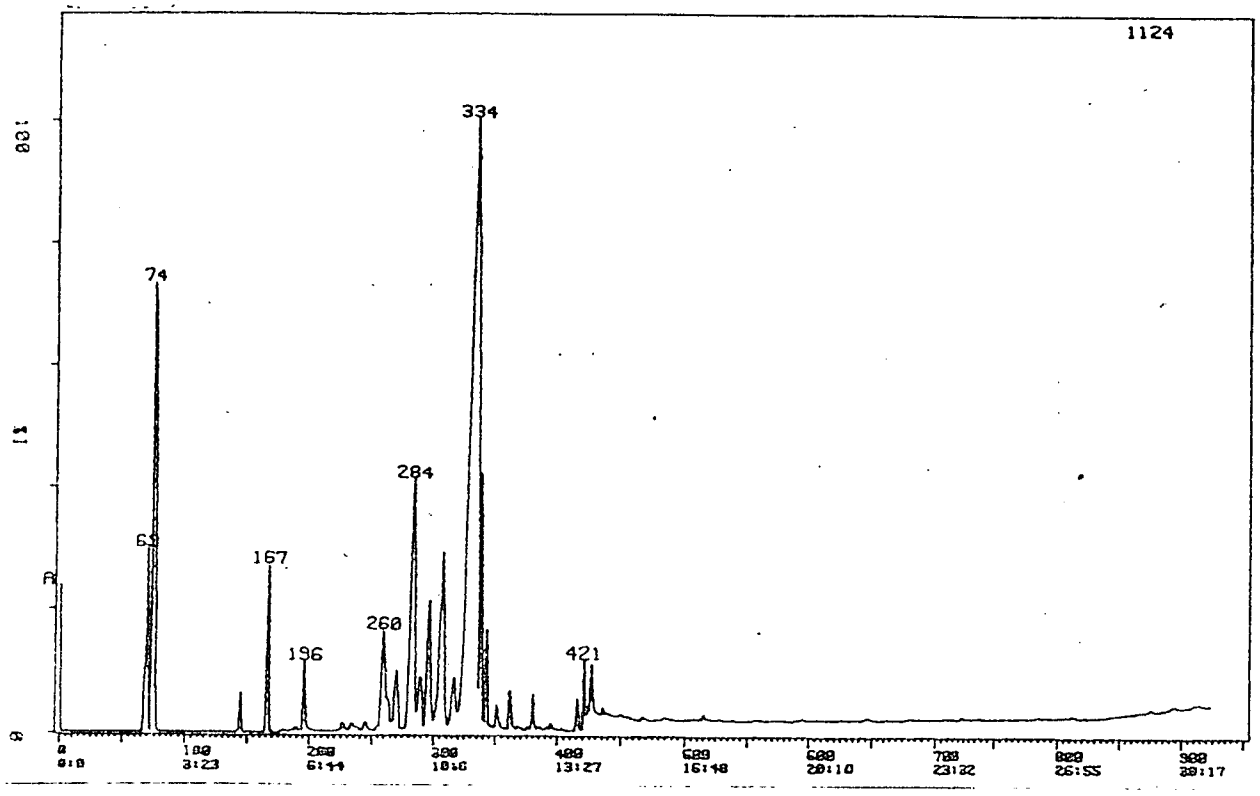


Figure XL. TIC Trace of Bark Oil P. radiata Below Girdle.
OV101 Capillary Col. 50-200 deg. C. at 4 deg./min.

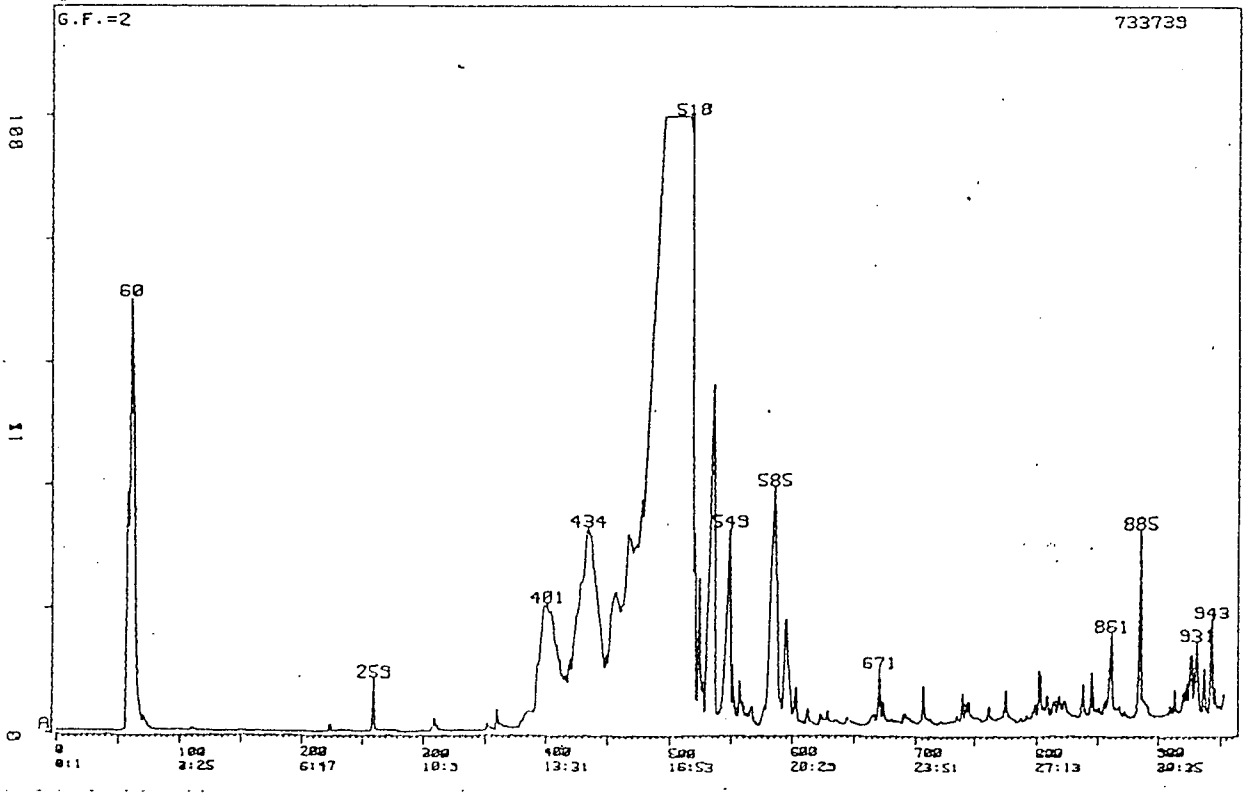


Figure XLI. TIC Trace of Bark Oil P. radiata Above Girdle.
OV101 Capillary Col. 50-200 deg. C. at 4 deg./min.

Peak No.	Identify	Rel.Ret. Time	Percentage Composition Below Girdle	Above Girdle
1	tricyclene ?	0.974	4.8	3.0
2	∝-pinene	1.000	28.9	16.1
3	β-pinene	1.056	57.8	66.8
4	pinane	1.077	0.3	<0.1
5	myrcene	1.090	1.2	1.2
6	βphellandrene	1.103	0.7	<0.1
7	limonene	1.114	1.3	2.3
8	?	1.132	1.1	0.7
9	?	1.146	0.1	<0.1
10	?	1.159	<0.1	<0.1
11	fenchone	1.177	<0.1	<0.1
12	?	1.188	<0.1	0.1
13	fenchol	1.219	0.2	0.2
14	?	1.325	<0.1	0.1
15	?	1.627	<0.1	0.2
16	?	1.772	<0.1	<0.1
17	?	1.786	<0.1	0.3
18	?	1.900	<0.1	<0.1
19	transpinocarveol	1.922	0.1	0.3
20	?	1.963	<0.1	0.1
21	borneol	1.976	<0.1	0.1
22	?	1.988	<0.1	<0.1
23	terpinene-4-ol	2.031	<0.1	0.1
24	∝ terpineol	2.050	0.6	1.8
25	myrtenol	2.067	<0.1	0.1
26	verbenone	2.081	<0.1	0.3
27	?	2.107	<0.1	0.3
28	citronellol	2.115	<0.1	0.6
29	mixture	2.139	0.3	1.1
30	?	2.169	0.3	0.4
31	?	2.219	<0.1	0.3
32	thymol (or carvecrol)	2.227	0.2	1.2
33	?	2.238	<0.1	0.5
34	?	2.249	<0.1	<0.1
35	?	2,264	0.2	1.1
36	?	2.317	<0.1	0.6
37	?	2.344	0.1	0.4
Other			0.3	0.4

Table XXIV. Peak Numbers and Percentage Composition of Steam Distillate of Bark Oil Below and Above Girdle of Pinus radiata.

The bark oil below the girdle contained a larger proportion of the more volatile components but generally, the two oils were very similar in the oxygenated and sesqui-terpene regions of the trace. The oil below the

girdle contained a slightly larger quantity of solvent hence the relative difference in peak area ratios in the traces.

Quantitative interpretation of the results on the basis of the one set of samples is suspect and further samples would be required to confirm any differences such as the apparent increase in relative concentrations of the oxygenated sesqui-terpenes eluting towards the end of the chromatogram in Figure XXXIX.

Comparison of the GC traces of Figures XXXVII and XXXIX with the corresponding GC/MS traces (Figures XL and XLI) reveals loss of the α and β-pinene and early monoterpene components, and a massive increase in the relative proportion of α terpineol. This may be due to the use of a splitter in the inlet of the GC/MS unit reducing the amount of volatile components reaching the inlet of the GC column, or to evaporation during sample transfer operations. The initial percentage composition figures shown in Table XXIV represent an accurate reproduceable comparison of the bark oils as three sampling runs showed only small variations.

Ten microliters of Freon (dichloro difluoromethane) was injected into the headspace, prior to sampling, to act as an internal standard. In each case the recovery of the added solvent was within acceptable limits (90 percent for headspace components above the girdle and, 86 percent for headspace components below the girdle).

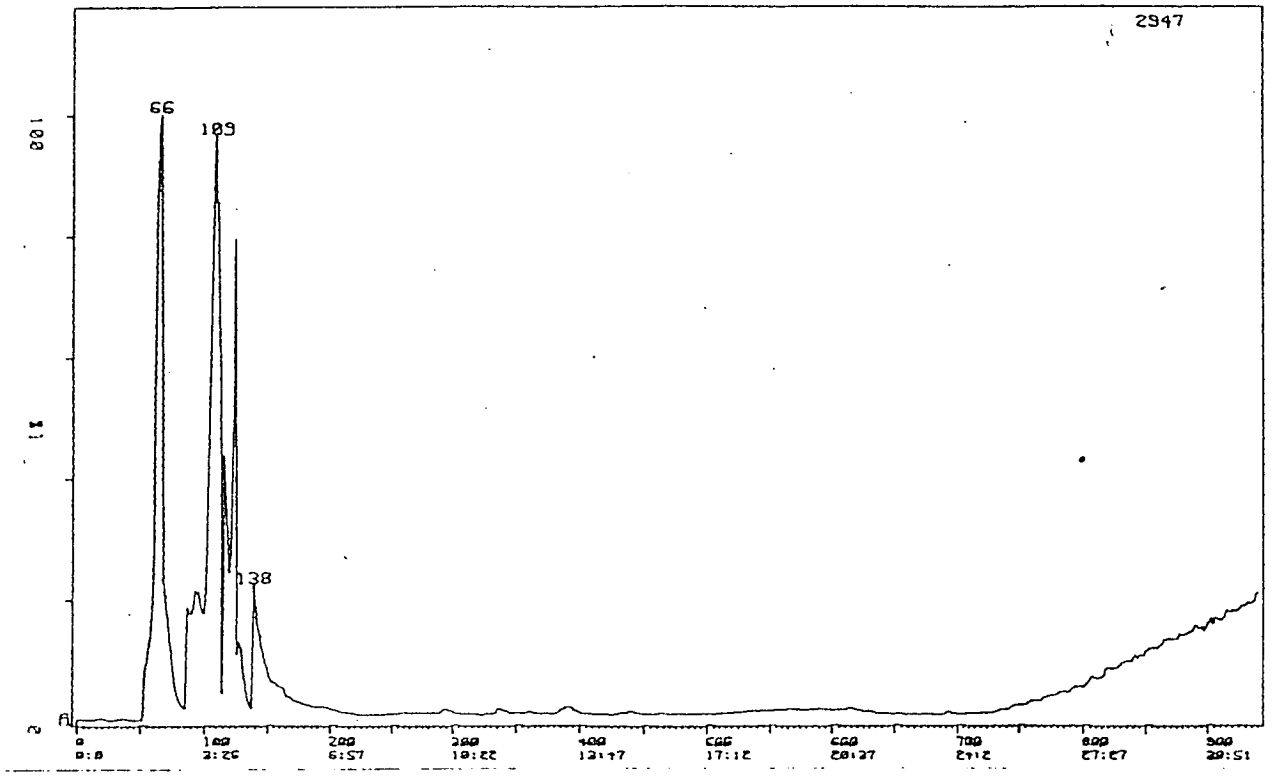


Figure XLII. TIC Trace Headspace P. radiata Below Girdle.
OV101 Capillary Col. 50-160 deg. C. at 4 deg./min.

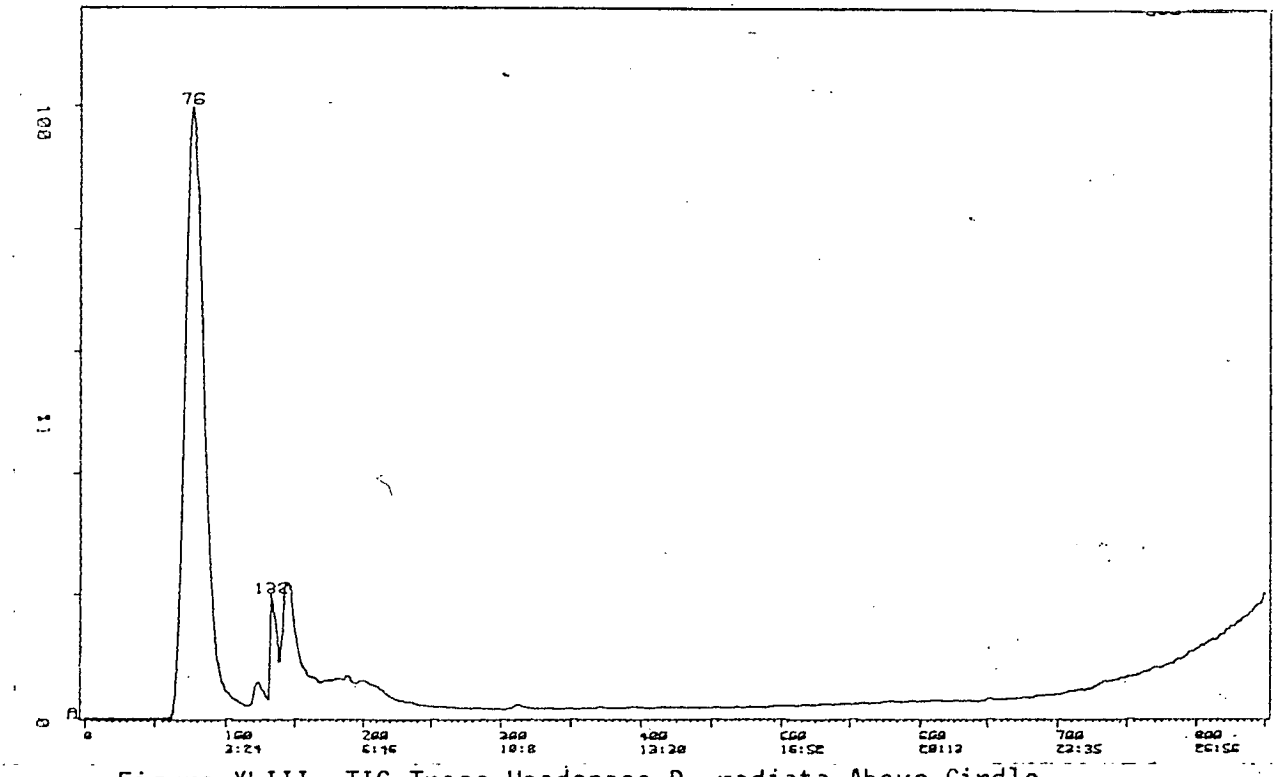


Figure XLIII. TIC Trace Headspace P. radiata Above Girdle.
OV101 Capillary Col. 50-160 deg. C. at 4 deg./min.

The volatile headspace TIC trace for components trapped from the bark below and above the girdle are shown in Figures XLII and XLIII. The traces show very few differences in the qualitative composition of the volatiles. Each sample was collected under identical conditions (2 hours sampling time at the same flow rate of 'dry' air), and quantitative measurements show that the amount of volatiles released from the bark above the girdle was greater than the amount released from below. This result in apparent contradiction with the composition of the oil distilled from the bark as shown in Table XXIV. Table XXV details the quantitative information determined from GC runs on duplicate headspace samples and related back to the MS traces.

Component Identity	H/S Below Girdle Scan No.	% Comp.	H/S Above Girdle Scan No.	% Comp.
tricyclene ?	198	0.1	220	0.8
∝-pinene	307	29.4	229	27.3
camphene	317	1.0	235	2.9
/3-pinene	352	68.0	261	58.0
myrcene	nd	-	279	0.6
limonene	398	1.1	293	2.1
Other		0.4		8.3

Table XXV. Percentage Composition and Component Identification P.radiata Headspace Above and Below Girdle.
nd - not detected

The trace components present in the headspace were difficult to identify due to the large proportions of ∝ and /3 - pinene. A greater number of components were present in the headspace from above the girdle, however many were present at a level below the detection limit of the GC/MS.

Attack by S.noctilio occurs in greater numbers below the girdled or injured section of a tree [220], and therefore, the attractive component, if such a component exists may be present at a very low concentration. Alternatively, the presence of oxygenated components may act as a repellent to the insect and reduce the incidence of attack above the girdled section of the tree [225]. Headspace sampling using porous polymer trapping techniques may not provide sufficient capacity to trap low concentration components ($\lesssim$0.1%) in the presence of massive quantities of other components.

D. Composition Changes of Bark Headspace of P. radiata.

Changes in the volatile components emitted from the bark of a number of trees were examined using a gas tight syringe and direct injection onto a packed GC column. Wide variations in the quantitative composition of monterpene components of P.radiata have been reported [217], and bark samples were collected from 7 trees of similar age and appearance to determine the range of the two major components.

A 50mm wide section of bark was removed from round the circumference of each tree and placed in a glass jar fitted with a lid containing a rubber septum. The containers were immediately taken to the laboratory and heated to 40 deg.C and 4mL of the headspace was injected onto a 2m CW20M packed GC column. The FID traces of the 7 samples recorded at an isothermal column temperature of 60 deg.C are presented in Figure XLIV. Peak identities and concentrations are recorded in Table XXVI.

After 6 and 14 days, aditional headspace samples were taken for analysis using the same method as outlined above. The traces recorded on the sixth day were similar to the ones illustrated in Figure XLIVa however marked changes had occured by day fourteen. Rearrangement of α-pinene to tricyclene had occured with many of the bark samples in the closed glass container [226],(Figure XLV).

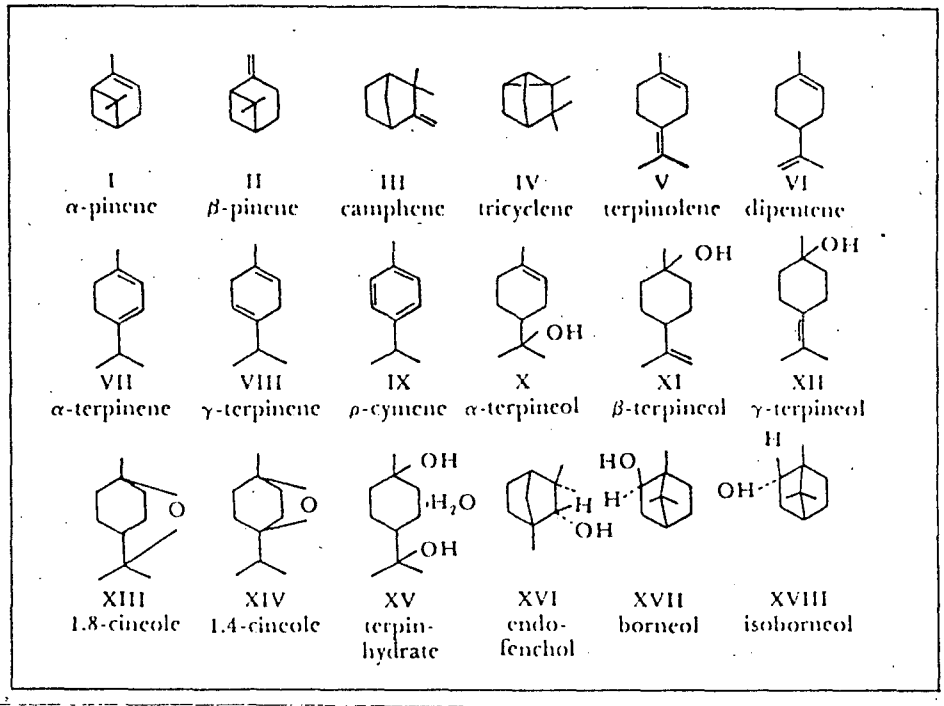


Figure XLV. Terpene Products Resulting From Hydration and Isomerisation of ∝-pinene [226].

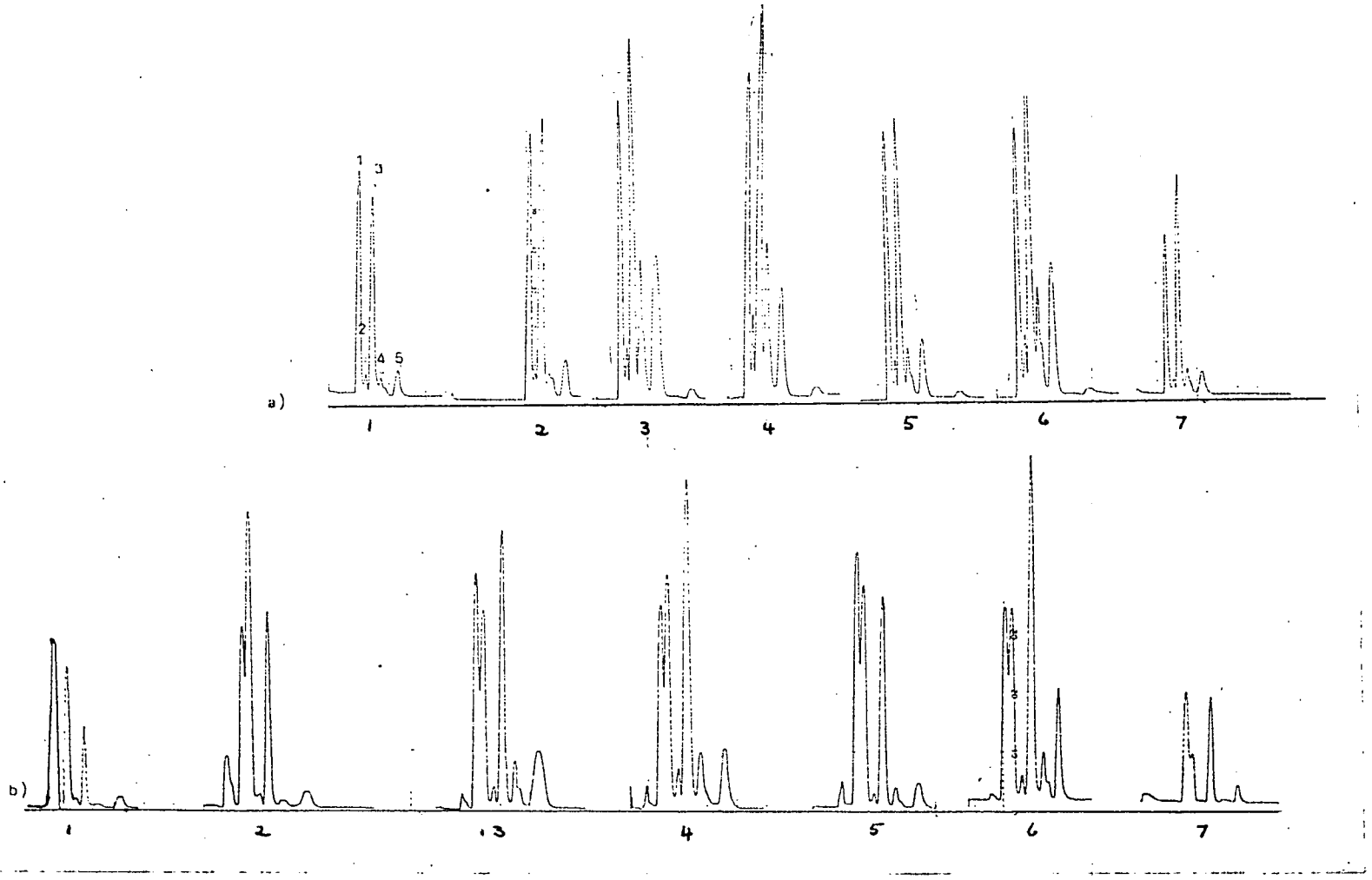


Figure XLIV. P. radiata Bark Headspace. 4mL direct injection on CW20M packed col.
a) Day 0. b) Day 14.

Component	Tree Number 1	2	3	4	5	6	7
1. α-pinene	42.3	36.1	24.5	26.3	34.1	23.7	31.4
2. camphene	3.4	3.8	3.3	4.9	3.9	4.1	2.9
3. β-pinene	41.3	38.0	32.5	37.9	39.4	38.6	48.5
4. myrcene	1.8	12.0	13.8	13.9	6.3	12.5	5.7
4a. unident.	0.4				2.1		1.7
5. limonene	8.0		23.4	13.4	11.6	18.6	9.2

Table XXVI. Percentage Composition of Headspace from Samples of P.radiata Bark. CW20M Packed GC Col.

Trees 5 and 2 selected for the previously described headspace work, and samples of the headspace were collected from above and below the girdle by filling a Teflon gas sample bag. Direct injection of 4mL samples of headspace onto the packed CW20M column confirmed the higher rate of release of monoterpenes from the bark above the girdle (Table XXVII).

Component	H/S Above Girdle Peak Area	% Comp.	H/S Below Girdle Peak Area	% Comp.
Unknown	1234	4.6	1043	20.7
α-pinene	10249	38.4	1094	21.8
camphene	632	2.4	1167	23.2
β-pinene	14565	54.6	1721	34.2

Table XXVII. A Comparison of Peak Areas (arbitary units) and Percentage Composition of Headspace Components Collected by Gas Sample Bag from P.radiata.

The relative error for the headspace sample collected from below the girdle would be high due to the small peak heights (Figure XLVI), but serve as an indication of the proportions of volatiles released.

CHAPTER VII

CONCLUSIONS

Techniques have been described for the sampling and identification of trace amounts of volatile organic compounds from natural products and air samples. Tenax has proved to be a versatile trapping medium for the collection of a wide range of organic compounds from gases to high molecular weight terpenes. The equipment used to trap the volatile components is relatively simple; consisting of a Tenax sample collection tube, a flowmeter and an air pump; thus enabling the collection of samples in field situations. The quantity of material trapped can be controlled by the volume of air passed through the trap, up to the point where breakthrough of the most volatile component occurs. This point is determined by conditions such as the temperature, flow rate, and chemical nature of the component, and can be monitored by the use of a second back-up sample tube in series with the first.

Limitations of the sample collection procedure include the early breakthrough of some low molecular weight gases, and the difficulties associated with the detection of trace quantities of components in the presence of large quantities of material eluting at the same time. The selection of other trapping mediums with different polarities and the use of subambient temperature programing on a GC would assist in overcoming some of the above problems.

Desorption of trapped components by heating and secondary trapping within a U tube enables optimium introduction of the sample onto the GC column using flash injection techniques. To prevent thermal degradation of the sample, elution temperatures and times need to be monitored to ensure adequate recoveries with minimum alteration of labile components.

The quantitation of components in complex mixtures of volatile unknowns presents problems. The adsorption and desorption efficiency of each component will vary according to the concentration of other components in the mixture and the chemical nature of the adsorbent, as well as on other factors such as flow rate and temperature. Tenax provides a versatile trapping medium for many complex mixtures and quantitation may be achieved using addition techniques for components of interest.

Identification of separated components was generally carried out "on the fly" using GC and GC/MS techniques as there are considerable difficulties involved in collecting the microgram to low nanogram quantities of material separated by the high resolution capillary GC columns, and performing off line identification. Additional spectral information was often required to complement the GC retention time and mass spectral information that was available. The introduction of a Fourier-transform infrared system coupled to the GC will assist in the confirmation of

the identity of many of the trace components detected in the samples examined in this work.

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APPENDIX

SECTION A. Paper Published During The Course of This Work.

SECTION B. Equipment Details.
Gas Chromatography Equipment.
Gas Chromatography/Mass Spectrometry Equipment Used During The Course of This Work.

SECTION C. Mass Spectral Information From GC/MS Runs (Arranged According to Chapter)

Chapter IV
Tenax Trap Volatiles.

Chapter V
Drimys lanceolata
Prostanthera lasianthos
Bronia megastigma

Chapter VI
Pinus radiata

Paper in attached pocket -
inside rear cover.

GAS CHROMATOGRAPHY

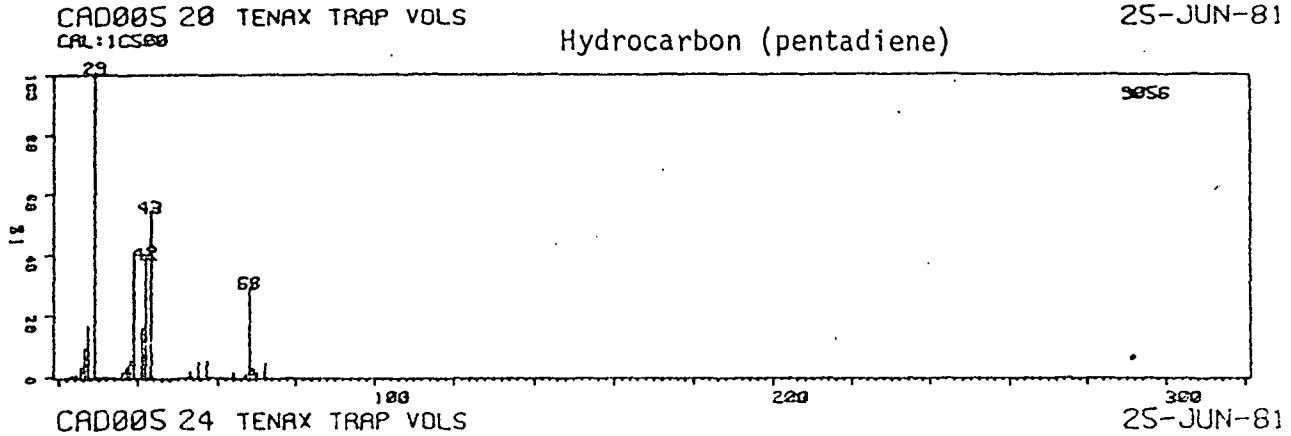
Packed column gas chromatography was performed on a Varian 3700 gas chromatograph equiped with flame ionisation detectors, and a temperature programme controlled oven. Two meter long by 4mm internal diameter glass columns were used with nitrogen carrier gas at a flow rate of 35mL per minute.

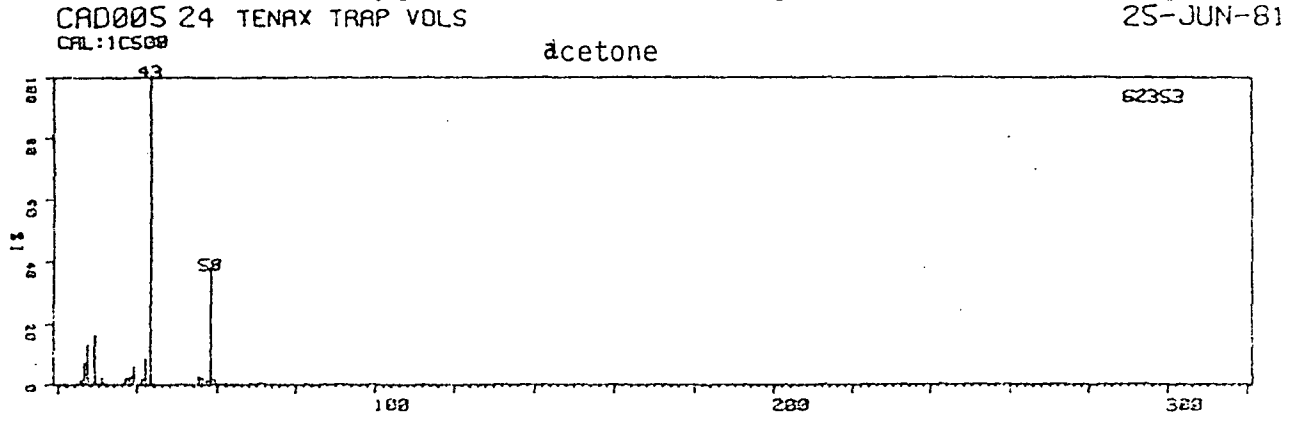
The same GC was used for capillary column gas chromatography using a SGE capillary column conversion kit to optimise gas flow.

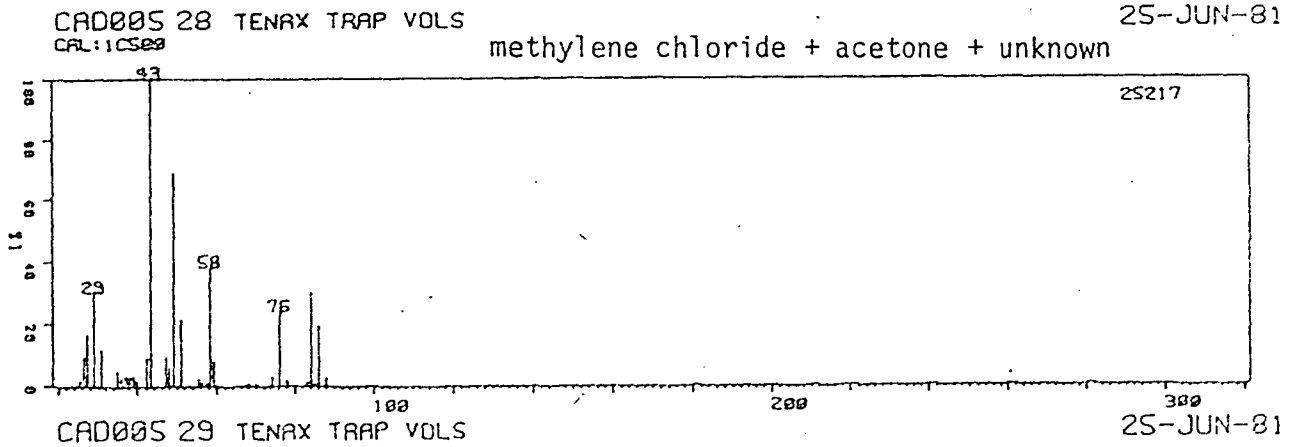
GAS CHROMATOGRAPHY/MASS SPECTROMETRY

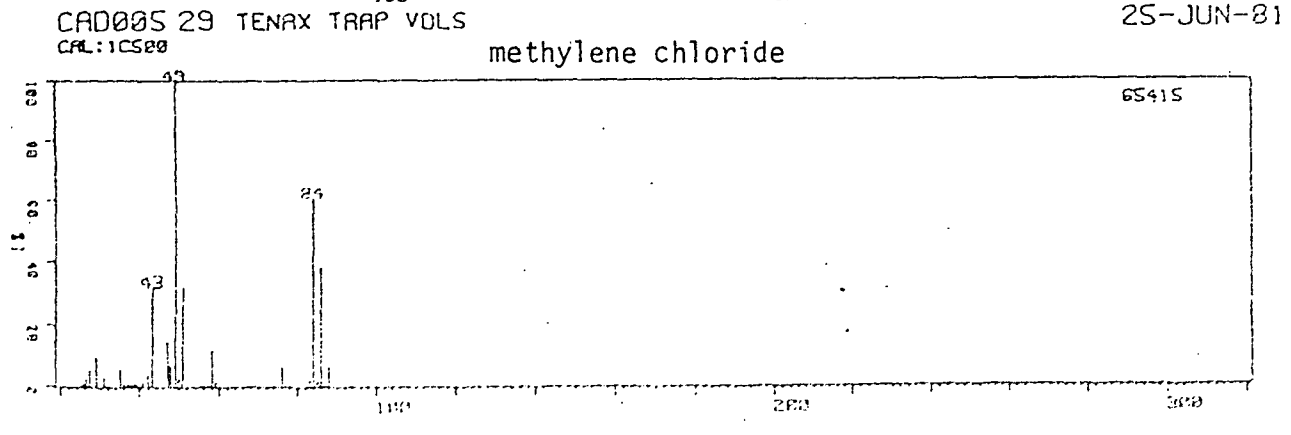
A Pye Unicam Series 204 gas chromatograph was coupled to a VG Micromass 7070F mass spectrometer via a VG jet separator (for packed column operation), and operated at a vacuum of $4*10^{-6}$ Torr. Capillary columns were coupled directly to the ion source. The system was operated at 70 EV and data was stored and processed on a VG 2235 system coupled to a PDP 8/A620 minicomputer. The electron impact (ei) mode was used on all GC/MS runs. Calibration of the system was performed by injection of fluorinated kerosene mixtures. The carrier used was either hydrogen or helium at a flow rate of 1 -1.5mL per minute.

COMPONENT MASS SPECTRA





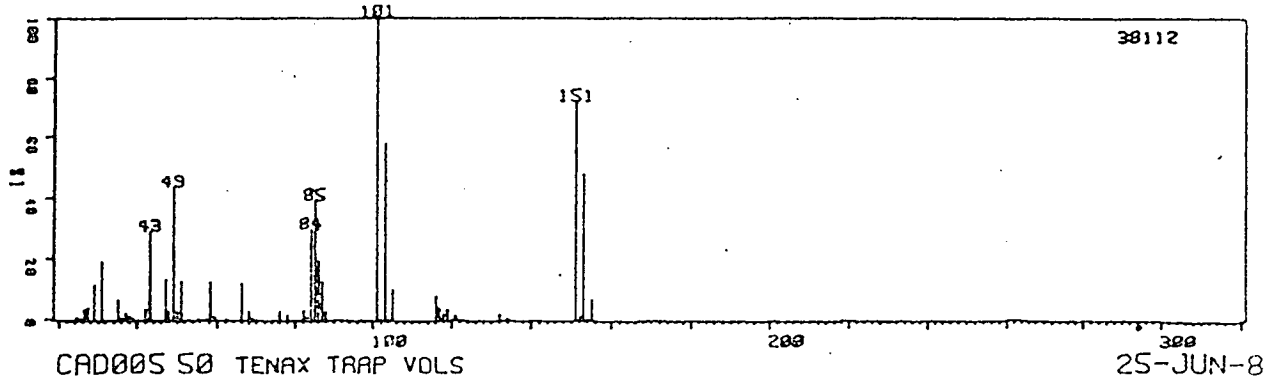




CAD005 32 TENAX TRAP VOLS
CAL:1CS00

Freon

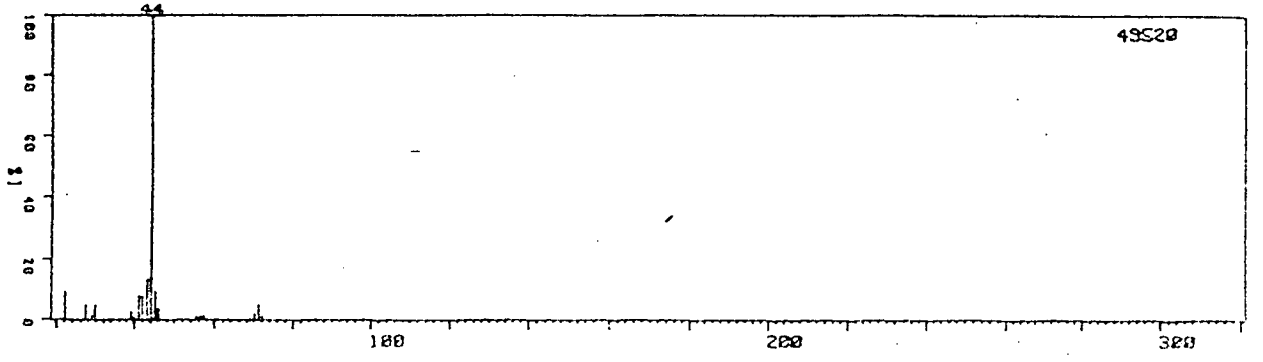
25-JUN-81



CAD005 50 TENAX TRAP VOLS
CAL:1CS00

carbon dioxide

25-JUN-81



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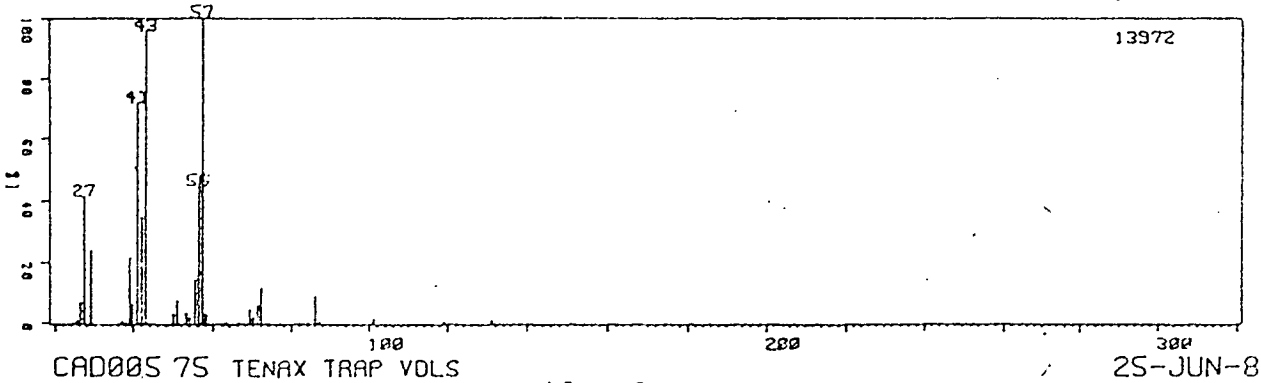
CAL:1CS00

n-pentane + methyl pentane

25-JUN-81



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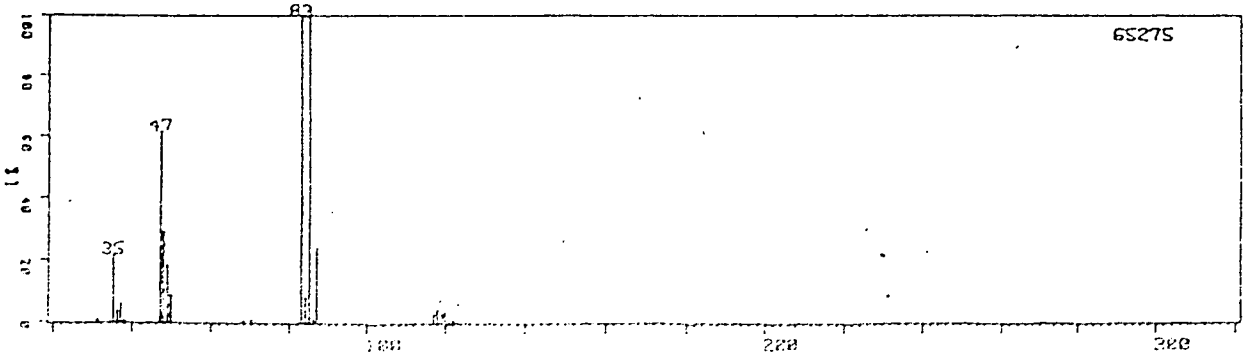
CAL:1CS00

chloroform

25-JUN-81



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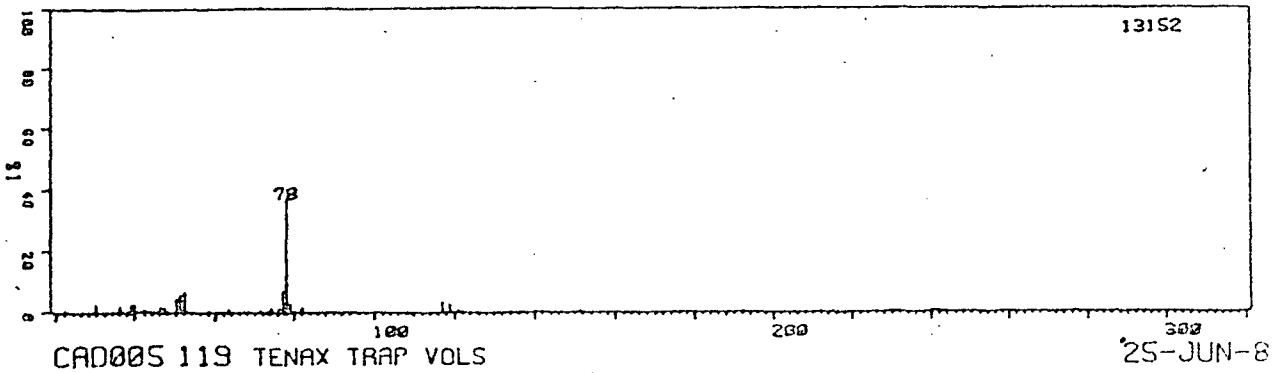
CAL:1CS00

benzene

25-JUN-81



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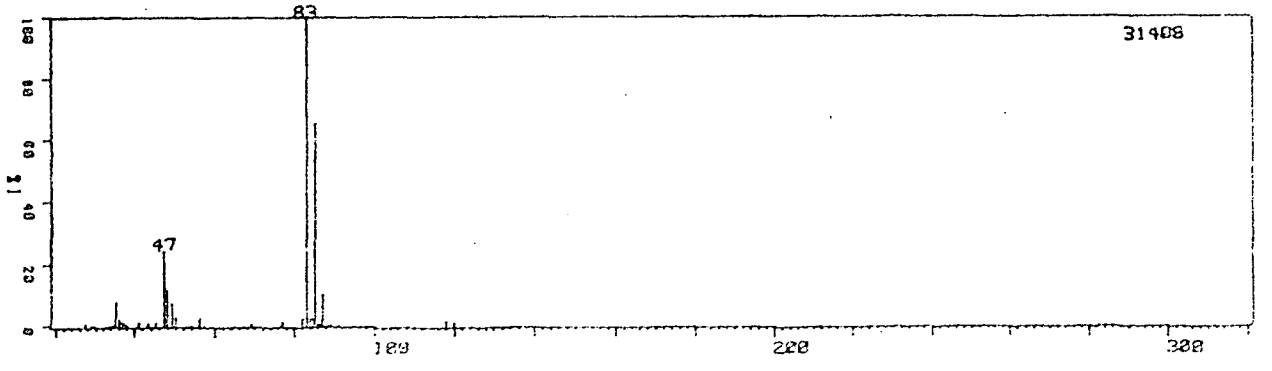
CAL:1CS00

chloroform

25-JUN-81



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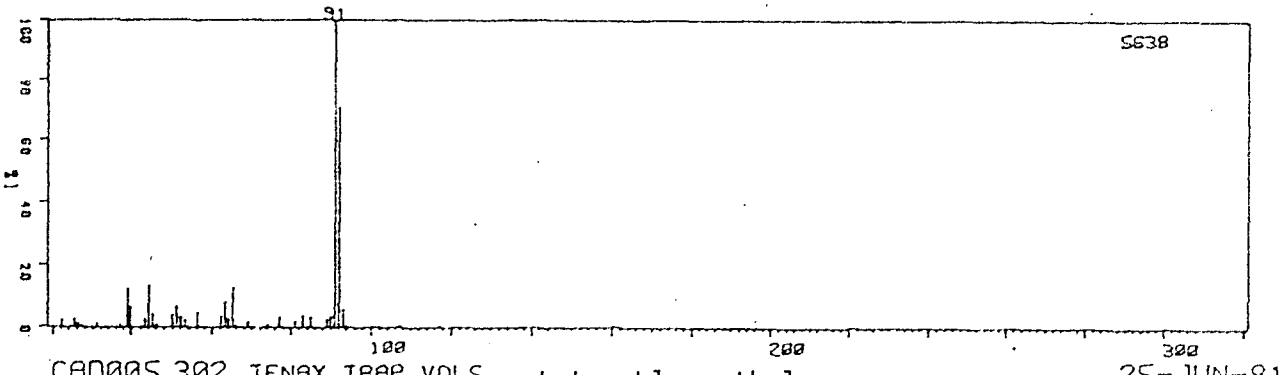
toluene

25-JUN-81



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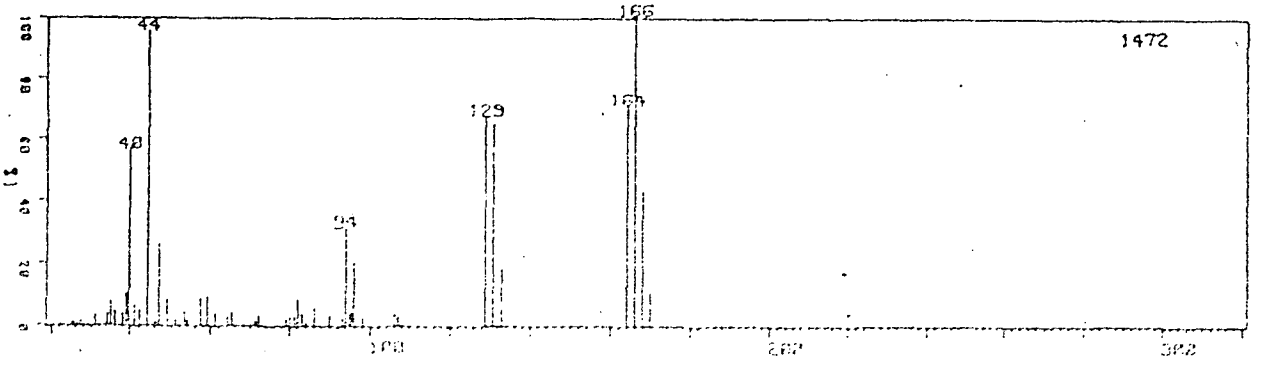
CAL:1CS00

tetrachloroethylene

25-JUN-81



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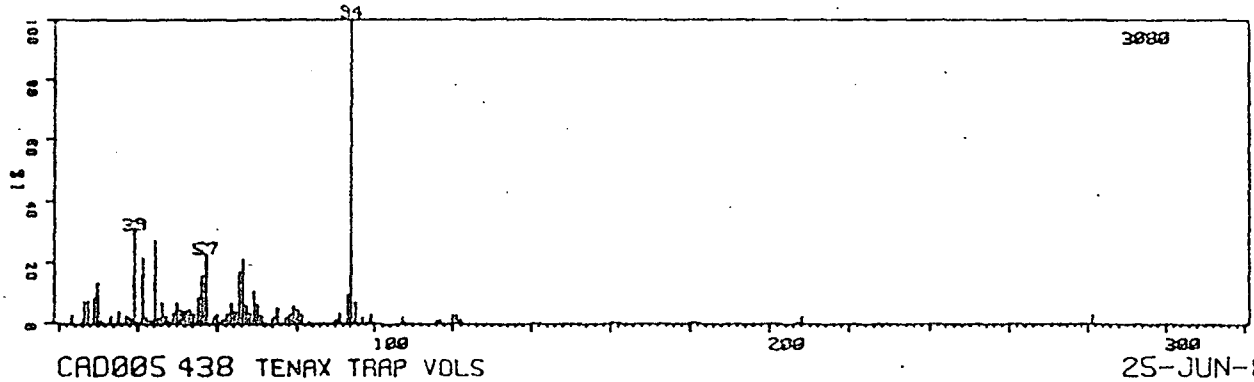
CAL:1CS00



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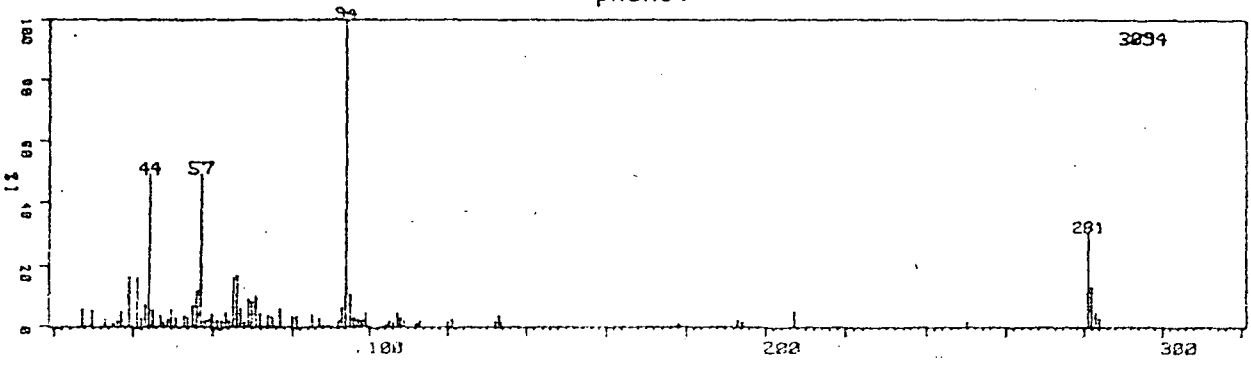
CAL:1CS60
phenol



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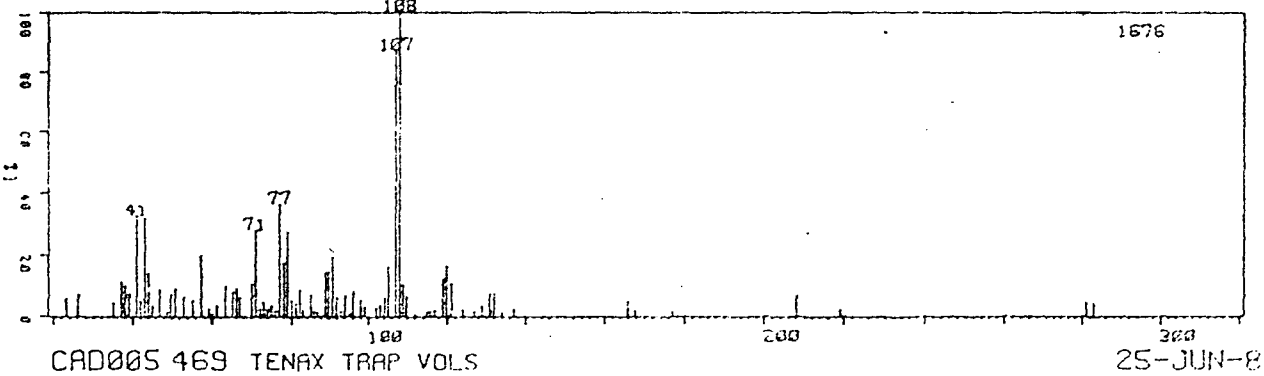
CAL:1CS00
cresol



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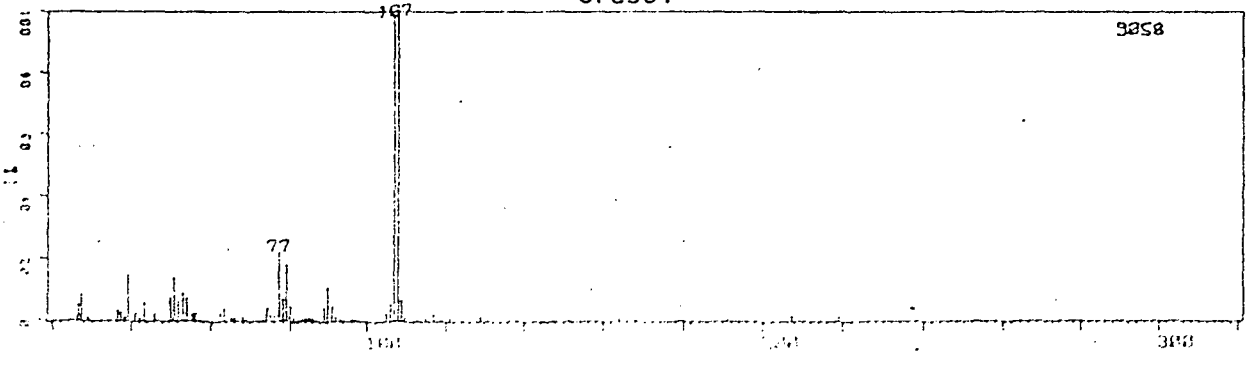
cresol



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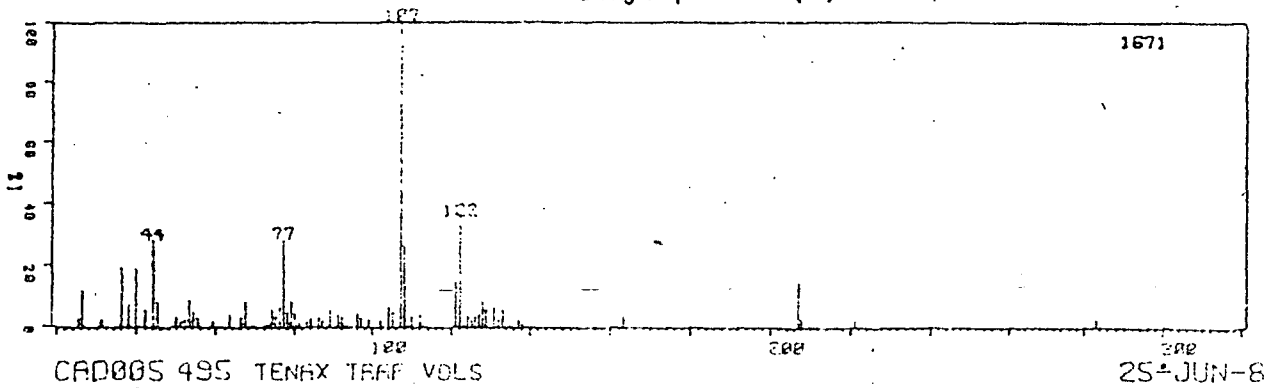
CAL:1CS00

ethyl phenol (?)



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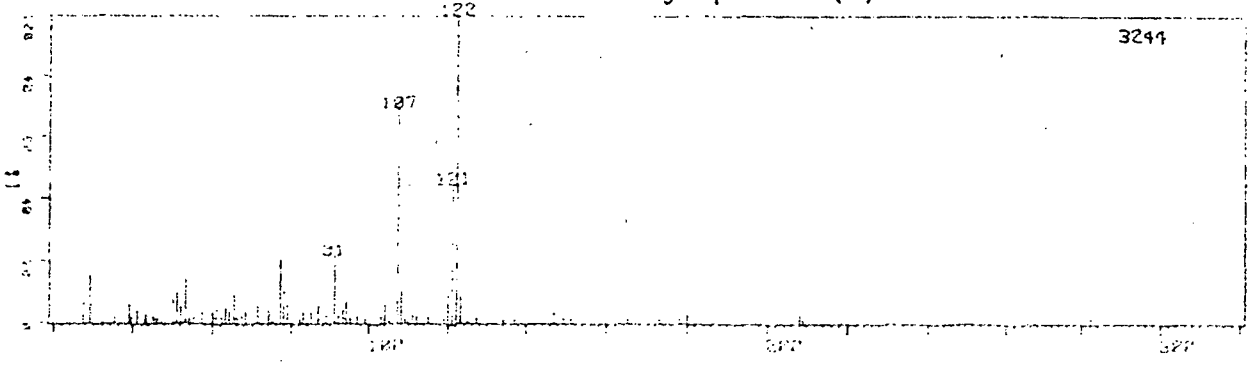
CAL:1CS00

dimethyl phenol (?)



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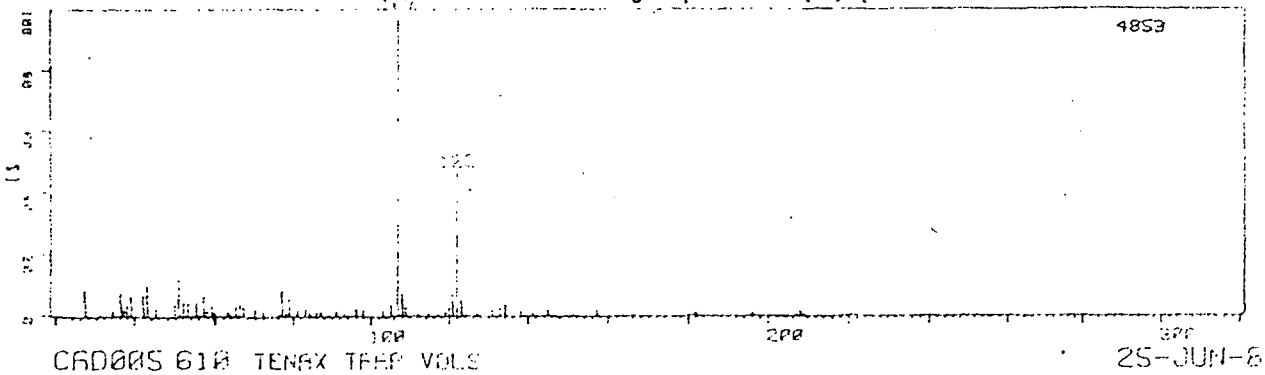
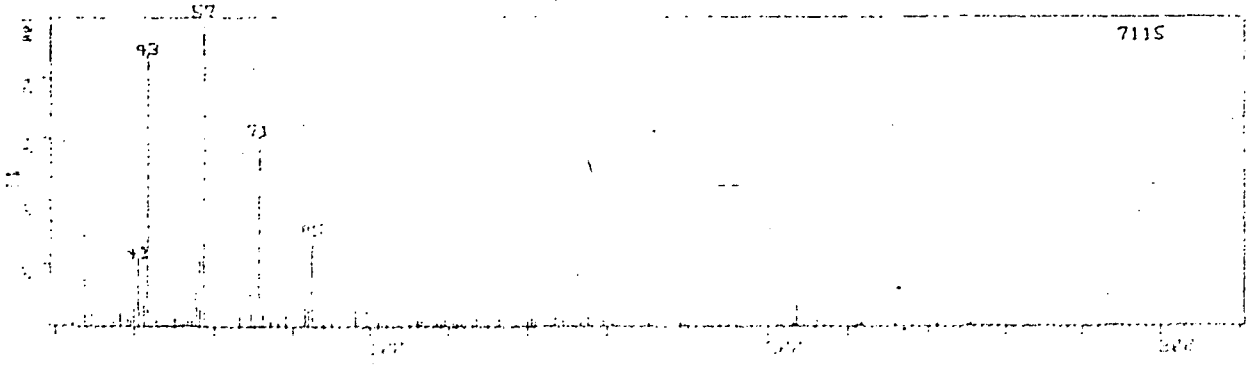
2 ethyl phenol (?)



CAD005 610 TENAX TRAP VOLS 25-JUN-81
CAL:1CS00

pentadecane



CAD00S 642 TENAX TRAP VOLS 25-JUN-81
CAL:1CS80

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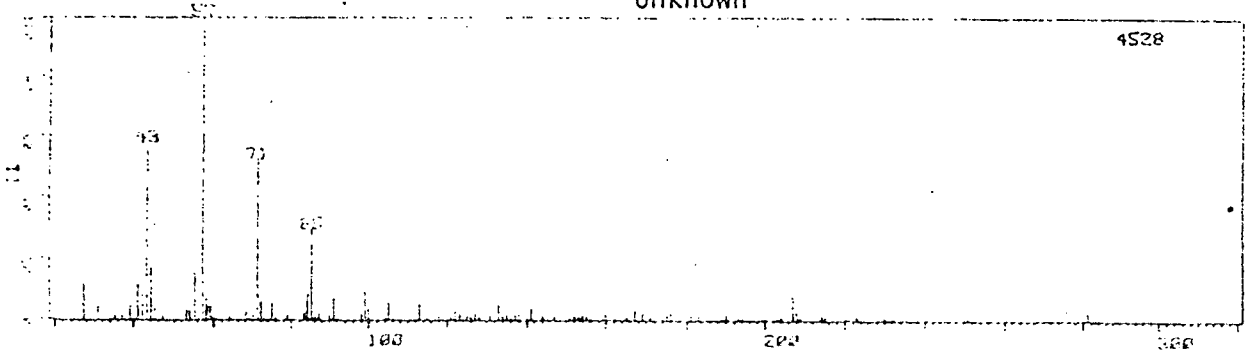
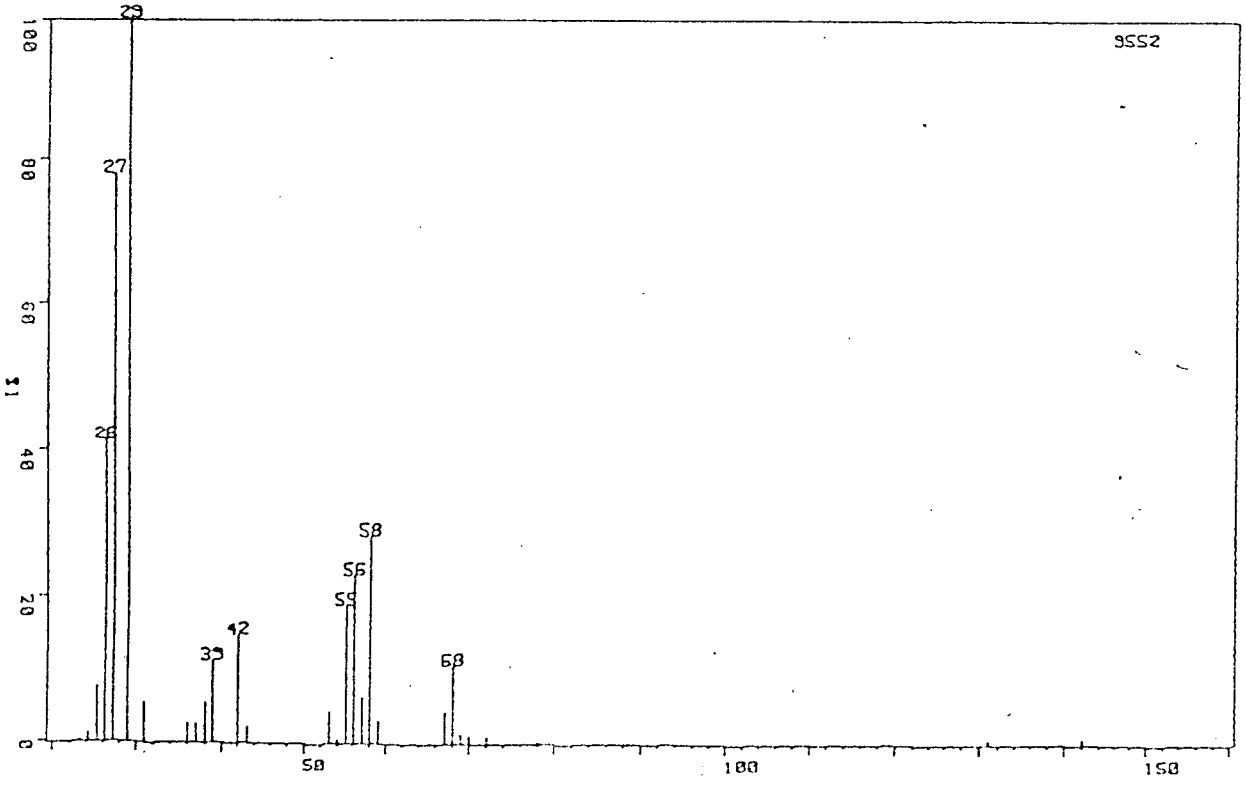
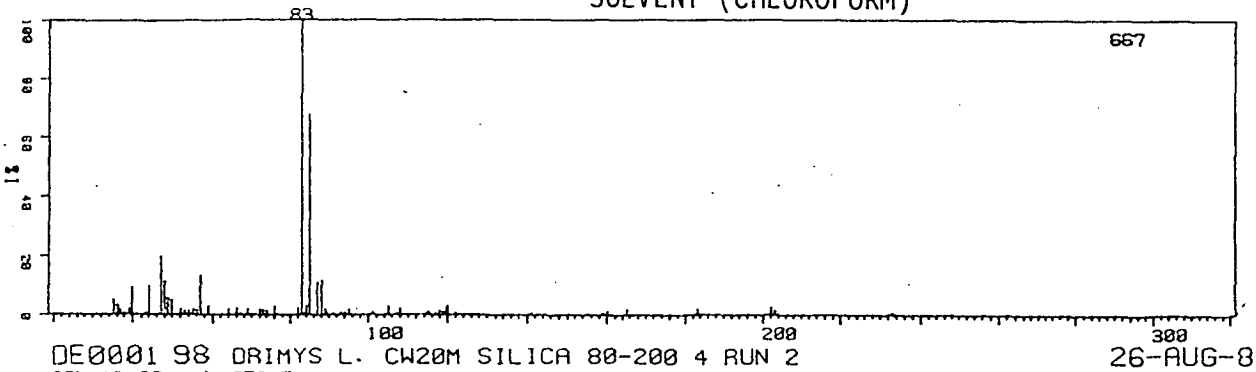


CAD00S 23 ACROLEIN + PENTADIENE ISOMER 25-JUN-81
CAL:1CS80



DE0001 96 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL: 1D400 STA: E. 3:1

SOLVENT (CHLOROFORM)



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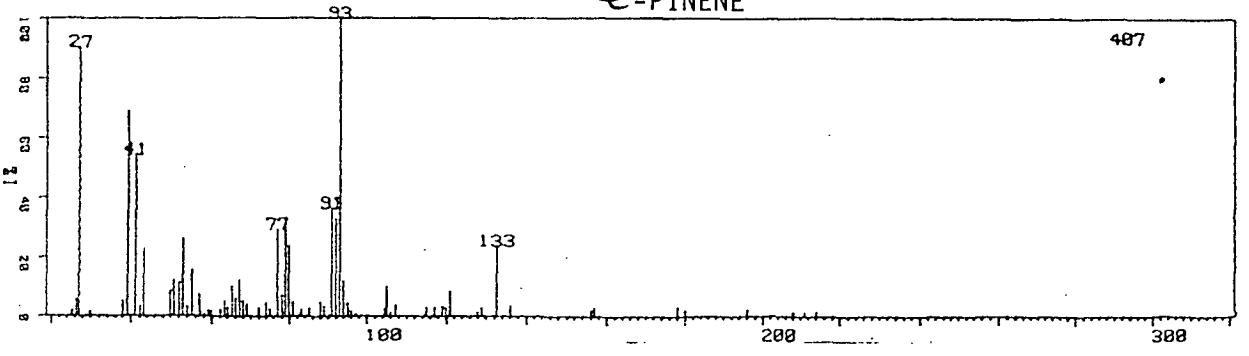
CAL: 1D400 STA: E. 3:S

α-PINENE



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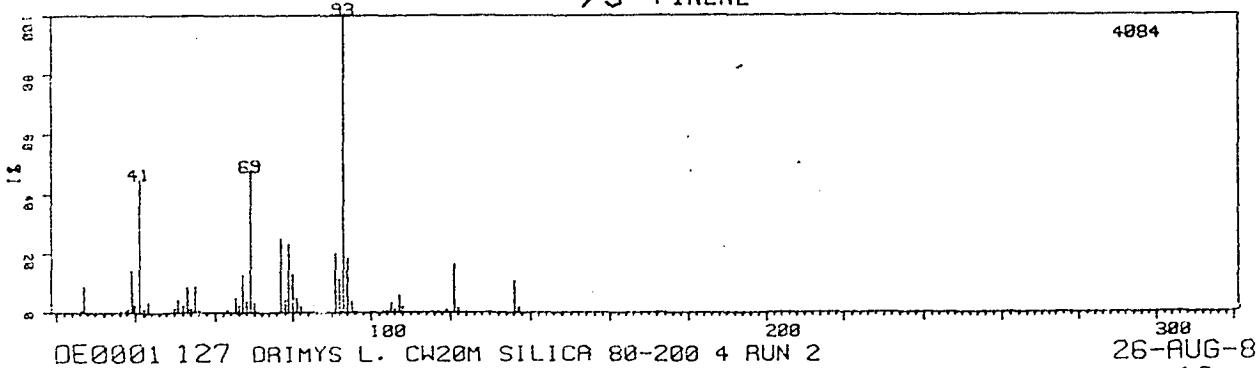
CAL: 1D400 STA: E. 3:39

β-PINENE



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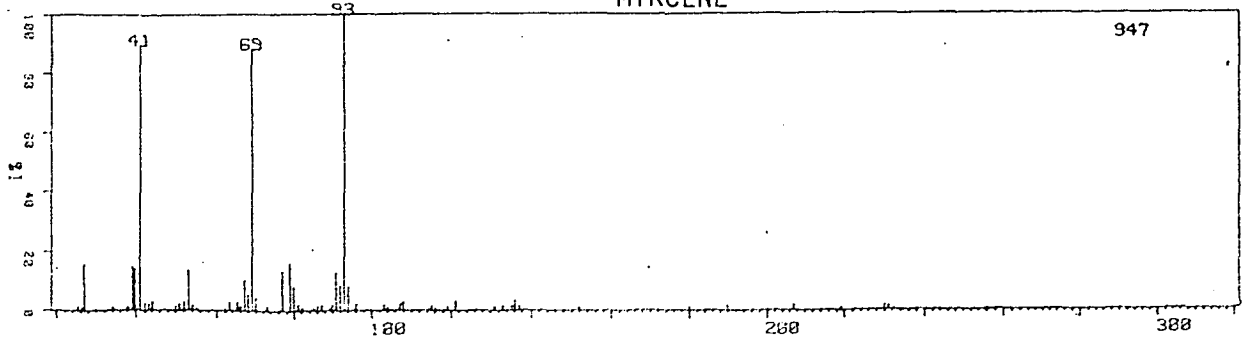
CAL: 1D400 STA: E. 4:0

MYRCENE



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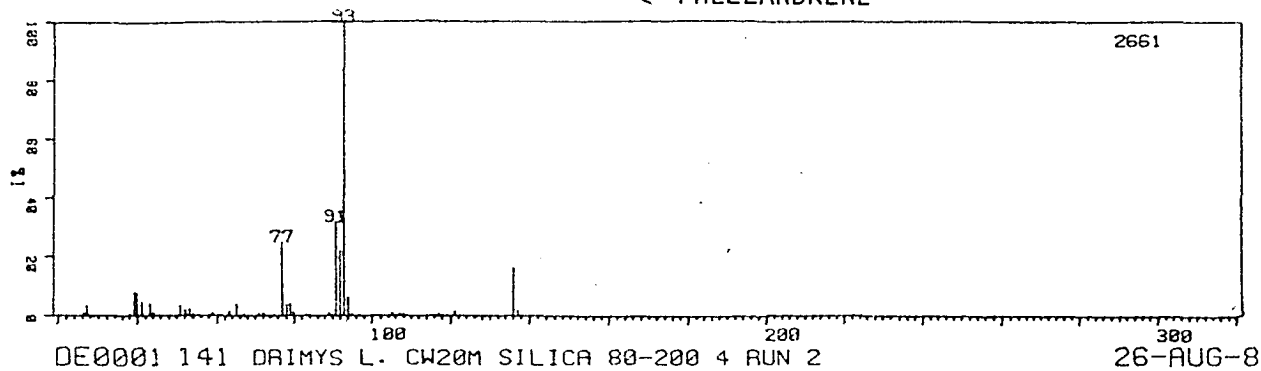
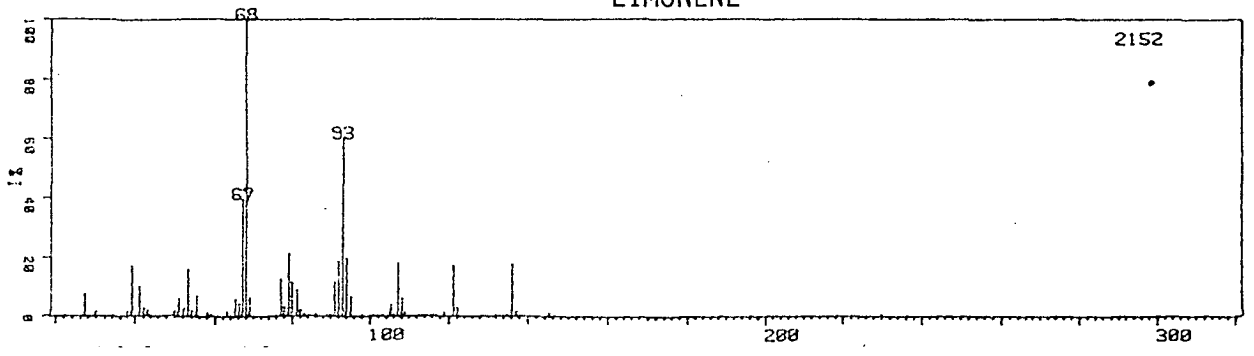
CAL:1D400 STA:E. 4:5

∝ -PHELLANDRENE



DE0001 141 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 4:26

LIMONENE



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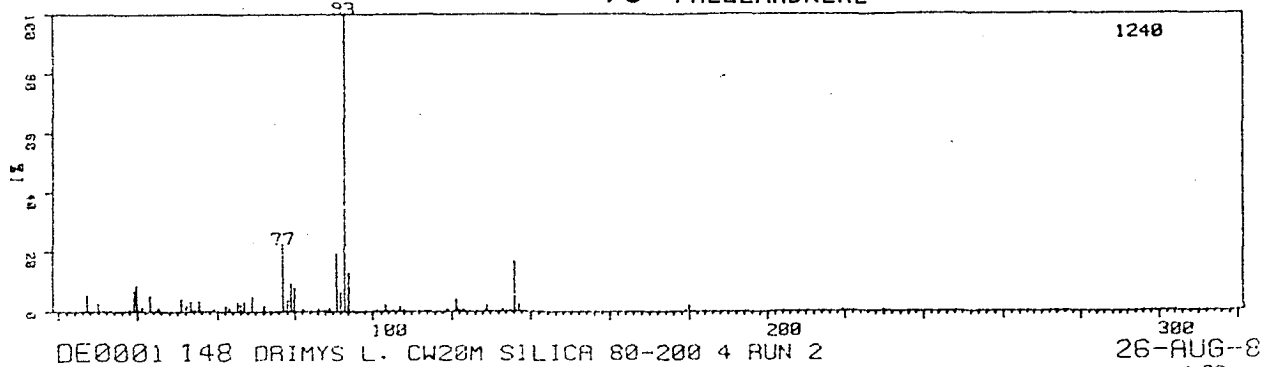
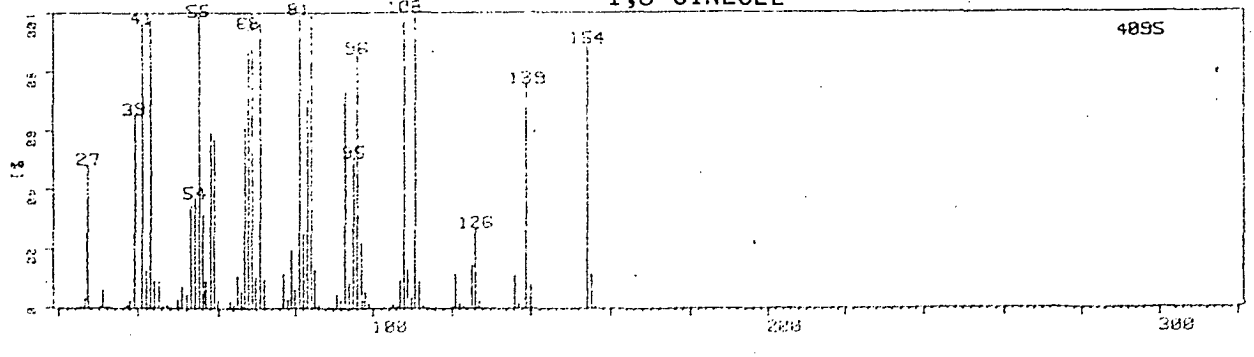
CAL:1D400 STA:E. 4:34

/3 -PHELLANDRENE



DE0001 148 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 4:39

1,8 CINEOLE



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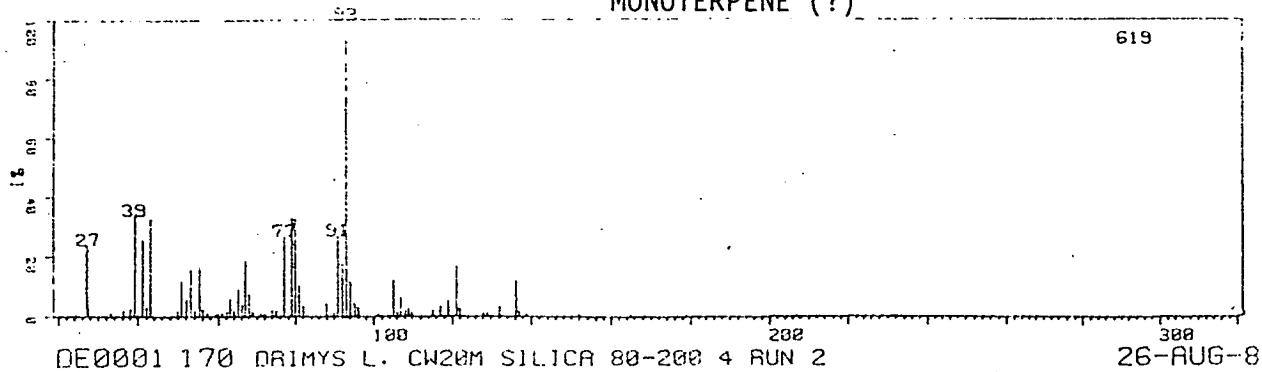
CAL:1D400 STA:E. 4:58

MONOTERPENE (?)



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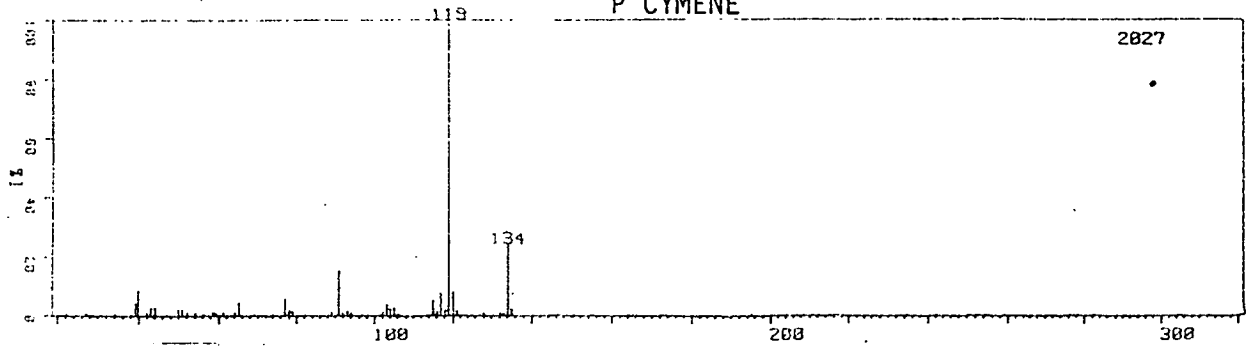
CAL:1D400 STA:E. 5:21

P CYMENE



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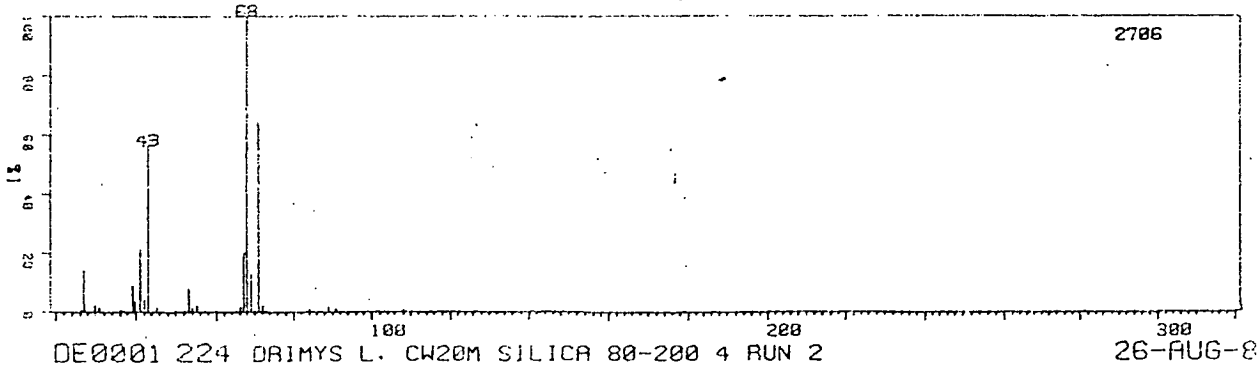
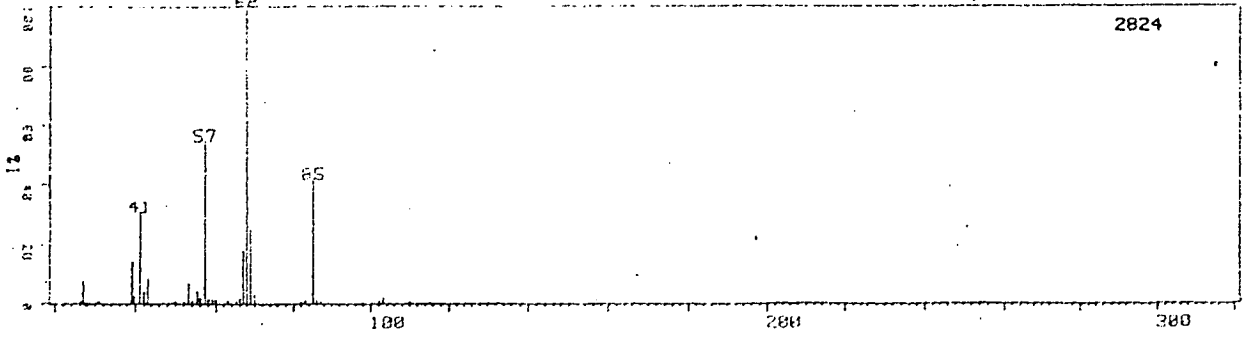
CAL:1D400 STA:E. 6:29

UNKNOWN



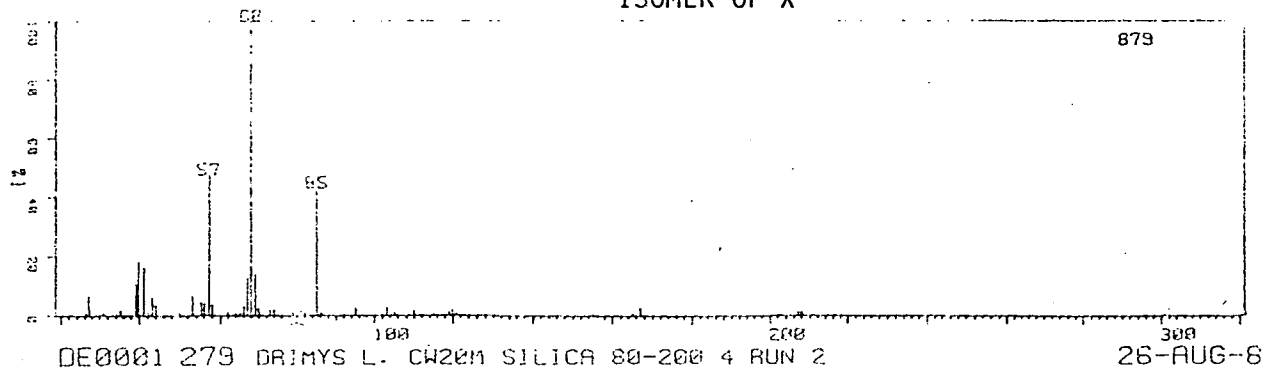
DE0001 224 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 7:3

ISOMER OF X



DE0001 268 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 8:25

ISOMER OF X



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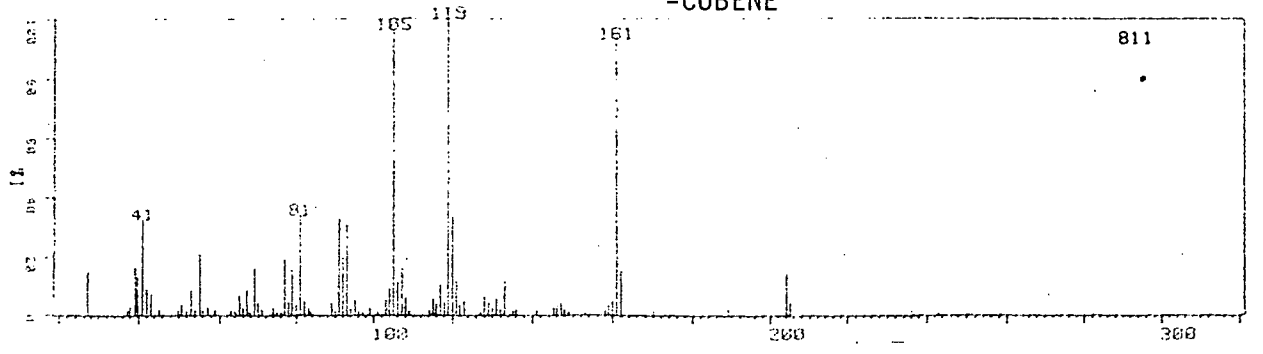
CAL:1D400 STA:E. 8:46

-CUBENE



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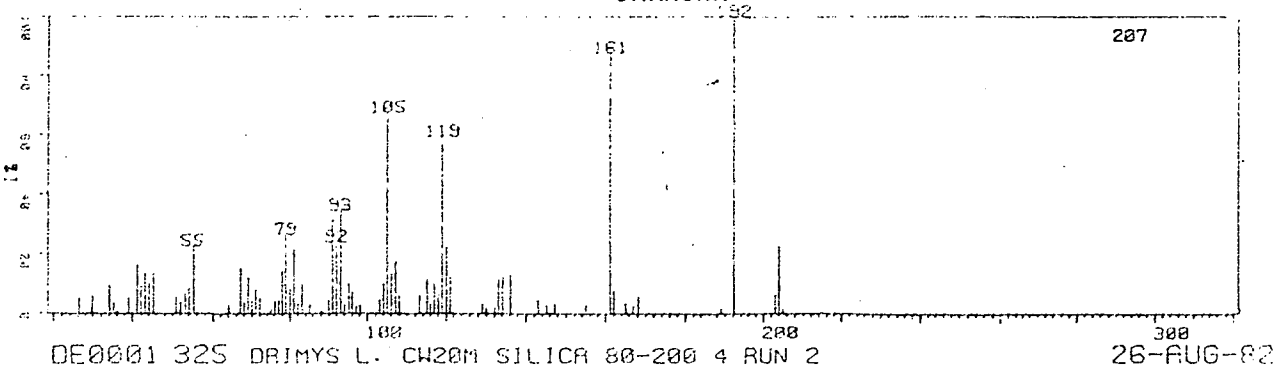

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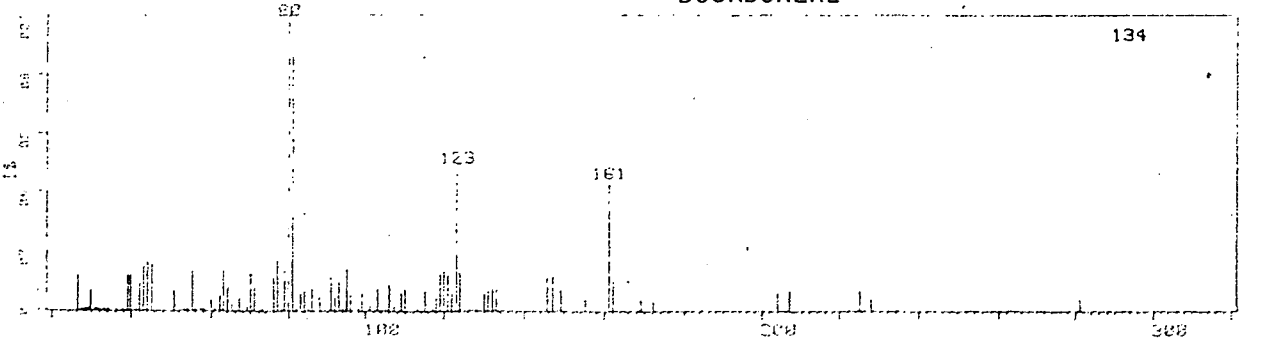
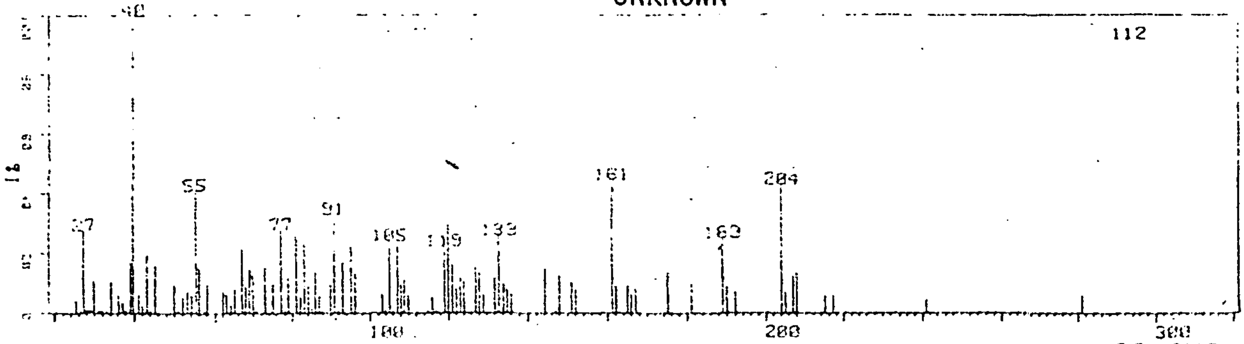
-BOURBONENE



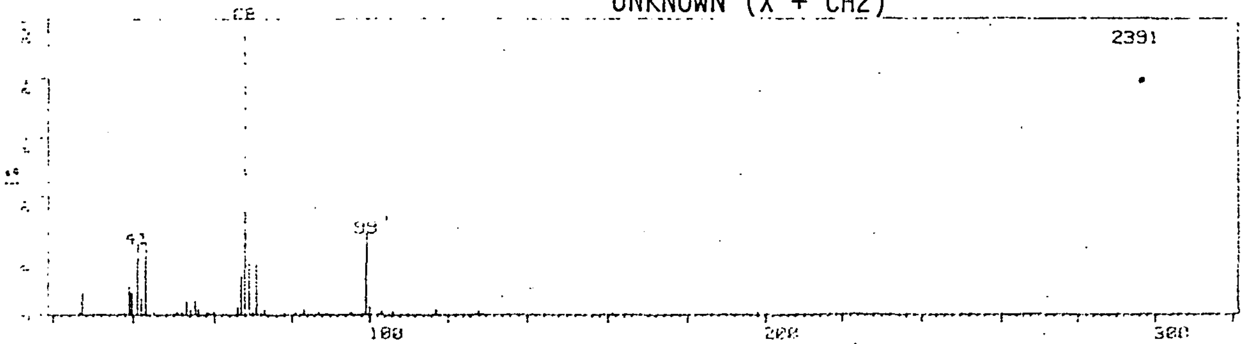
DE0001 332 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:10400 STA:E. 10:26

UNKNOWN



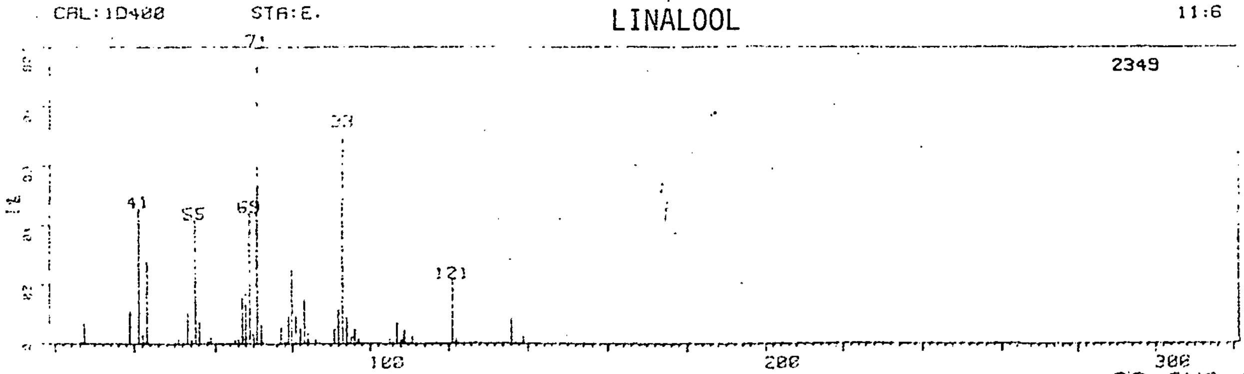
DE0001 342 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:10400 STA:E. 10:45

UNKNOWN (X + CH2)



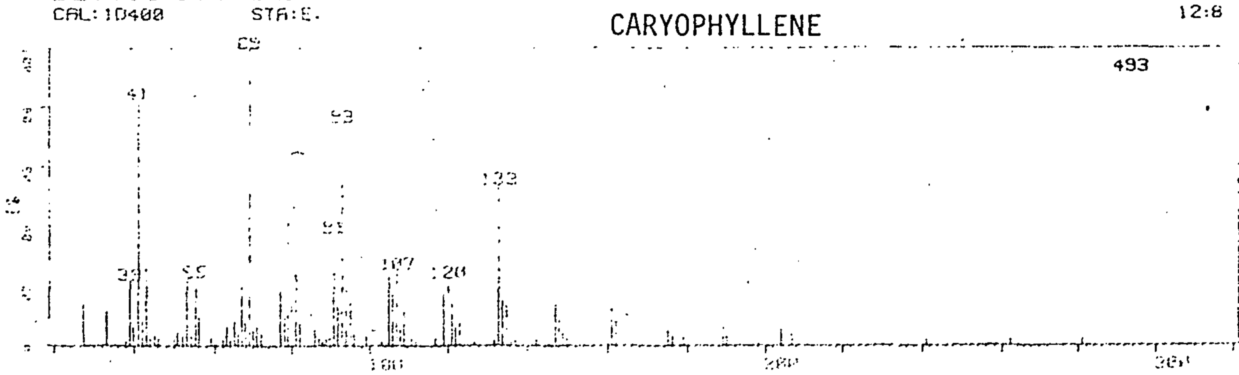
DE0001 353 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:10400 STA:E. 11:6

LINALOOL



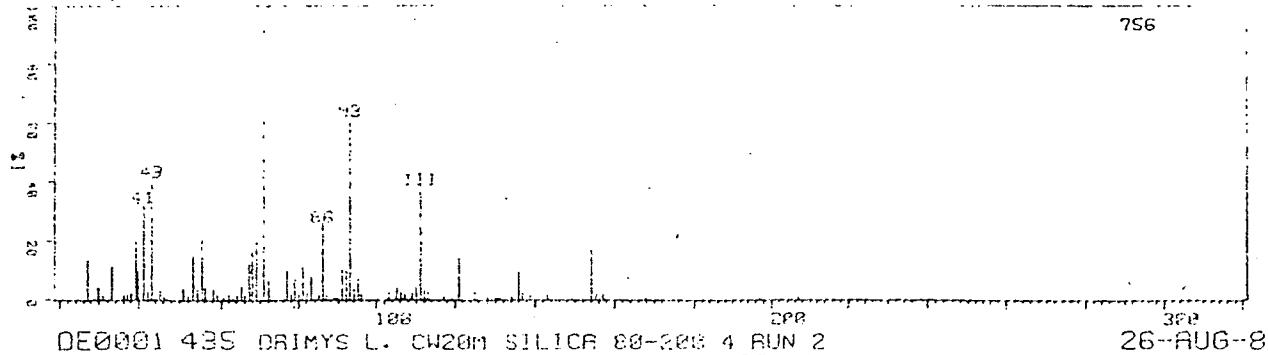
DE0001 386 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:10400 STA:E. 12:8

CARYOPHYLLENE



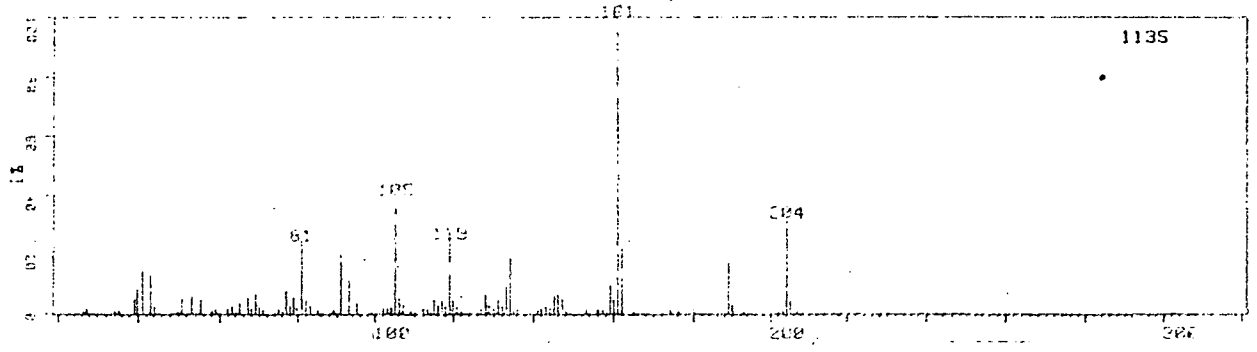
DE0001 395 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 12:25

TERPINENE-4-01



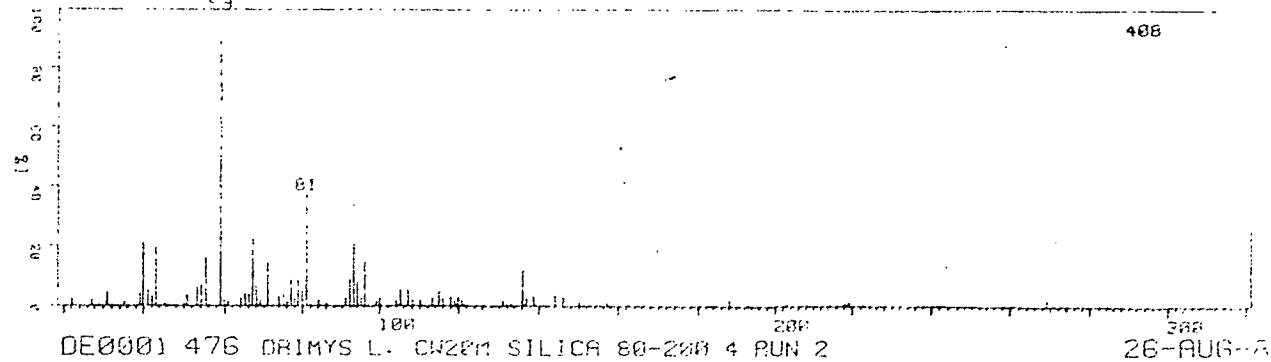
DE0001 435 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 13:40

SESQUITERPENE



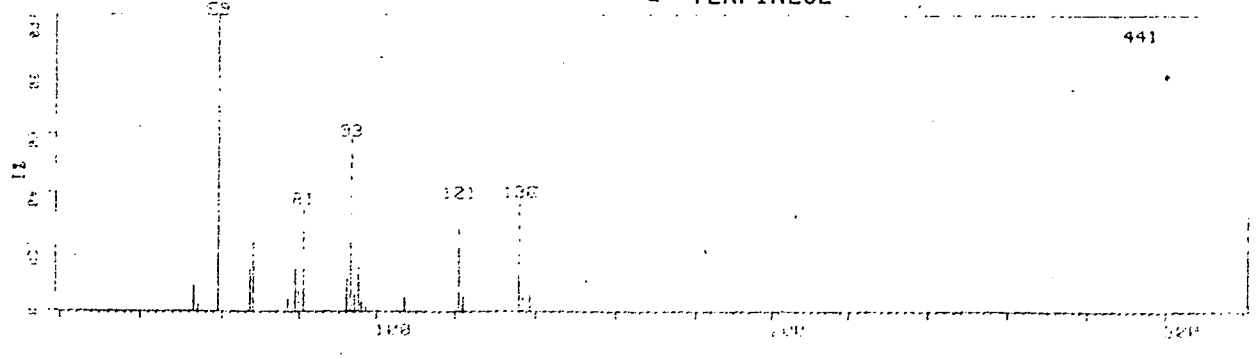
DE0001 455 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 14:18

MONOTERPENE ALCOHOL

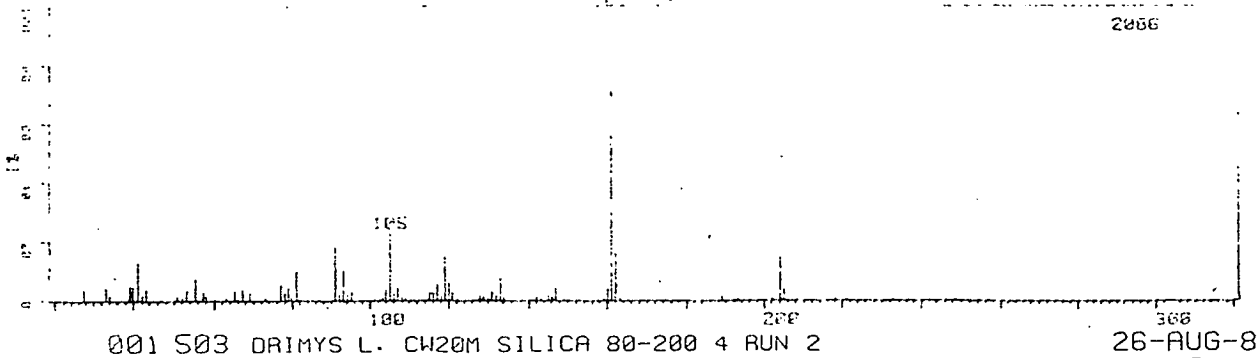


DE0001 476 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 14:57

α-TERPINEOL

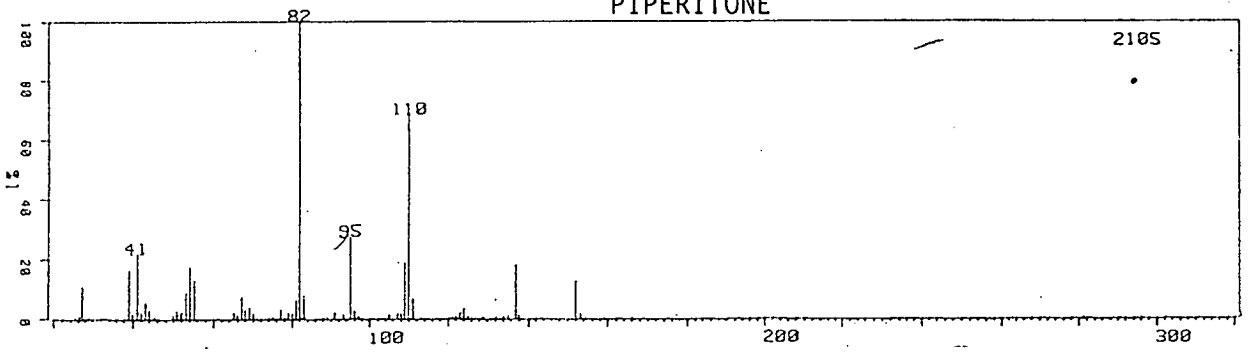


SESQUITERPENE



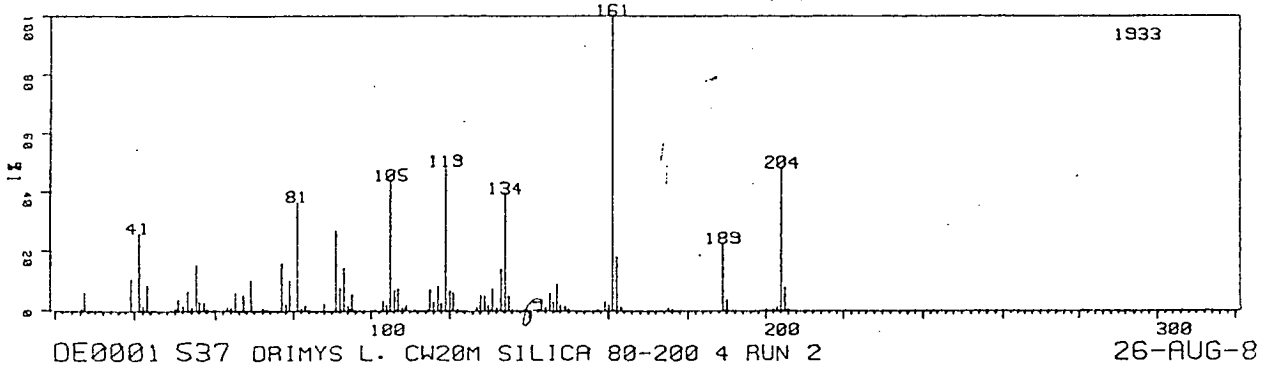
001 S03 DRIMYS L. CW20M SILICA 80-200 4 RUN 2
CAL:1D400 STA:E.
26-AUG-82
15:48

PIPERITONE



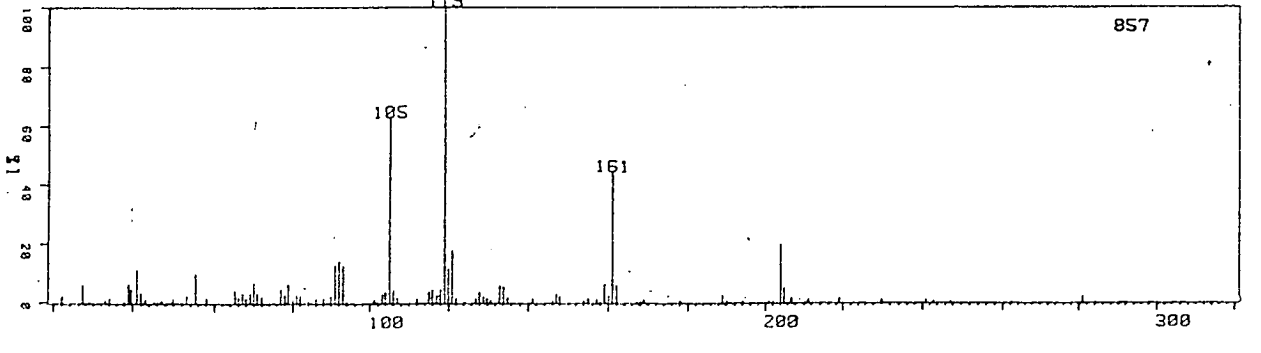
DE0001 S16 DRIMYS L. CW20M SILICA 80-200 4 RUN 2
CAL:1D400 STA:E.
26-AUG-82
16:13

CADINENE (?)



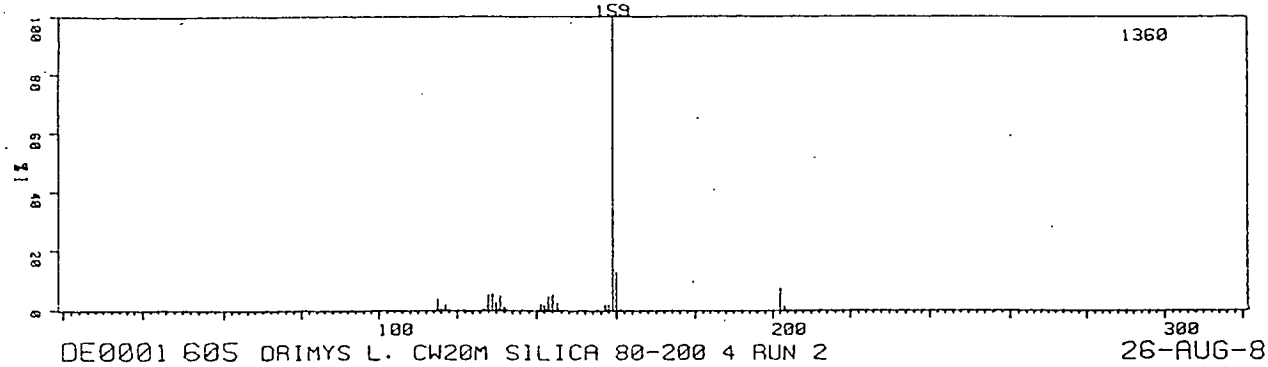
DE0001 S37 DRIMYS L. CW20M SILICA 80-200 4 RUN 2
CAL:1D400 STA:E.
26-AUG-82
16:52

CADINA 1,4 DIENE



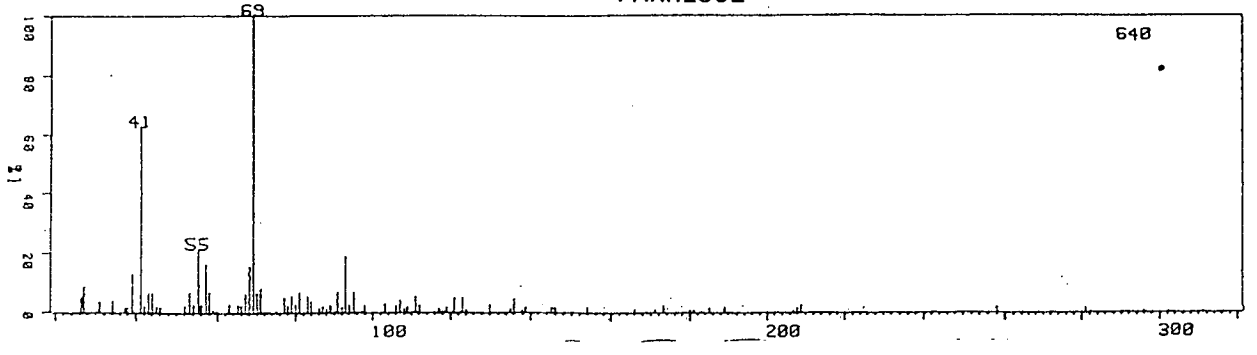
DE0001 581 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL: 1D400 STA: E. 18:15

CALAMANINE



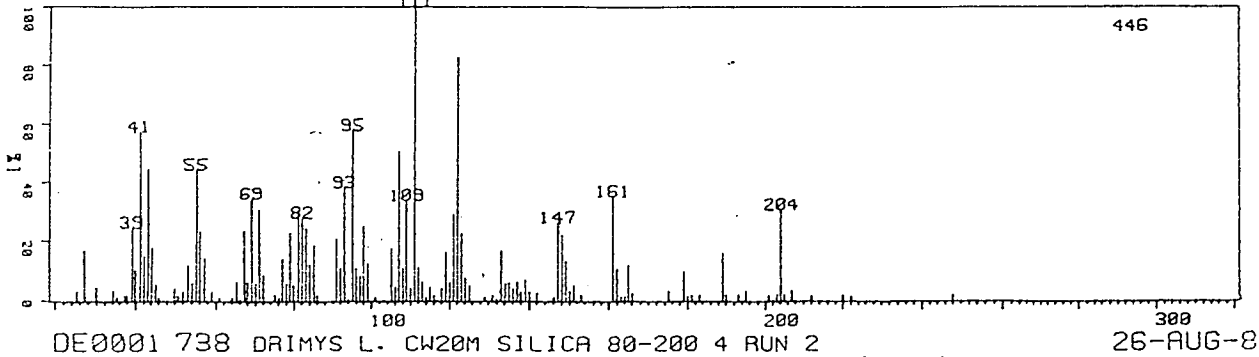
DE0001 605 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL: 1D400 STA: E. 19:0

FARNESOL



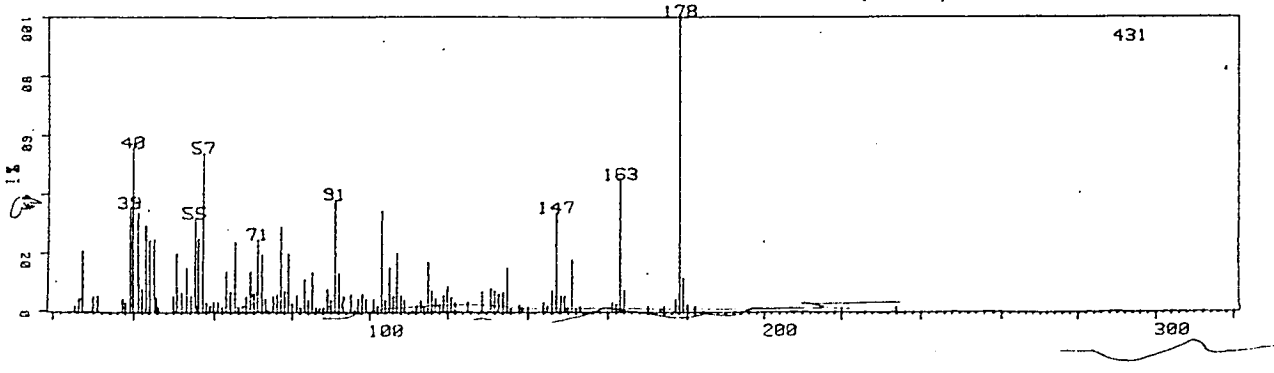
DE0001 666 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL: 1D400 STA: E. 20:55

UNKNOWN



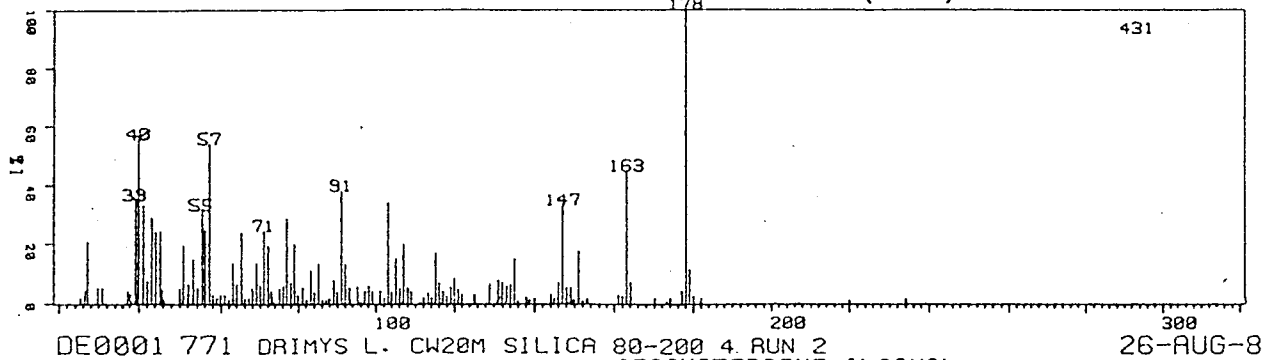
DE0001 738 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL: 1D400 STA: E. 23:11

METHYL EUGENOL (TYPE)



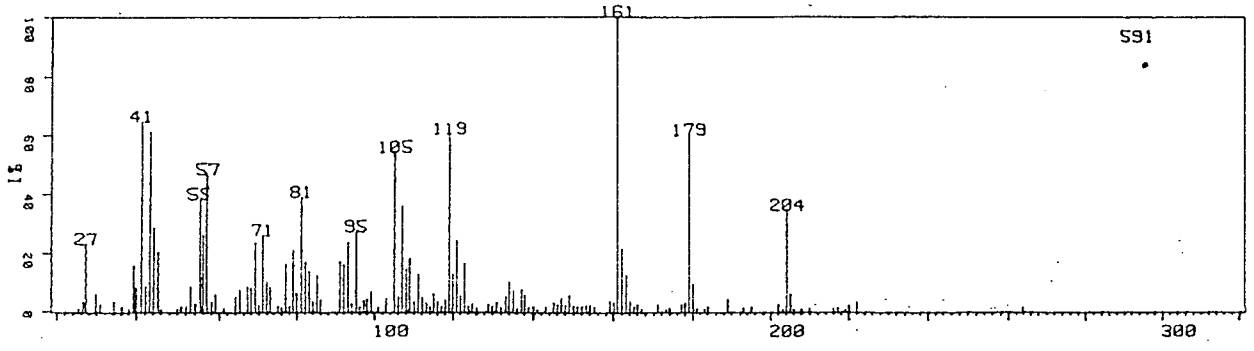
DE0001 738 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 23:11

METHYL EUGENOL (TYPE)



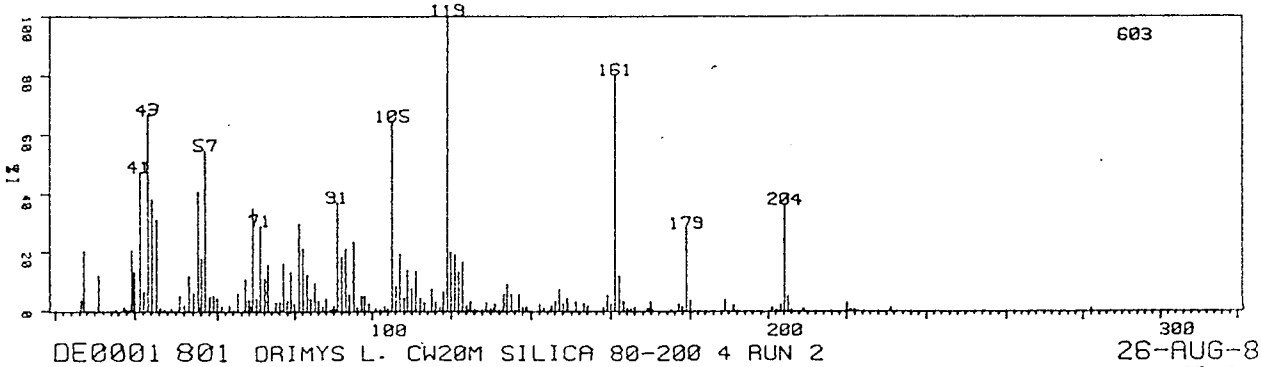
DE0001 771 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 24:13

SESQUITERPENE ALCOHOL



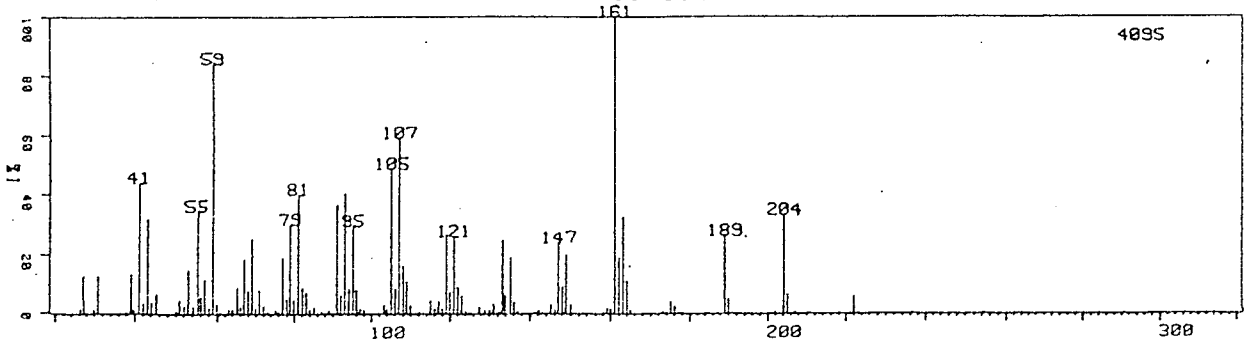
DE0001 779 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 24:28

SESQUITERPENE ALCOHOL



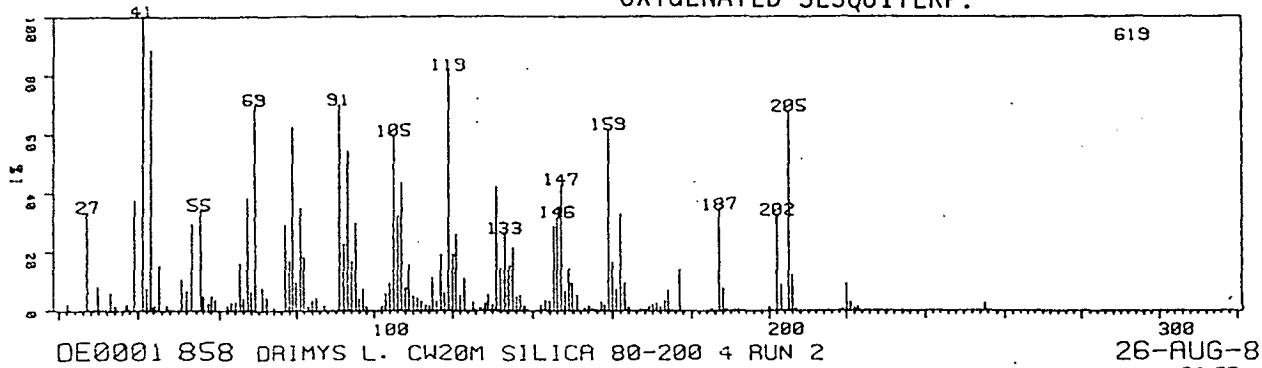
DE0001 801 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 25:10

GUAIOL



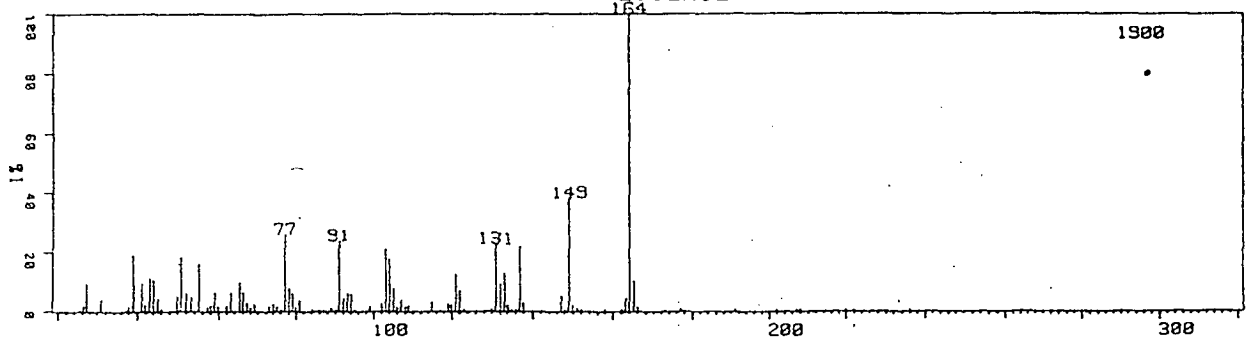
DE0001 826 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 25:57

OXYGENATED SESQUITERP.



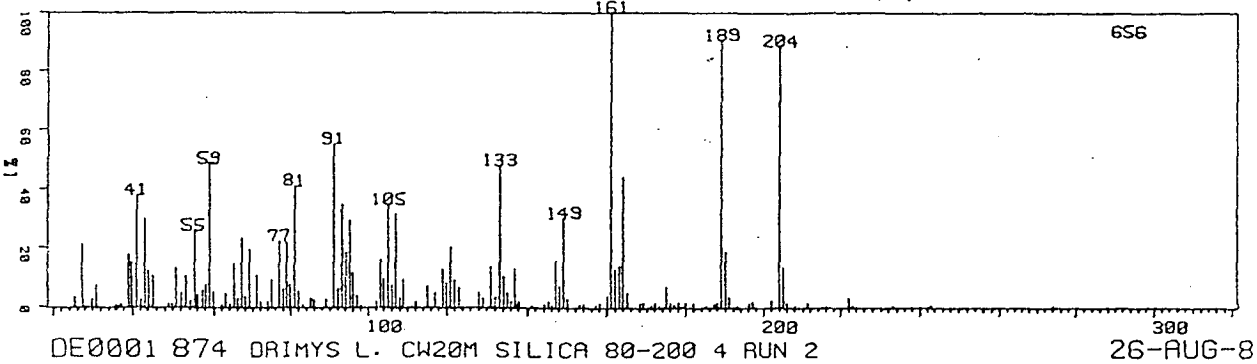
DE0001 858 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 26:57

EUGENOL



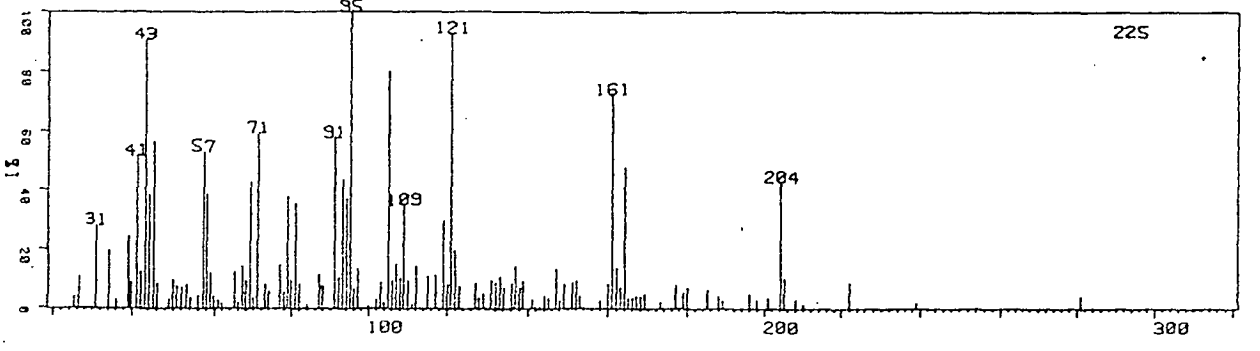
DE0001 861 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 27:3

ISOMERIC GUAIOL (?)



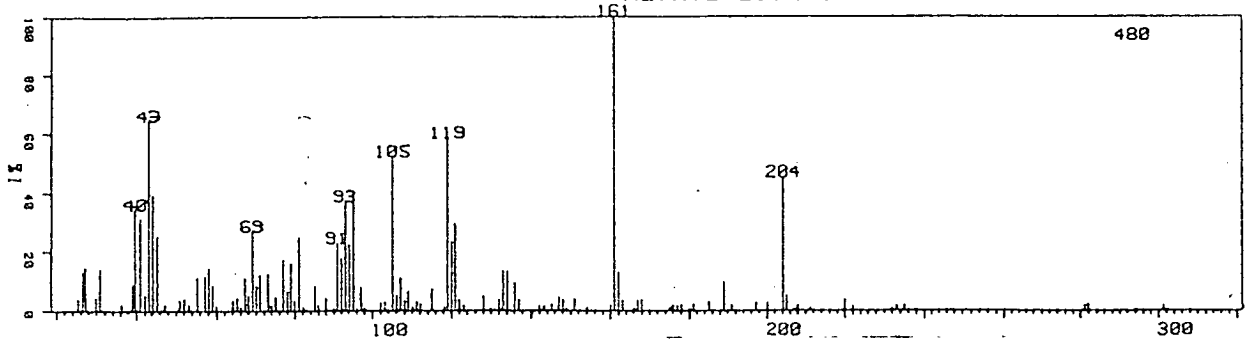
DE0001 874 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 27:27

UNKNOWN



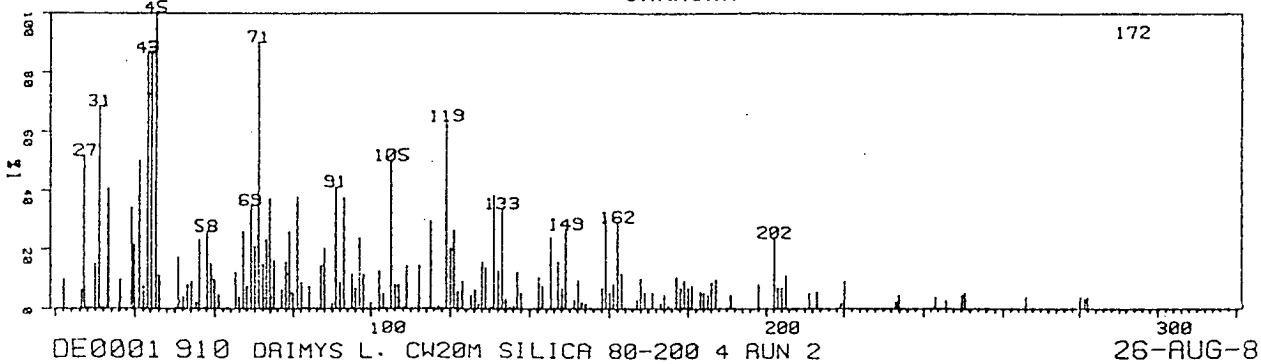
DE0001 88S DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 27:48

METHYL EUGENOL + CH2



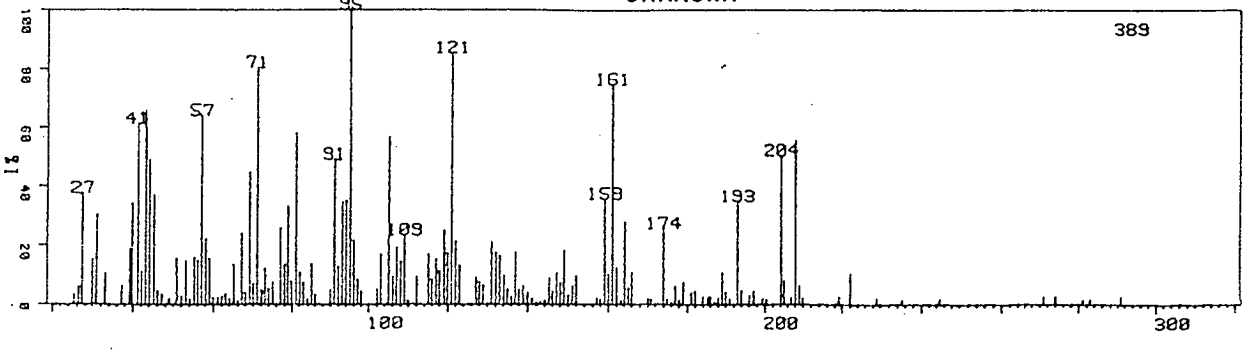
DE0001 90S DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 28:26

UNKNOWN



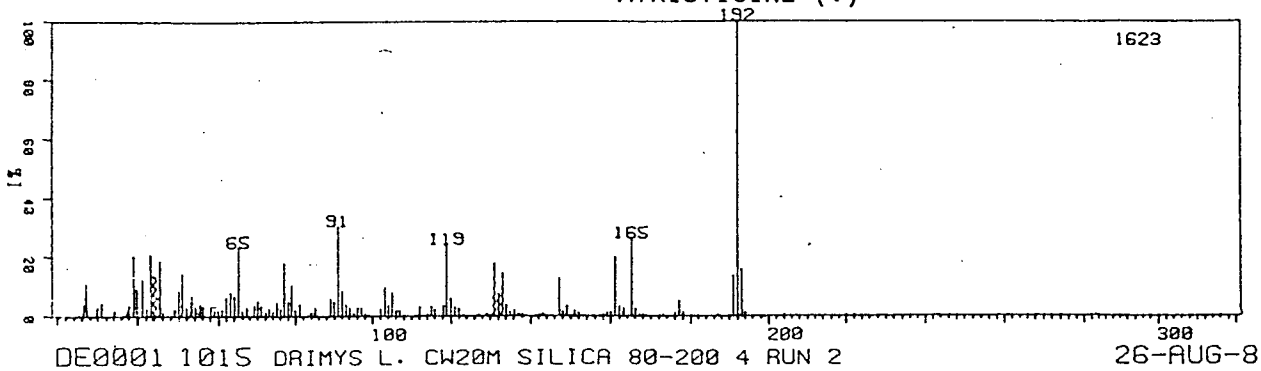
DE0001 910 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 28:35

UNKNOWN



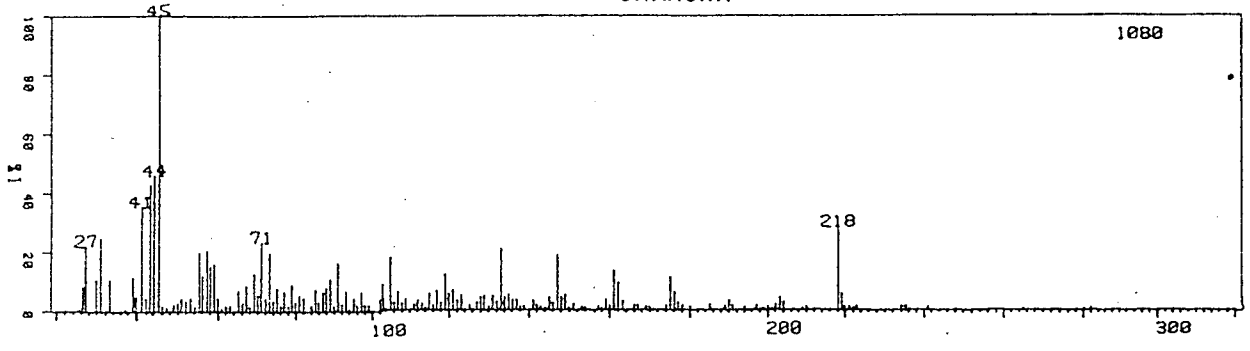
DE0001 929 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 29:11

MYRISTICINE (?)

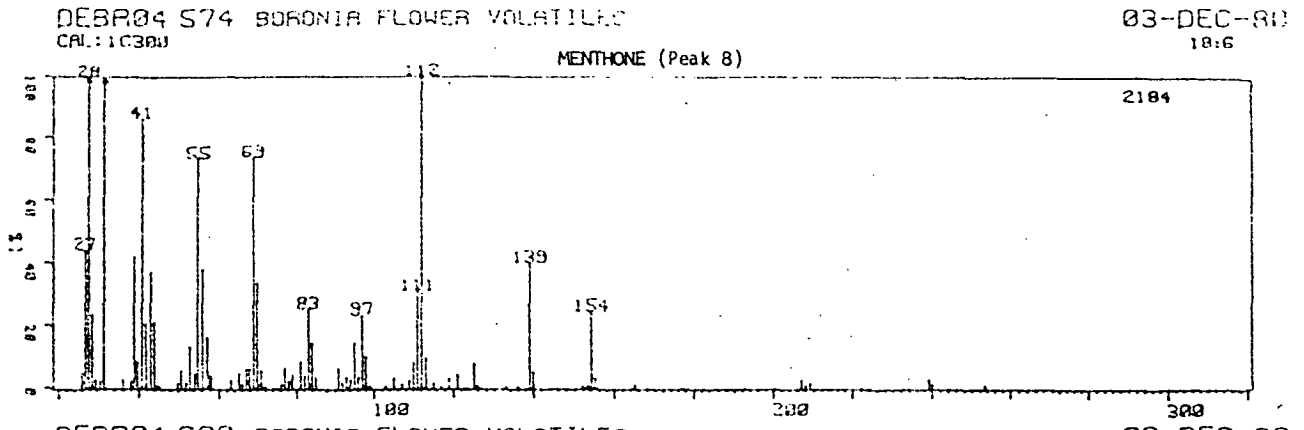


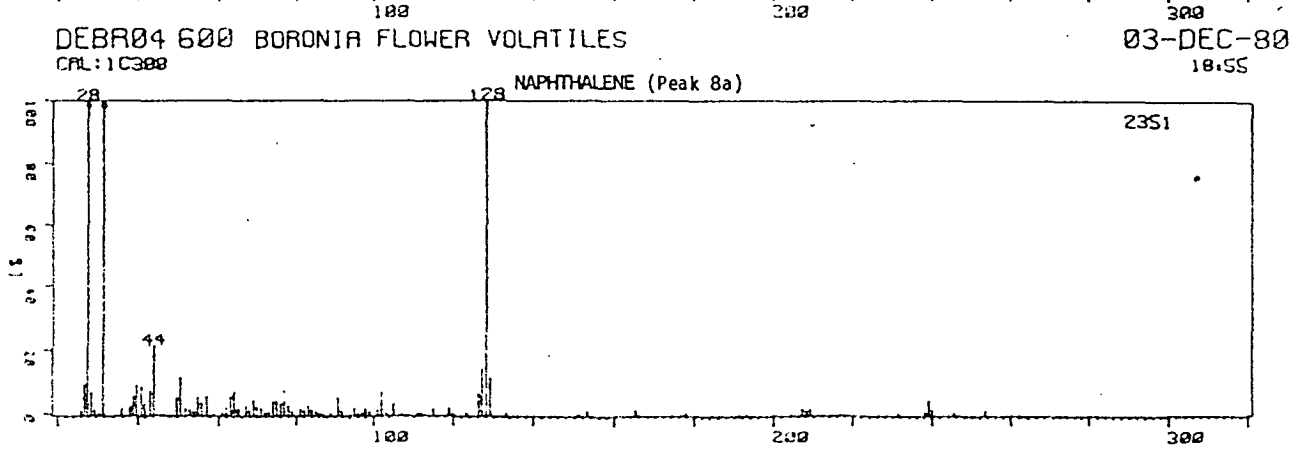
DE0001 1015 DRIMYS L. CW20M SILICA 80-200 4 RUN 2 26-AUG-82
CAL:1D400 STA:E. 31:53

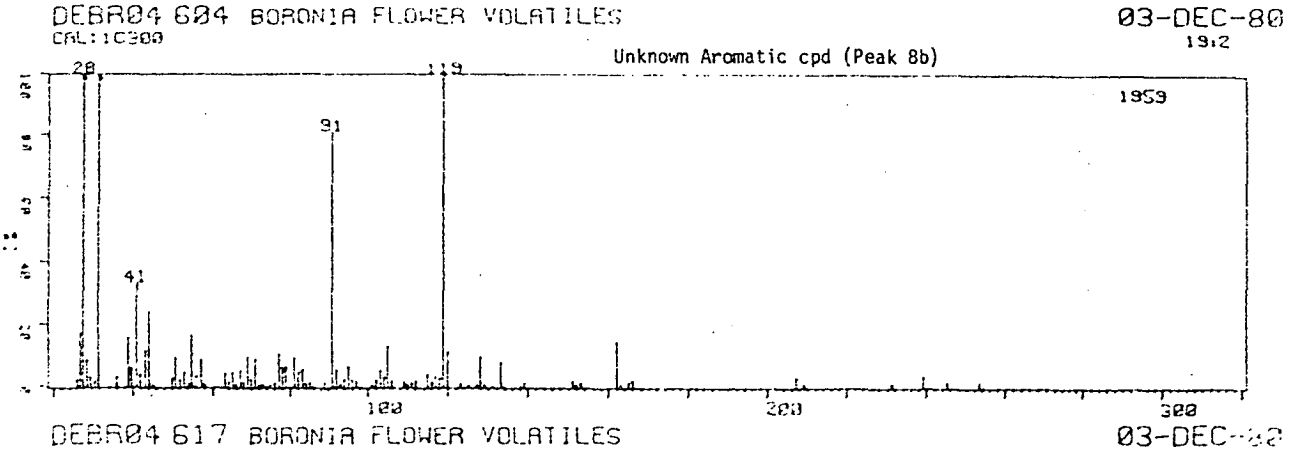
UNKNOWN

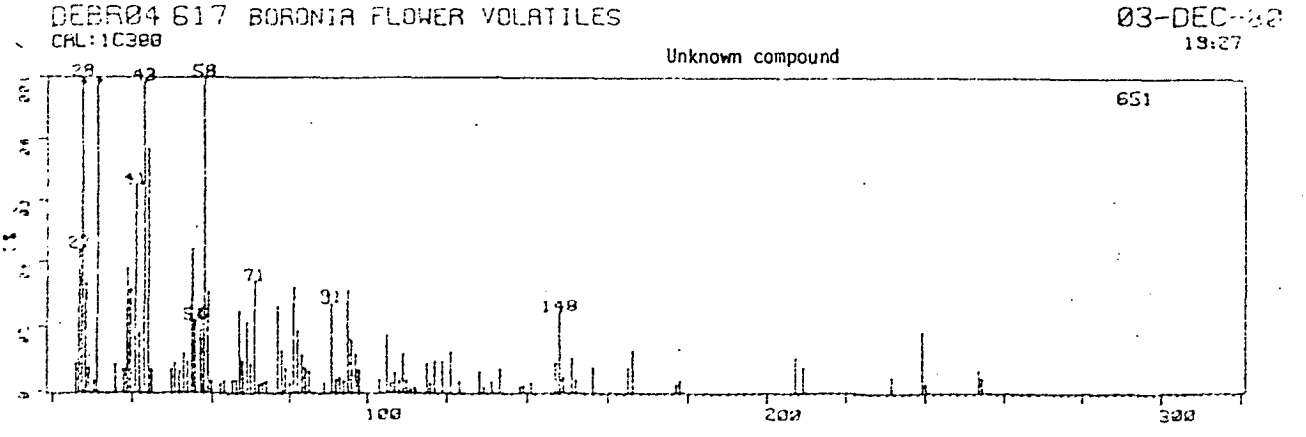


MASS SPECTRA



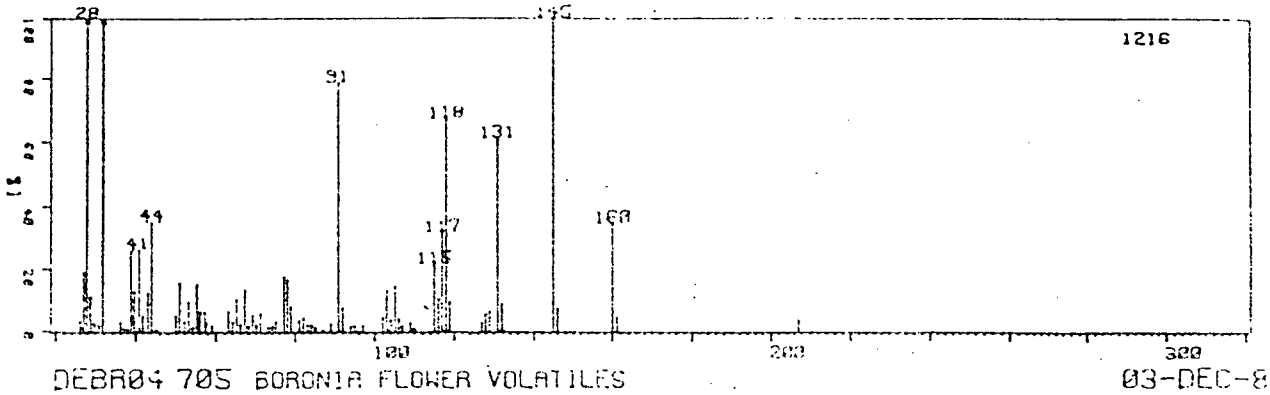




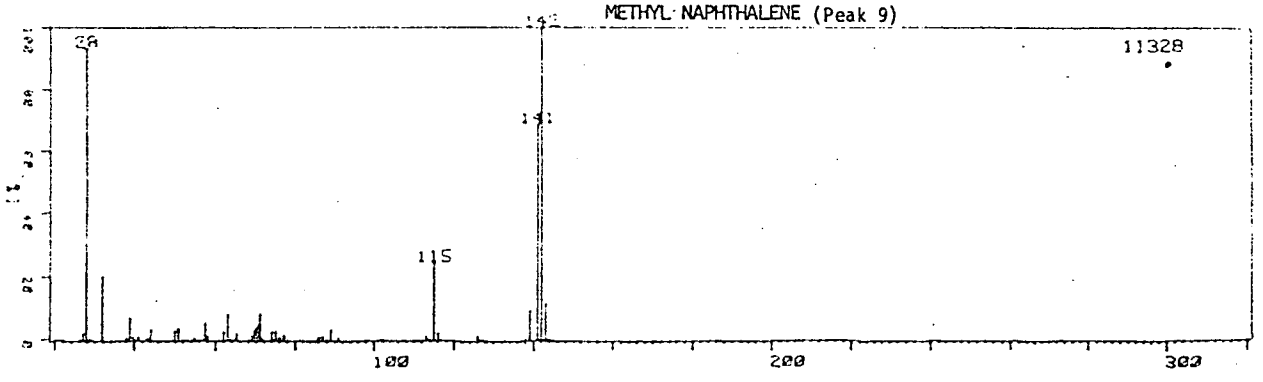


MASS SPECTRA

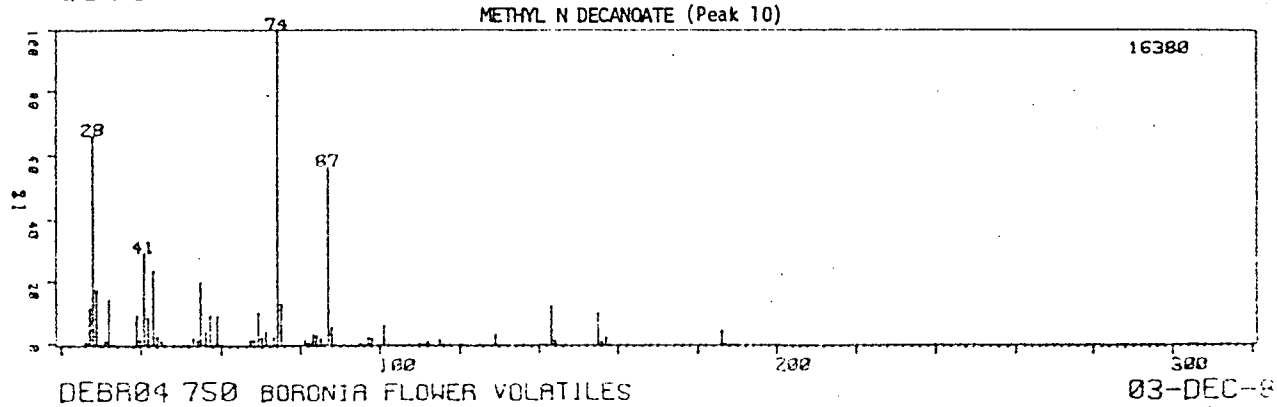
DEBR04 688 MIXTURE
CAL:1C300
MIXTURE TETRAHYDRONAPHTHALENE AND A DIMETHYLINDANE CPD. (Peak 8c)
03-DEC-88
21:41



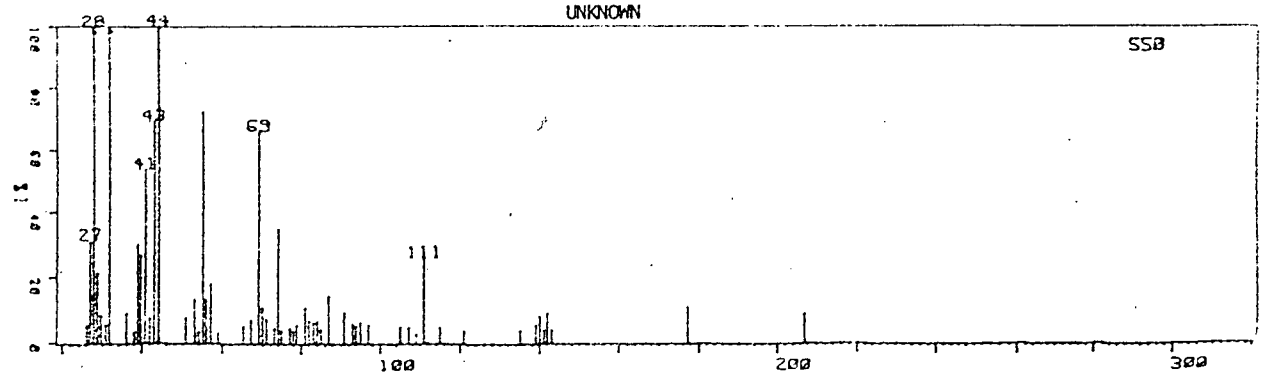
DEBR04 705 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-88
22:13
METHYL NAPHTHALENE (Peak 9)



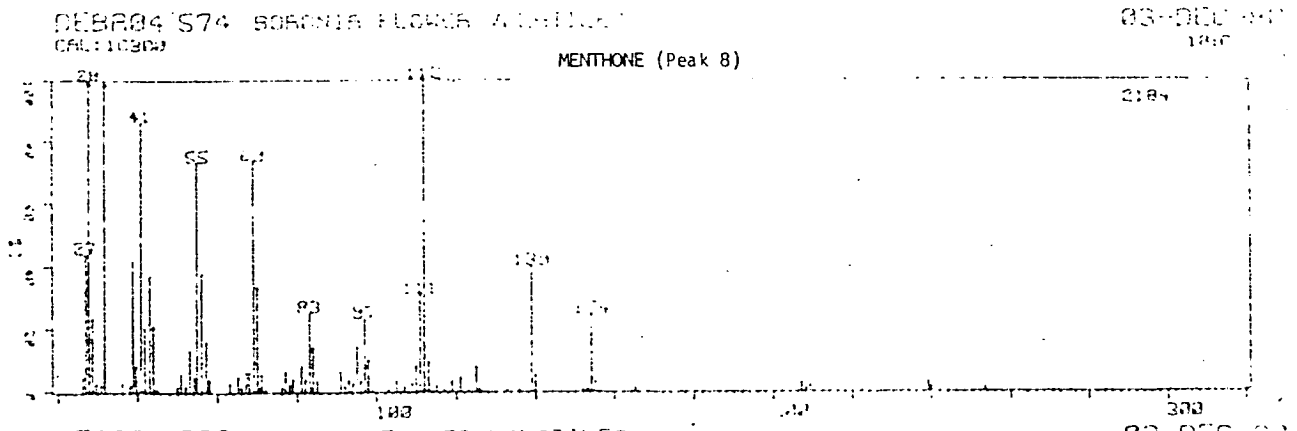
DEBR04 736 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-88
23:12
METHYL N DECANOATE (Peak 10)

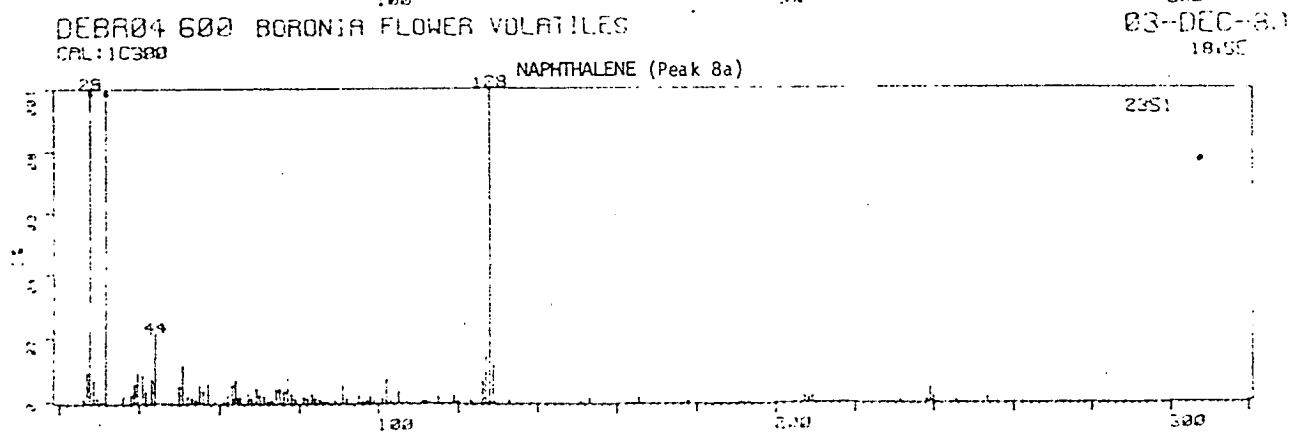


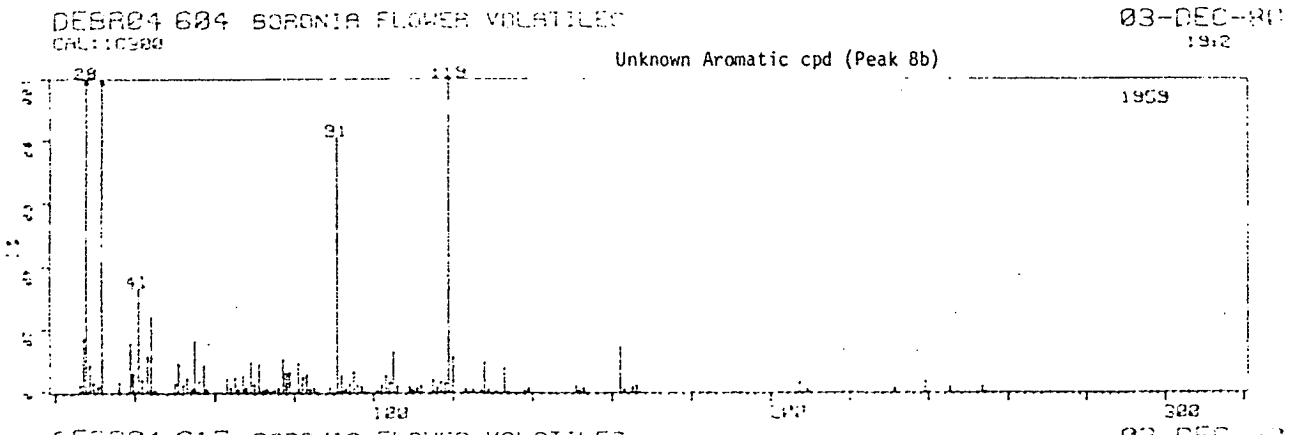
DEBR04 750 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-88
23:38
UNKNOWN

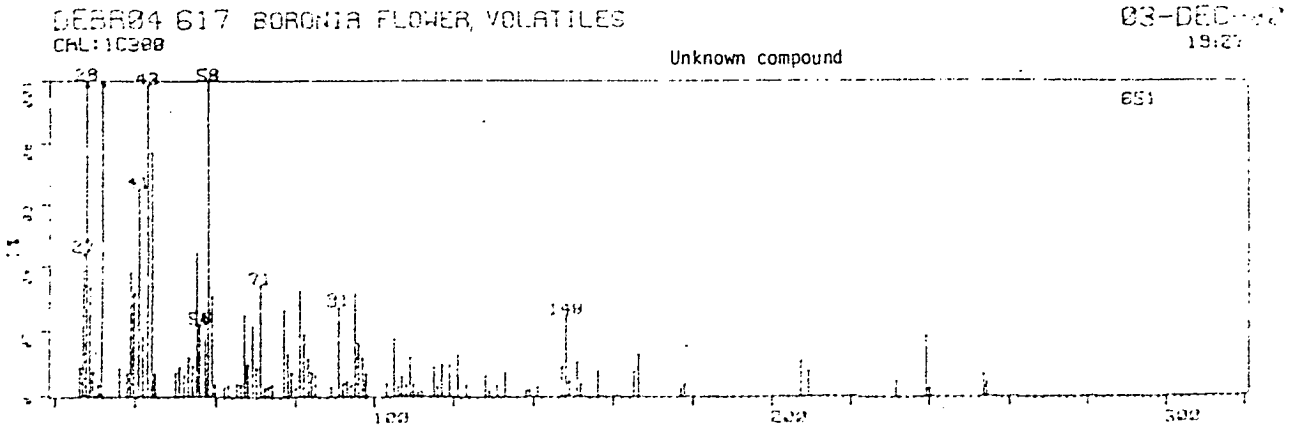


MASS SPECTRA

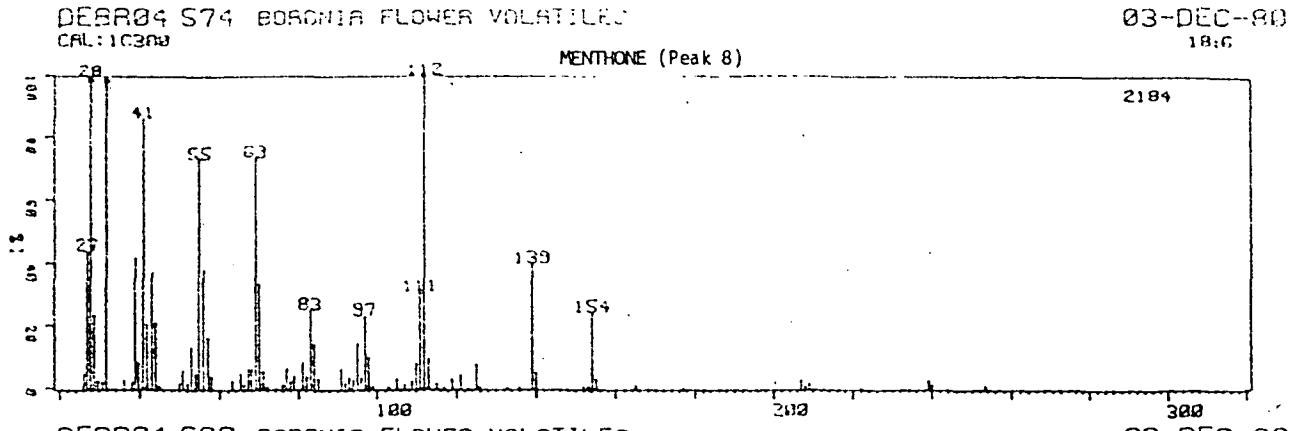


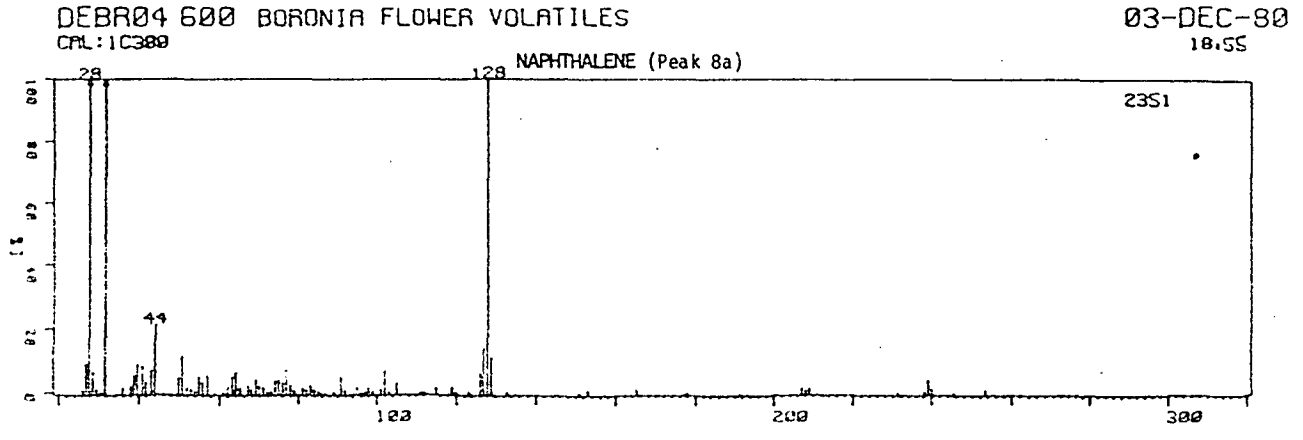


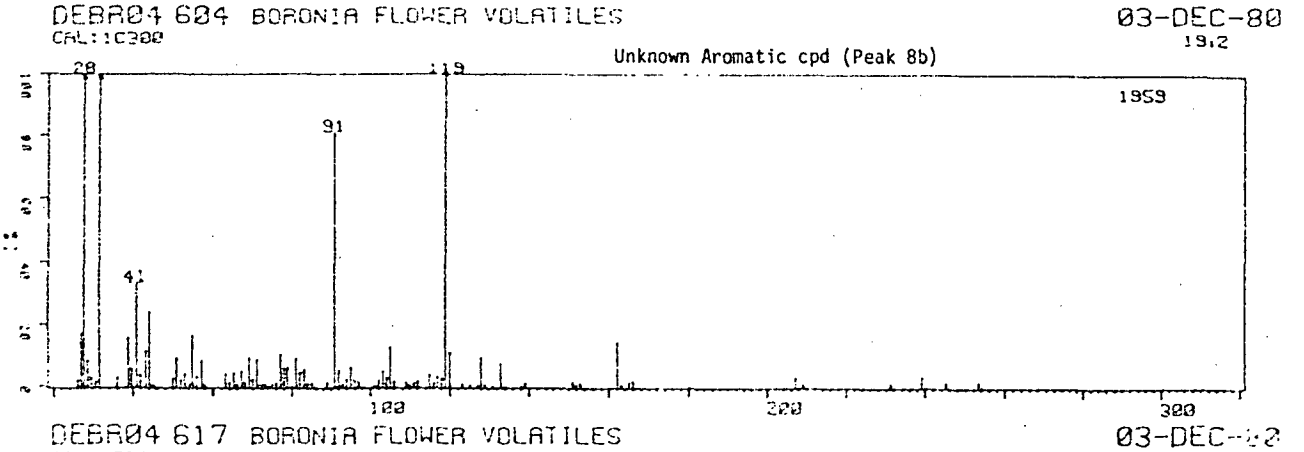


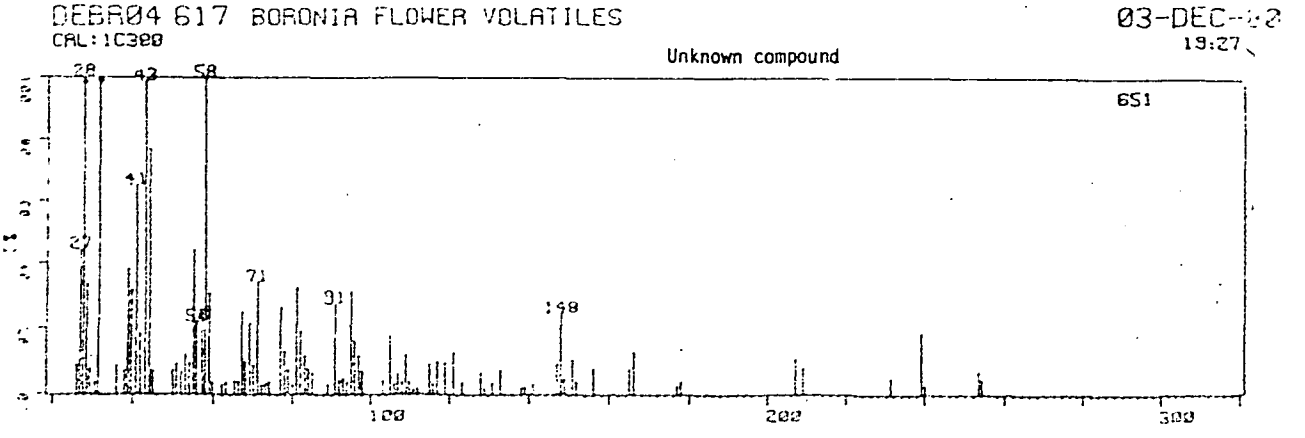


MASS SPECTRA





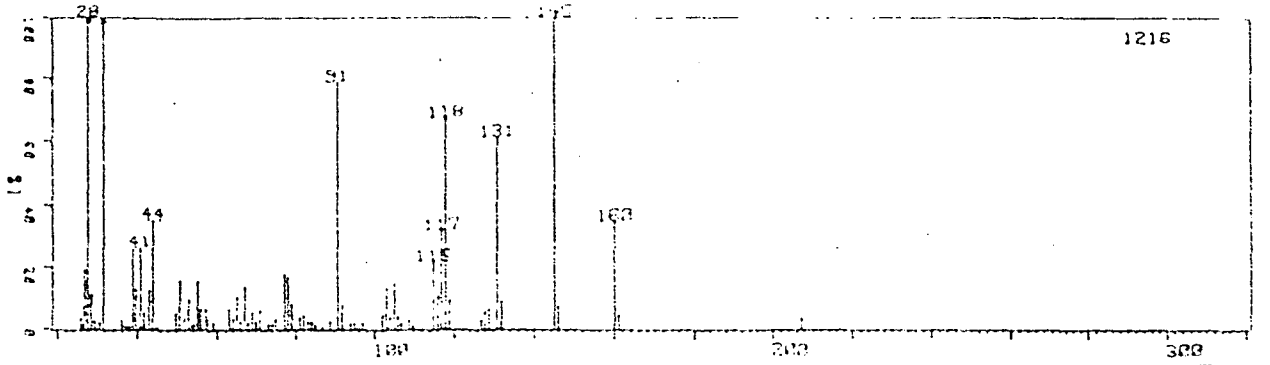




MASS SPECTRA

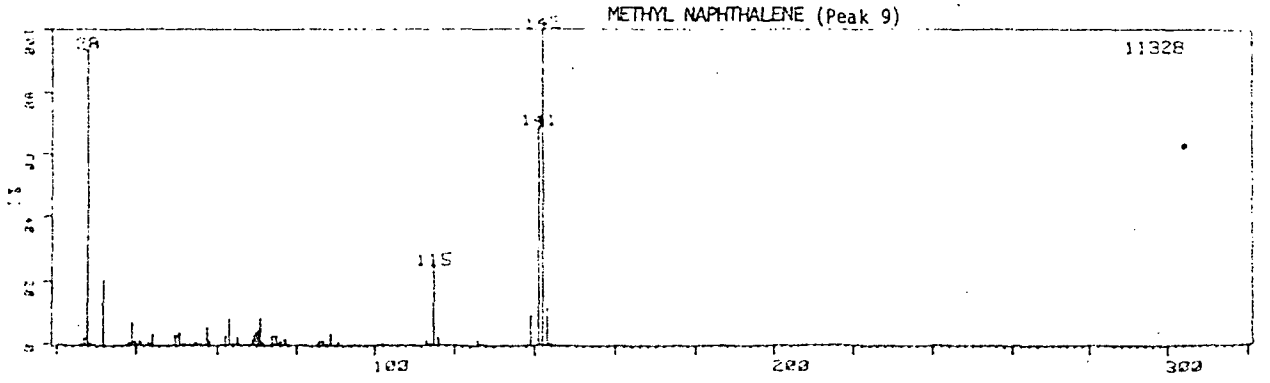
DEBR04 688 MIXTURE 03-DEC-80
CAL:1C300 21:41

MIXTURE TETRAHYDRONAPHTHALENE AND A DIMETHYLINDANE CPD. (Peak 8c)



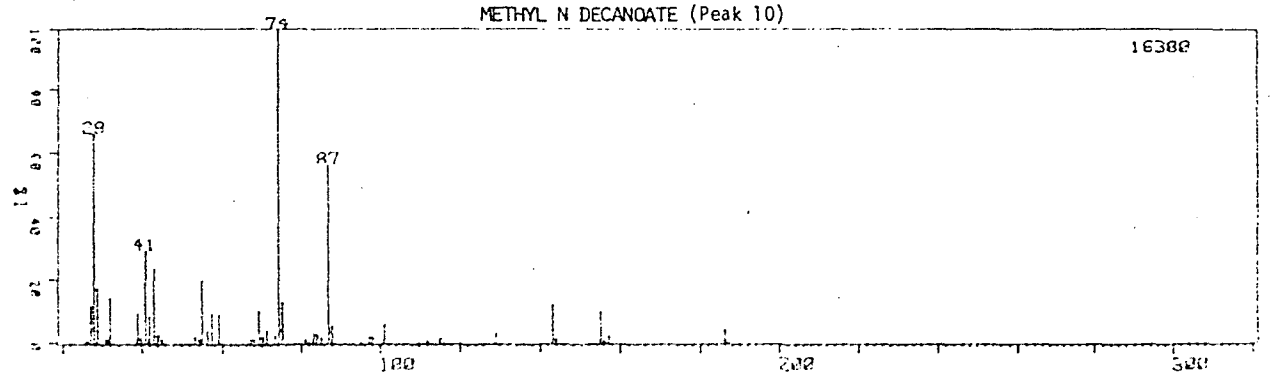
DEBR04 785 BORONIA FLOWER VOLATILES 03-DEC-80
CAL:1C300 22:13

METHYL NAPHTHALENE (Peak 9)



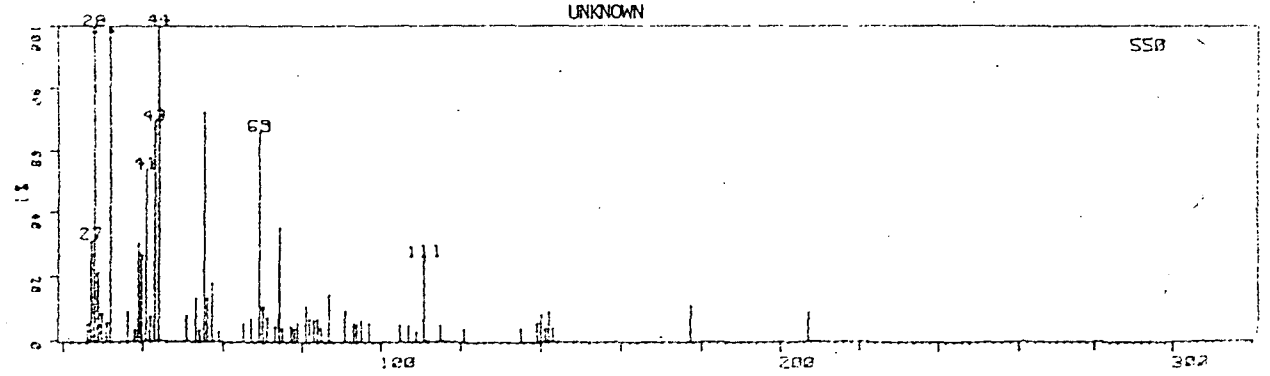
DEBR04 736 BORONIA FLOWER VOLATILES 03-DEC-80
CAL:1C300 23:12

METHYL N DECANOATE (Peak 10)

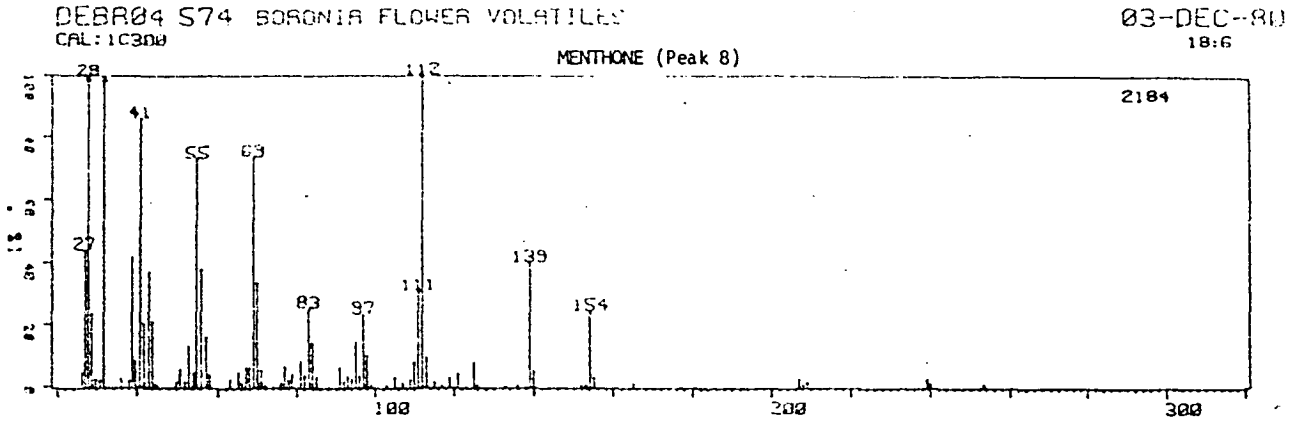


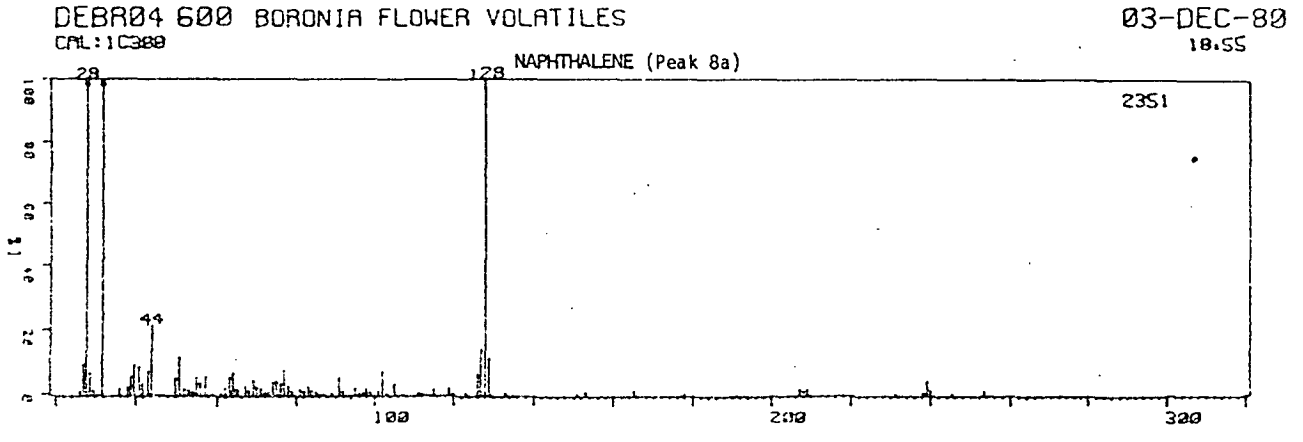
DEBR04 750 BORONIA FLOWER VOLATILES 03-DEC-80
CAL:1C300 23:38

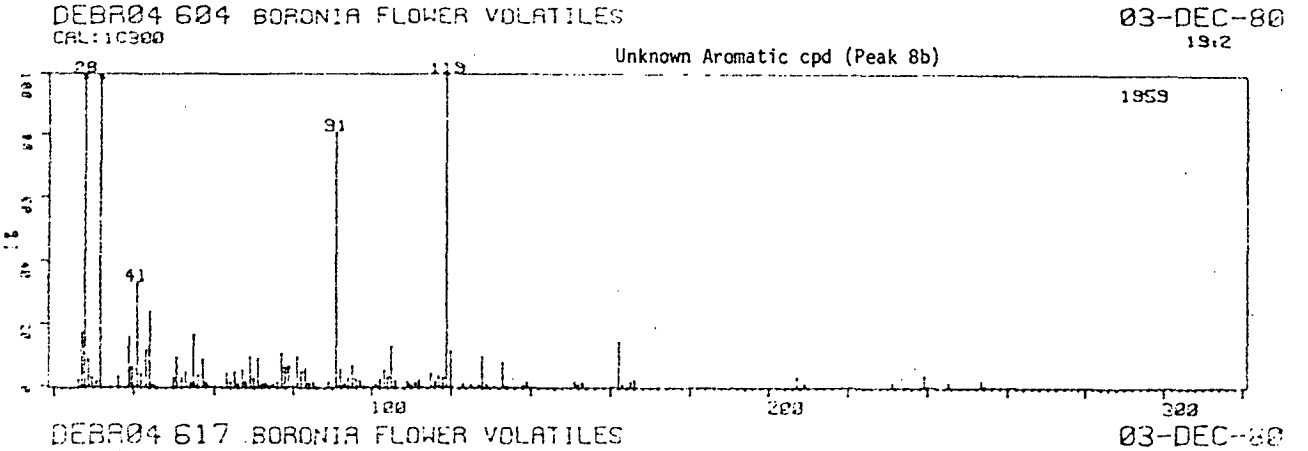
UNKNOWN

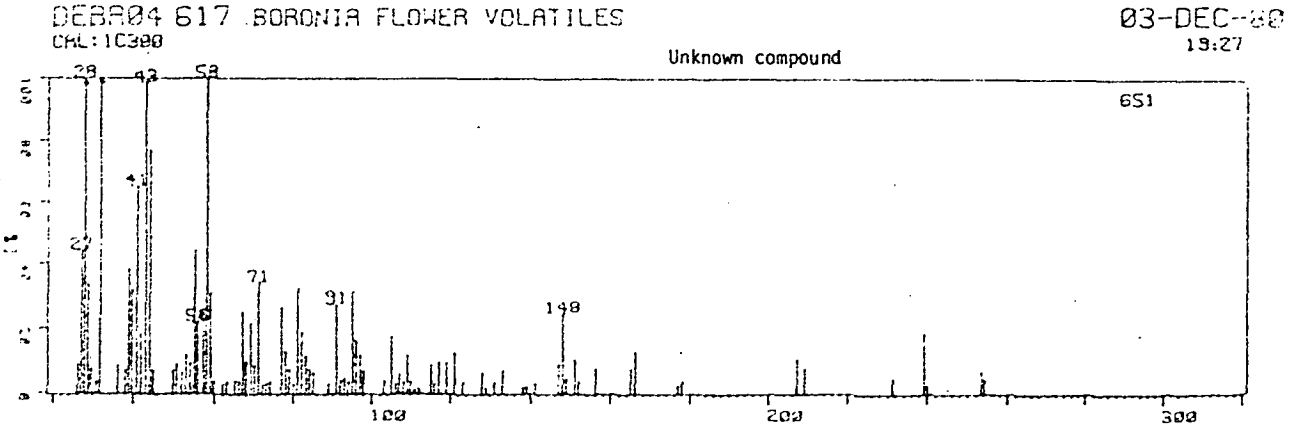


MASS SPECTRA



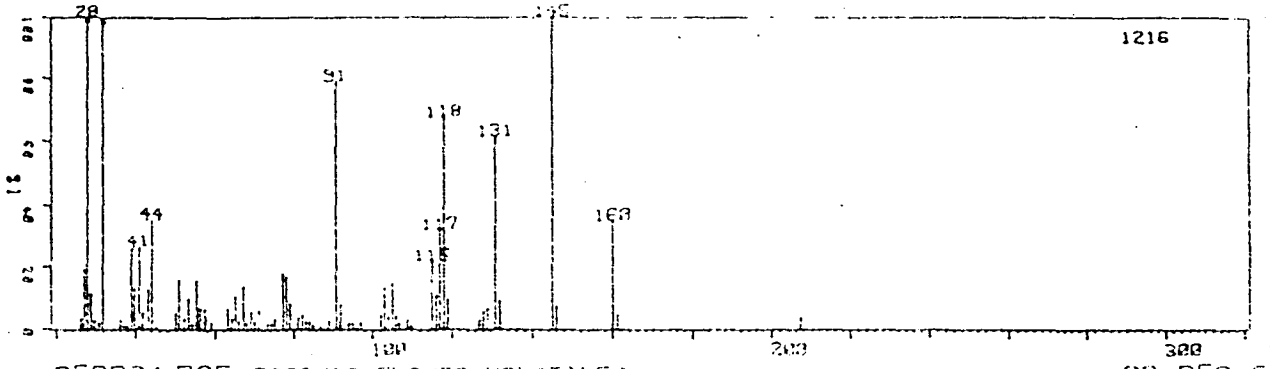




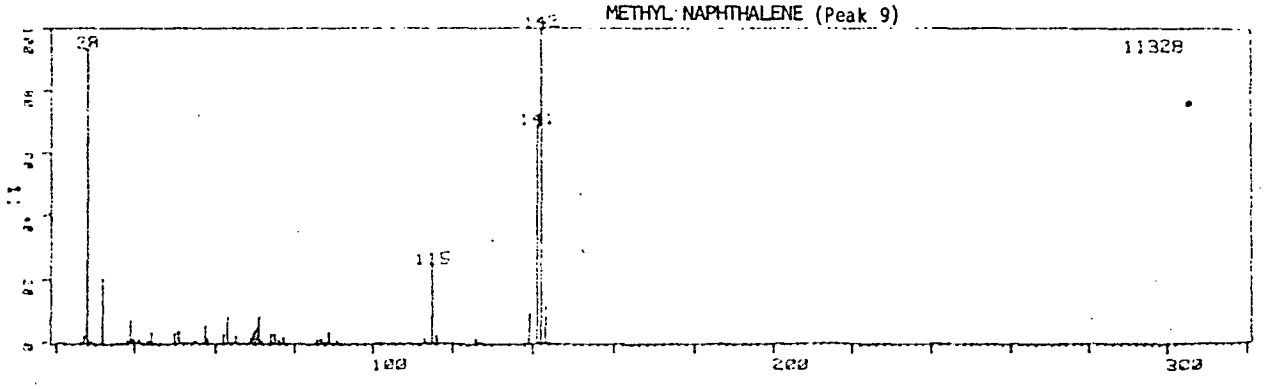


MASS SPECTRA

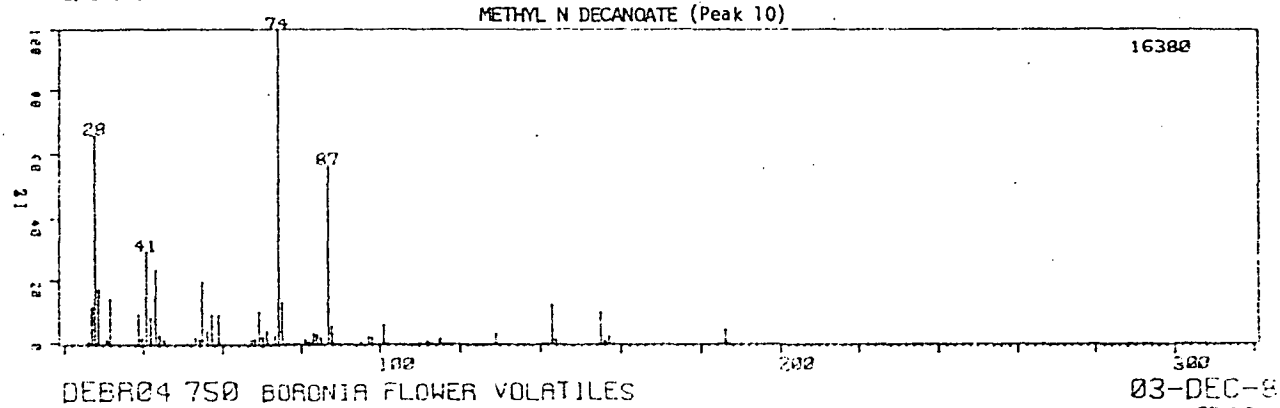
DEBR04 688 MIXTURE
CAL:1C300
MIXTURE TETRAHYDRONAPHTHALENE AND A DIMETHYLINDANE CPD. (Peak 8c)
03-DEC-80
21:41



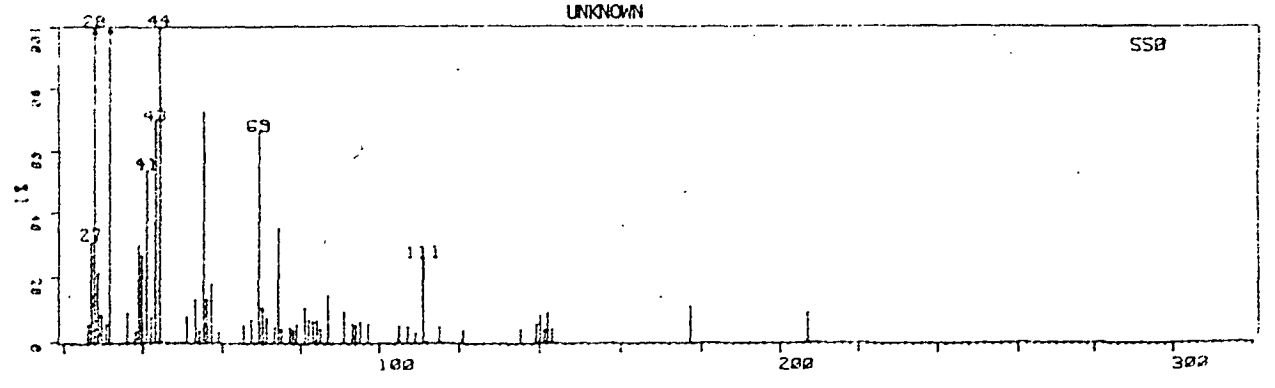
DEBR04 705 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-80
22:13
METHYL NAPHTHALENE (Peak 9)



DEBR04 736 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-80
23:12
METHYL N DECANOATE (Peak 10)



DEBR04 750 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-80
23:38
UNKNOWN



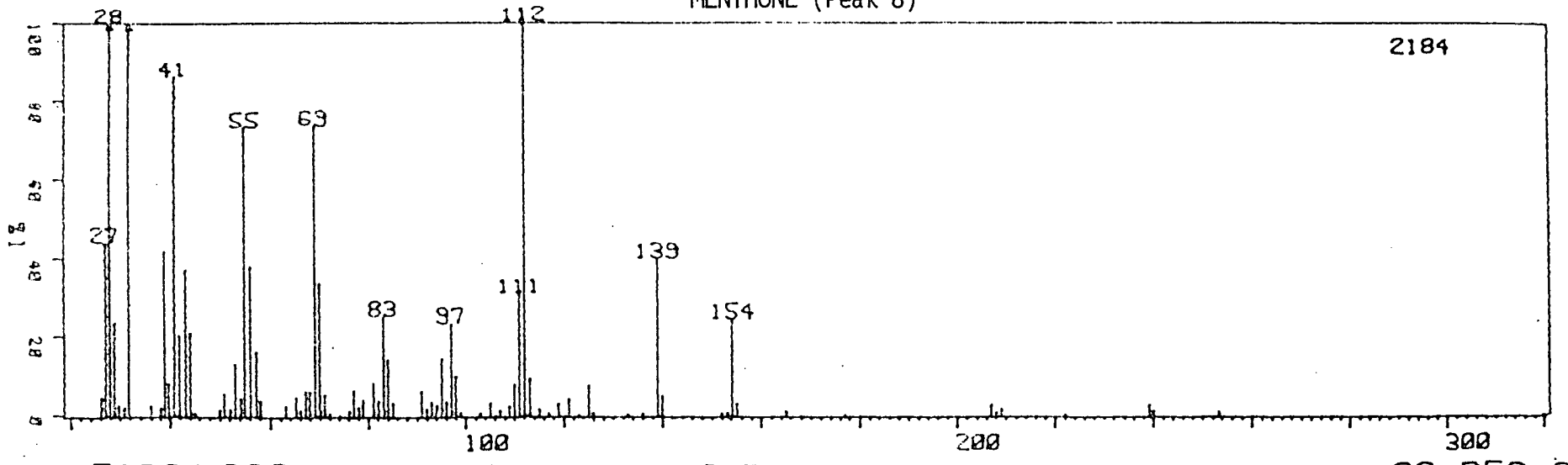
DEBR04 S74 BORONIA FLOWER VOLATILES

03-DEC-80

CAL:1C300

18:6

MENTHONE (Peak 8)



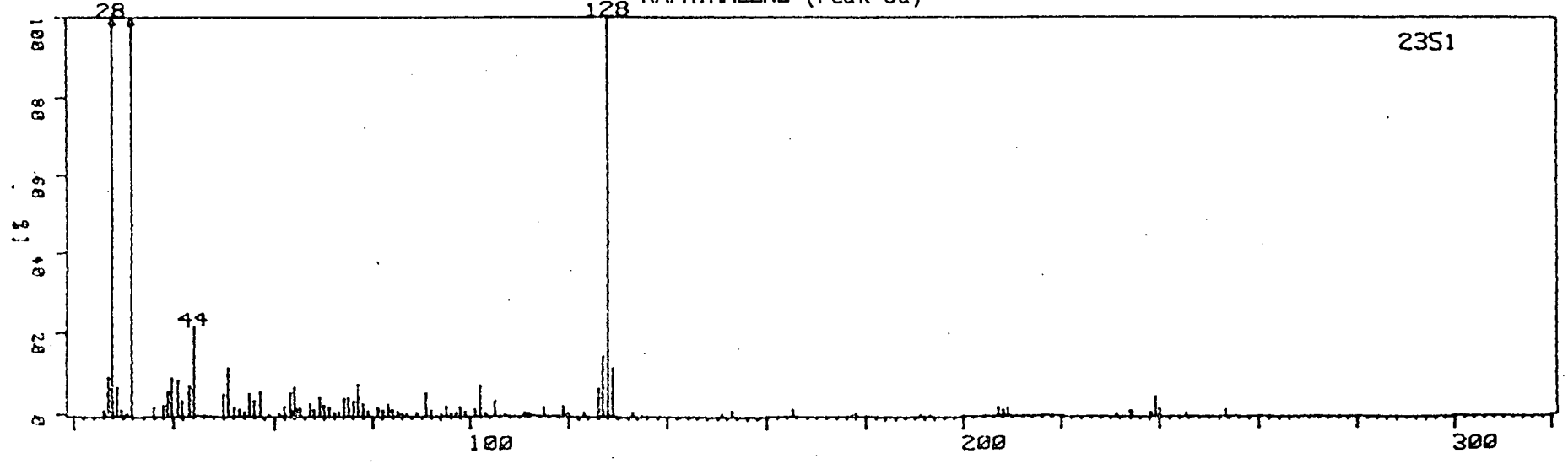
DEBR04 600 BORONIA FLOWER VOLATILES

03-DEC-80

CAL:1C300

18:55

NAPHTHALENE (Peak 8a)

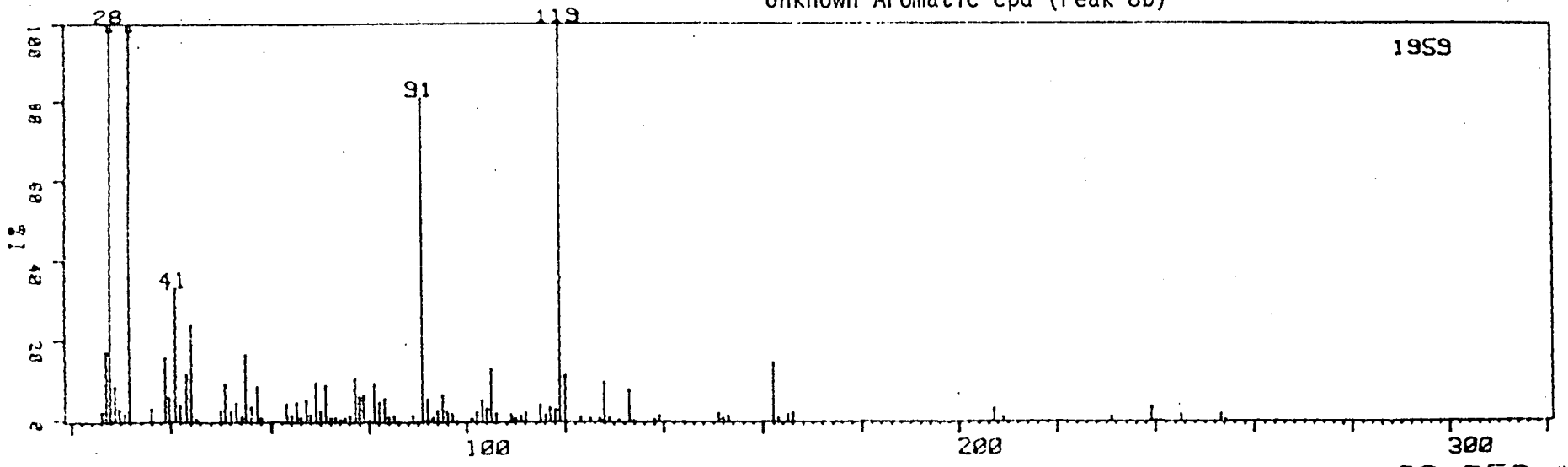


DEBR04 604 BORONIA FLOWER VOLATILES

03-DEC-80
19:2

CAL:1C300

Unknown Aromatic cpd (Peak 8b)

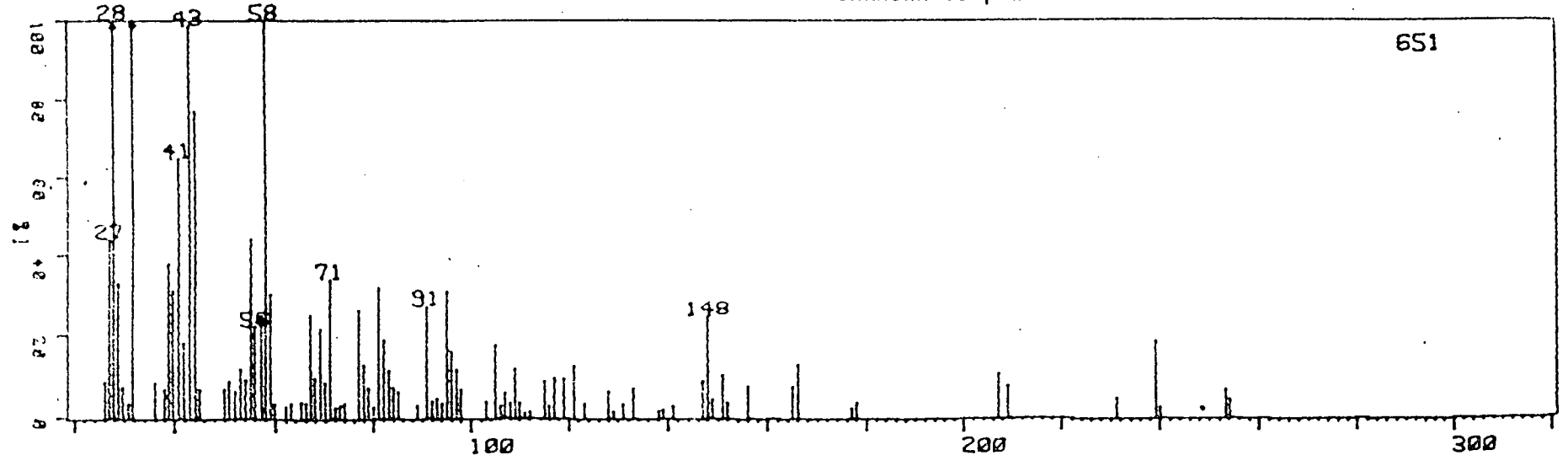


DEBR04 617 BORONIA FLOWER VOLATILES

03-DEC-80
19:27

CAL:1C300

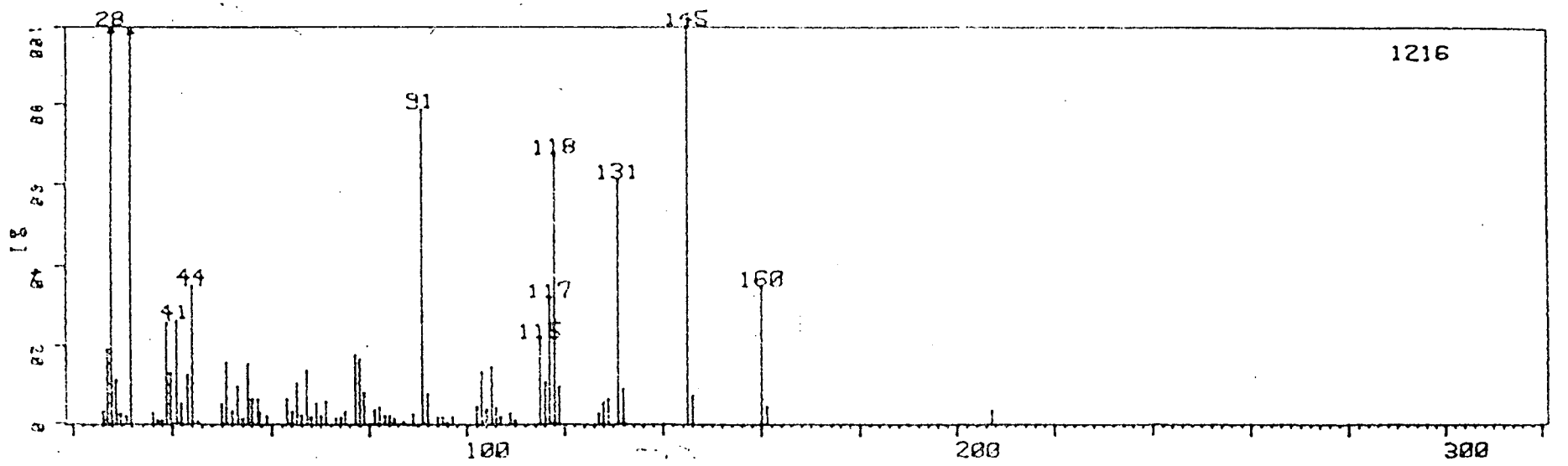
Unknown compound



DEBR04 688 MIXTURE
CAL:1C300

03-DEC-80
21:41

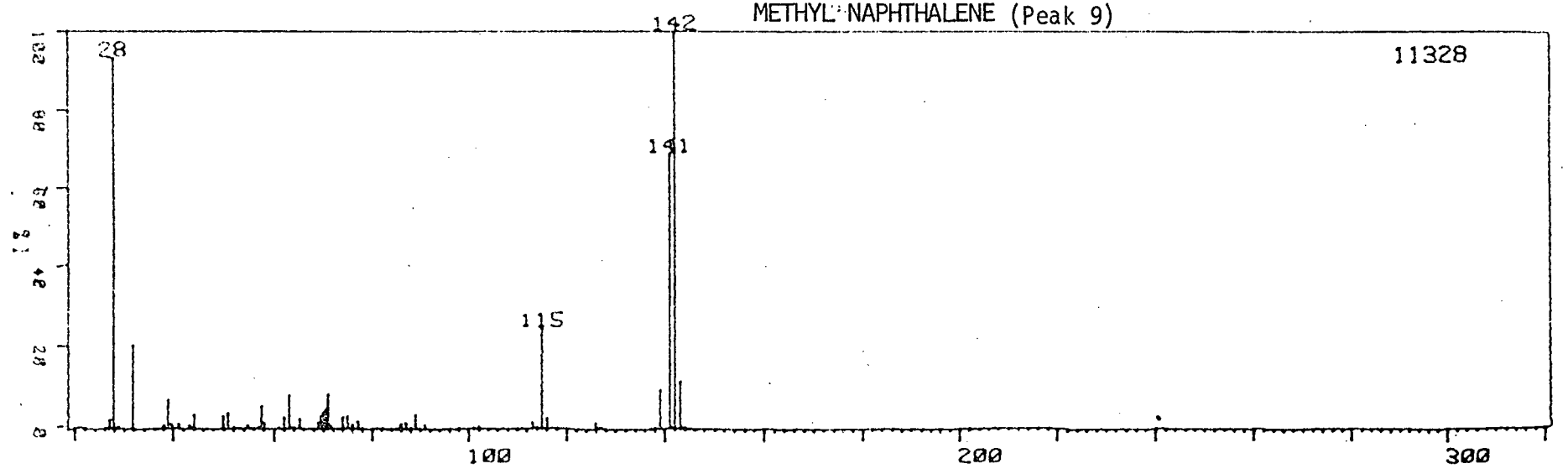
MIXTURE TETRAHYDRONAPHTHALENE AND A DIMETHYLINDANE CPD. (Peak 8c)



DEBR04 705 BORONIA FLOWER VOLATILES
CAL:1C300

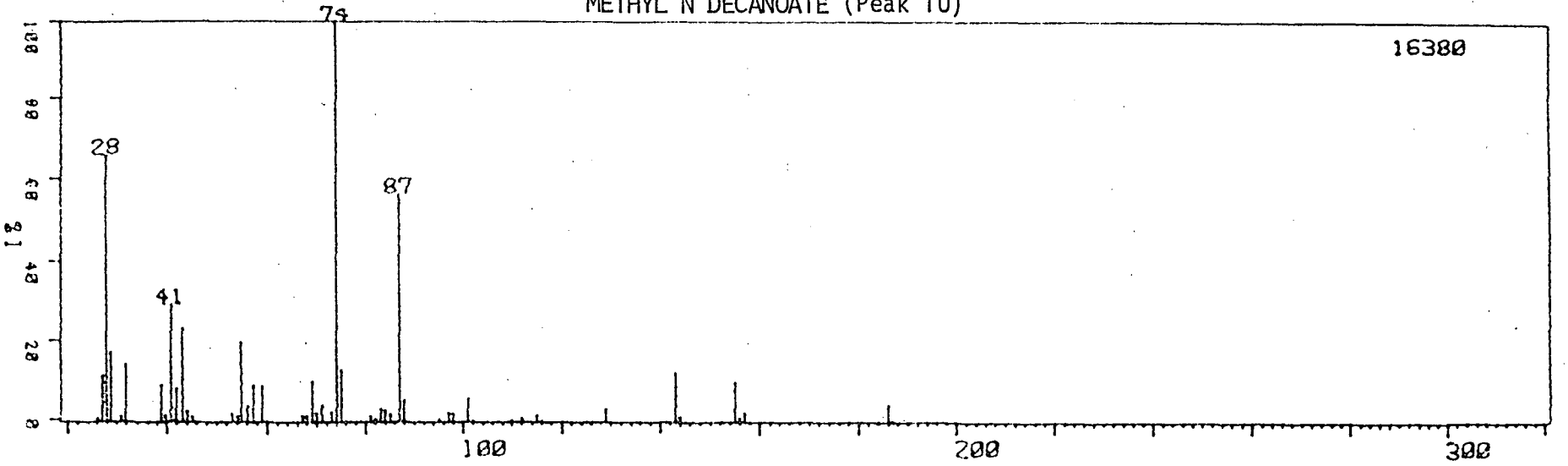
03-DEC-80
22:13

METHYL NAPHTHALENE (Peak 9)



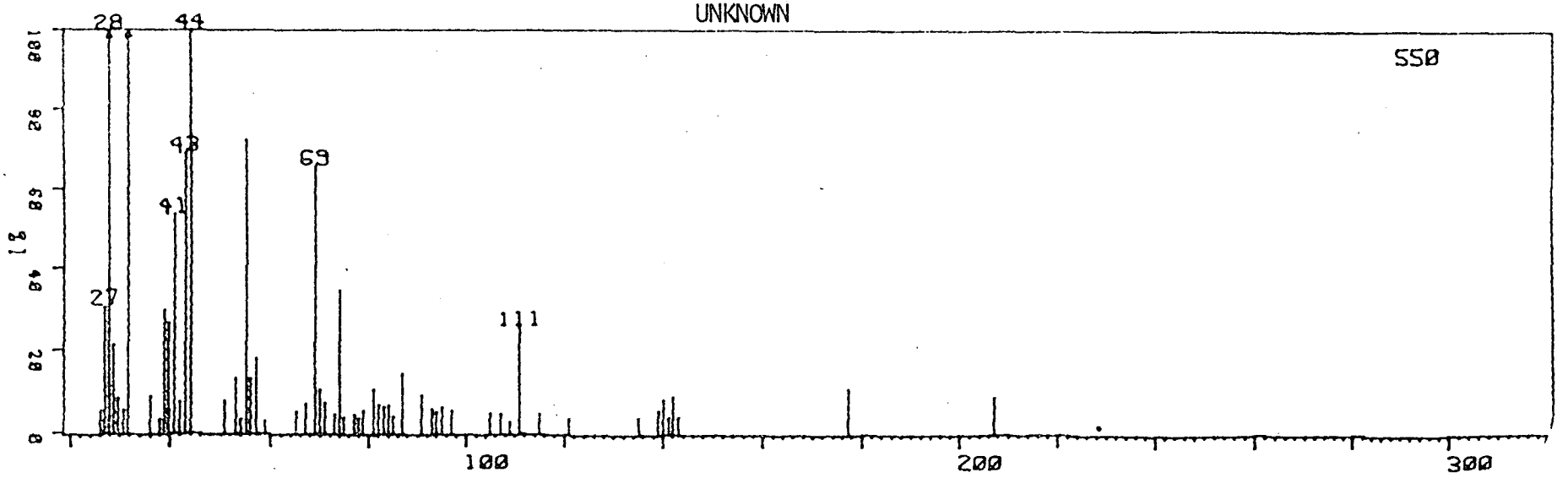
DEBR04 736 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-80
23:12

METHYL N DECANOATE (Peak 10)

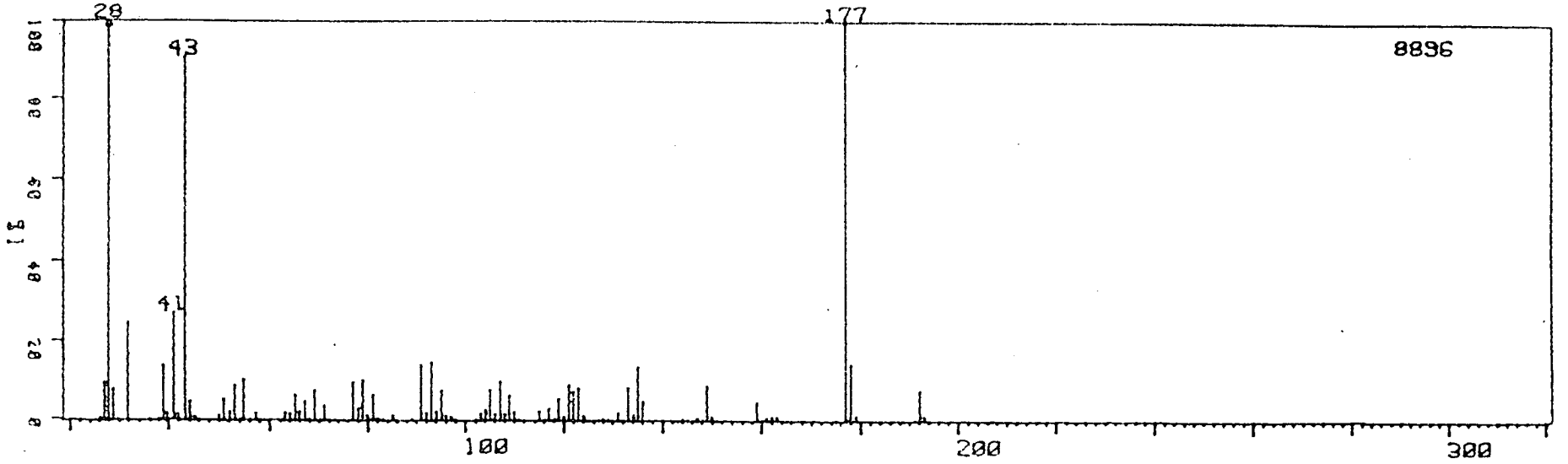


DEBR04 750 BORONIA FLOWER VOLATILES
CAL:1C300
03-DEC-80
23:38

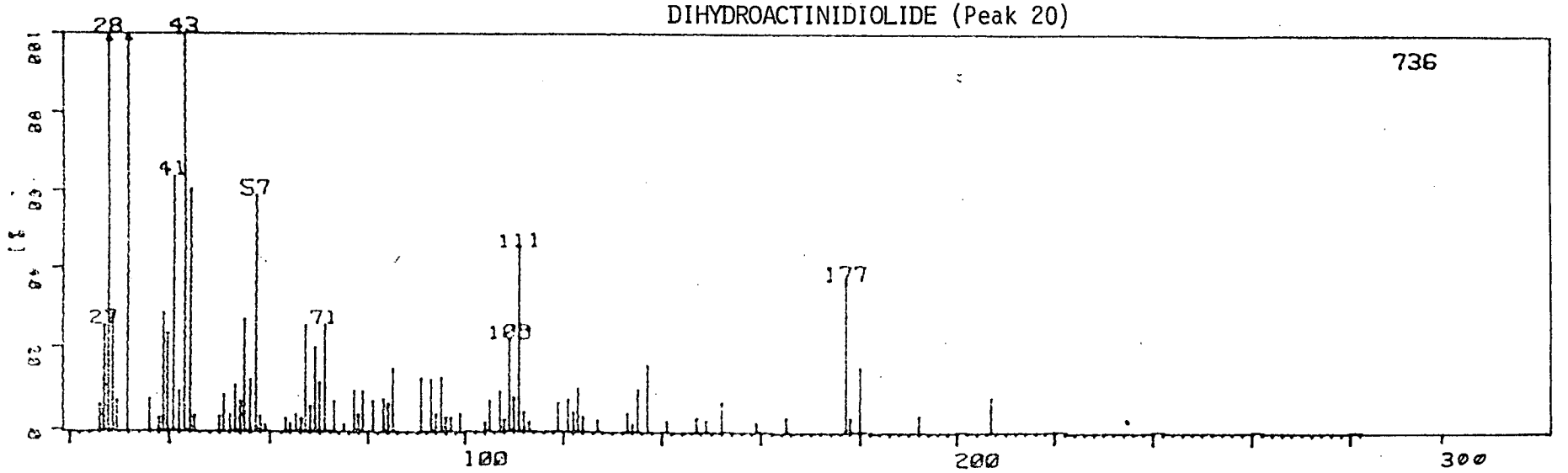
UNKNOWN



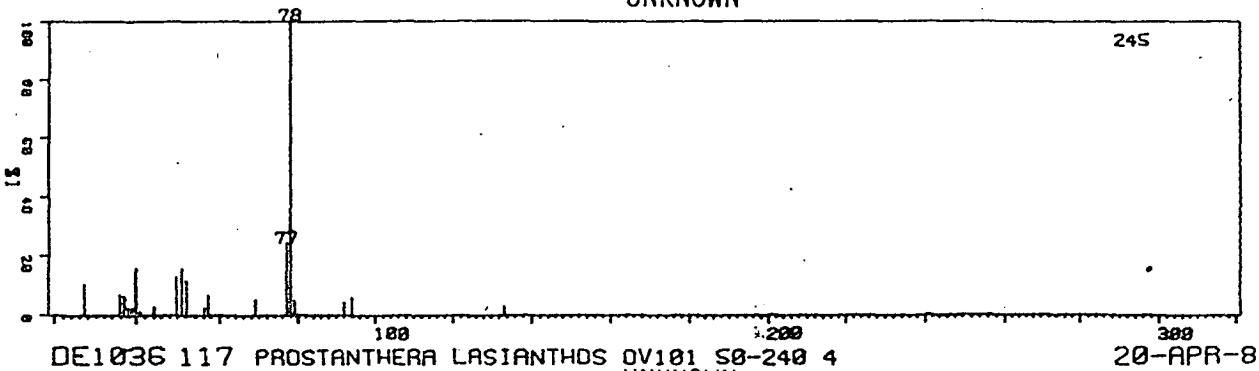
DEBR04 858 BORONIA FLOWER VOLATILES
CAL:1C300
β-IONONE (Peak 18)
03-DEC-80
27:2



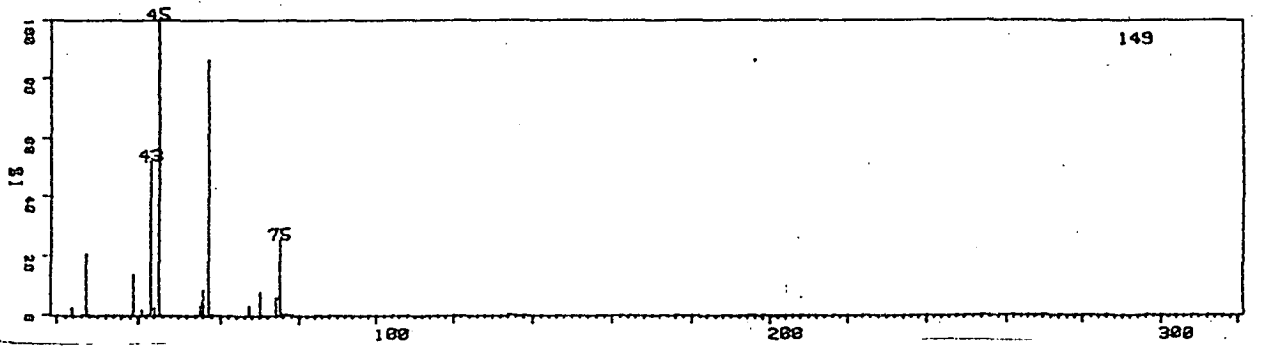
DEBR04 883 BORONIA FLOWER VOLATILES
CAL:1C300
DIHYDROACTINIDIOLIDE (Peak 20)
03-DEC-80
27:50



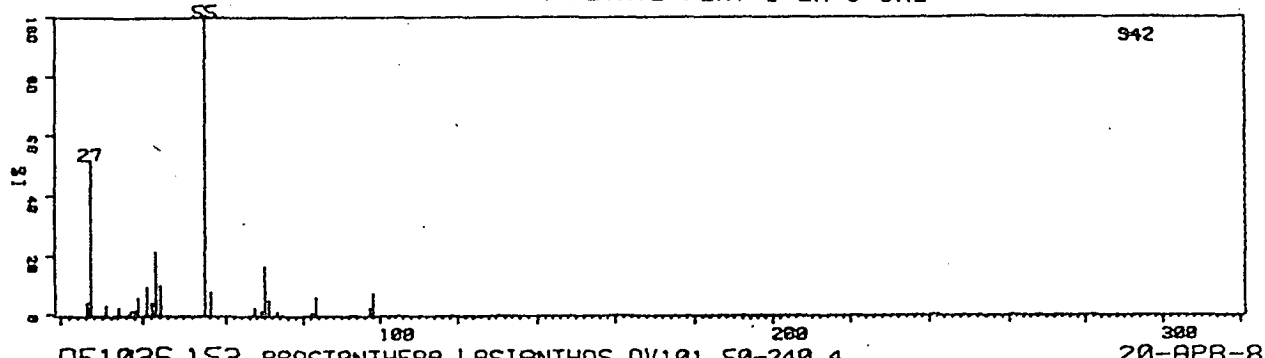
DE1036 92 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 2:54



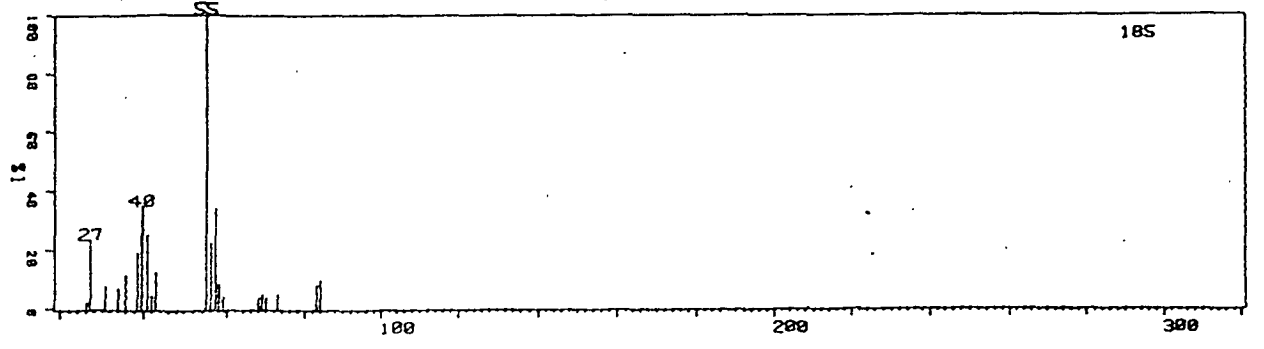
DE1036 117 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 3:42



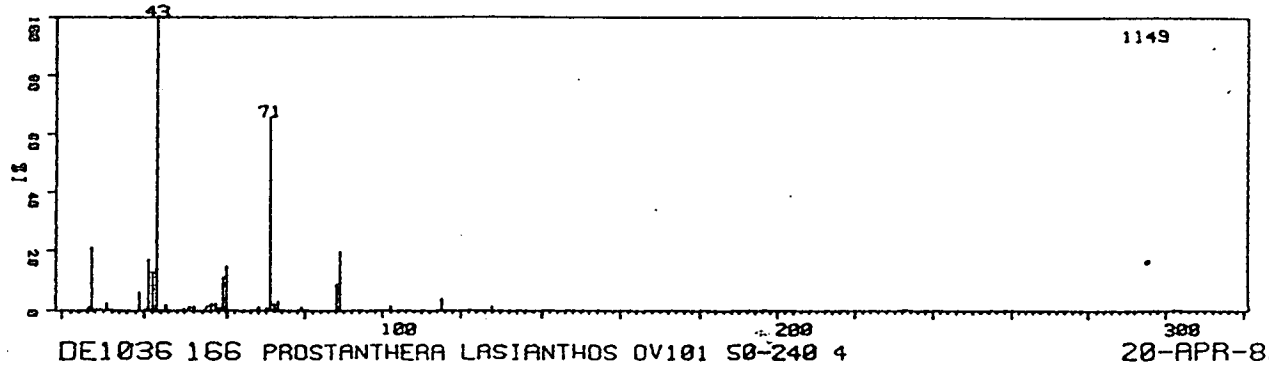
DE1036 123 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 4 METHYL-PENT-1-EN-3-ONE 3:53



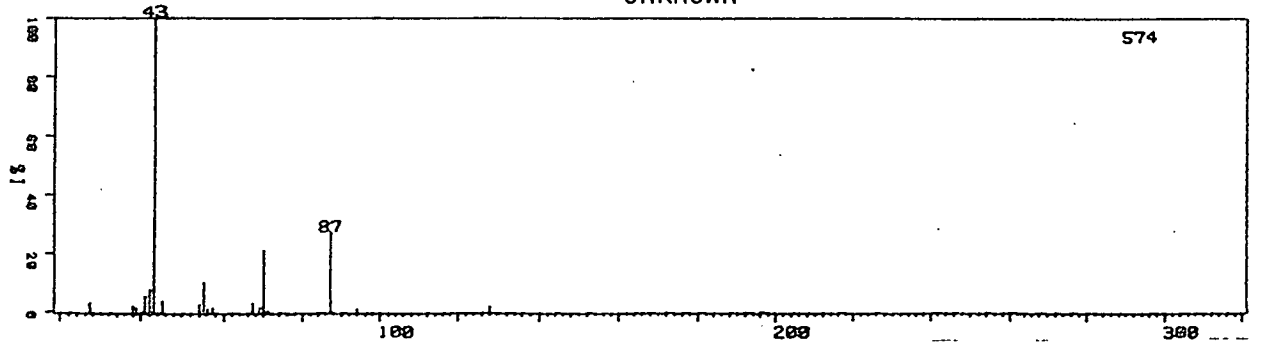
DE1036 153 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 4:58



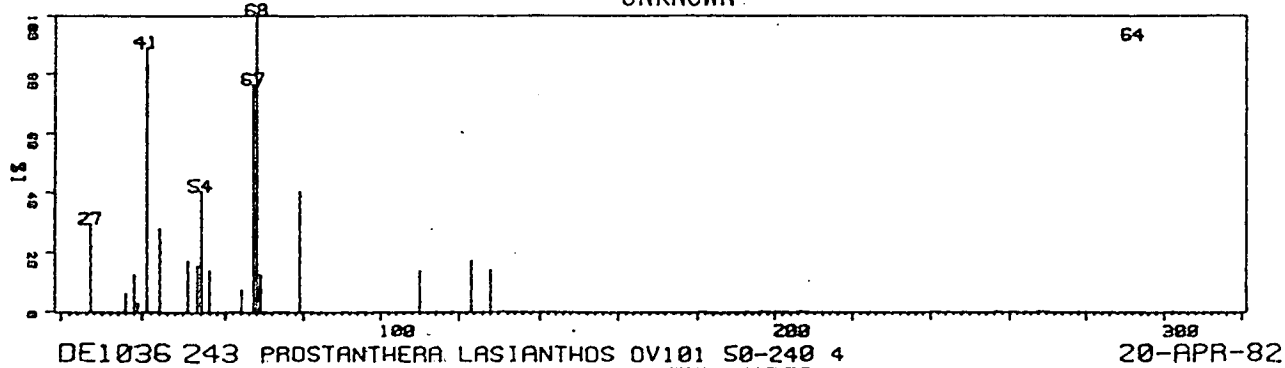
DE1036 161 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D480 STA:E. UNKNOWN S:S



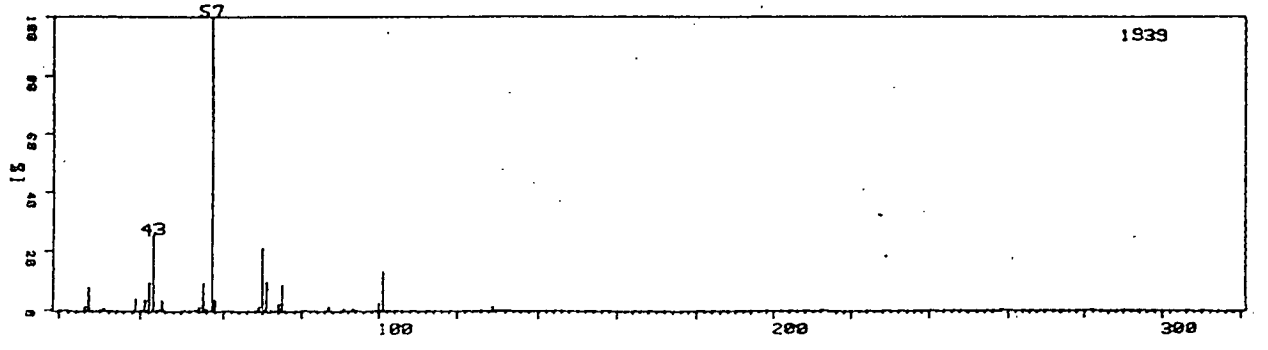
DE1036 166 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D480 STA:E. UNKNOWN S:14



DE1036 189 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D480 STA:E. UNKNOWN S:S7

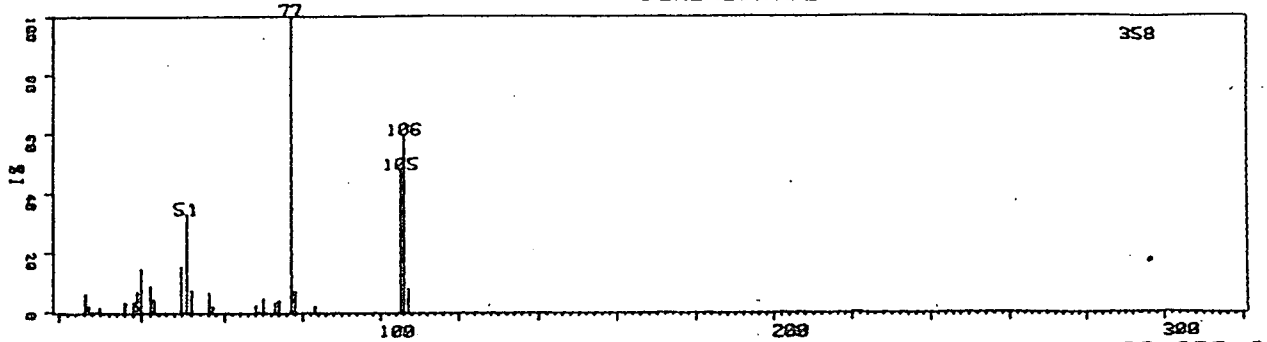


DE1036 243 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D480 STA:E. PENTYL ESTER 7:39



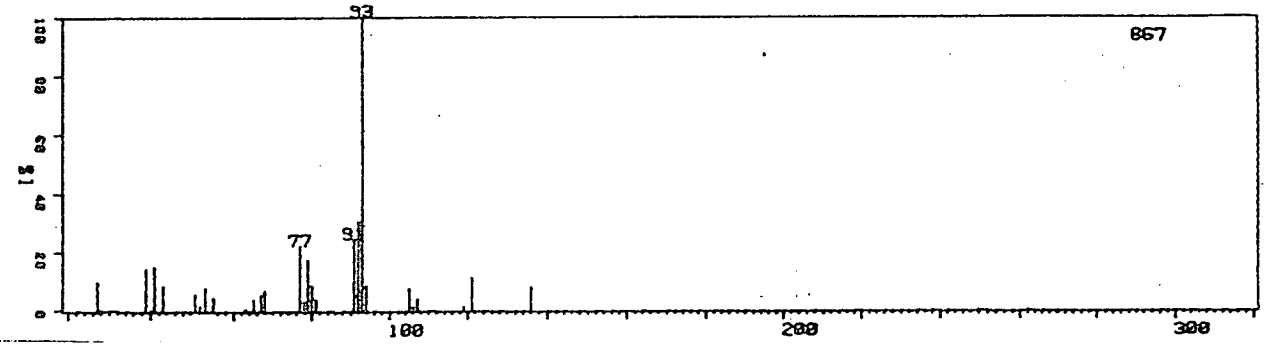
DE1036 250 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 7:53

BENZALDHYDE



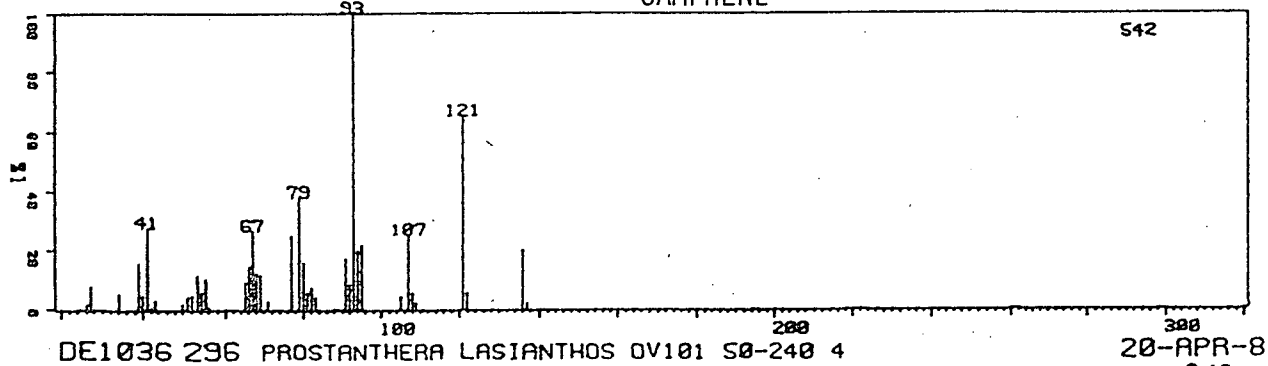
DE1036 254 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 8:0

α -PINENE



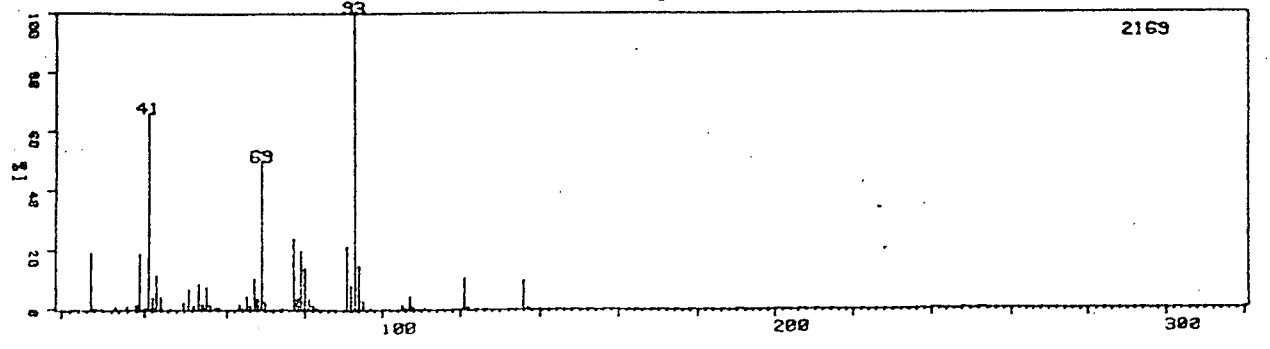
DE1036 267 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 8:25

CAMPHENE

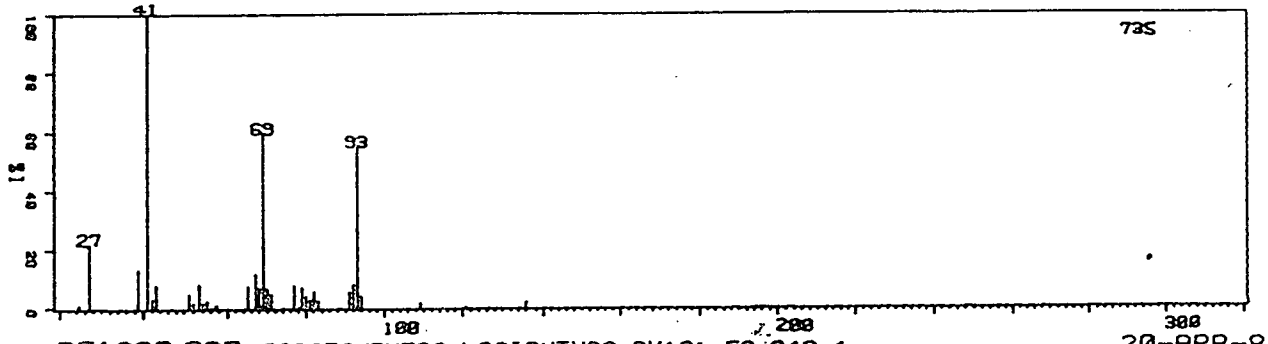


DE1036 296 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 9:19

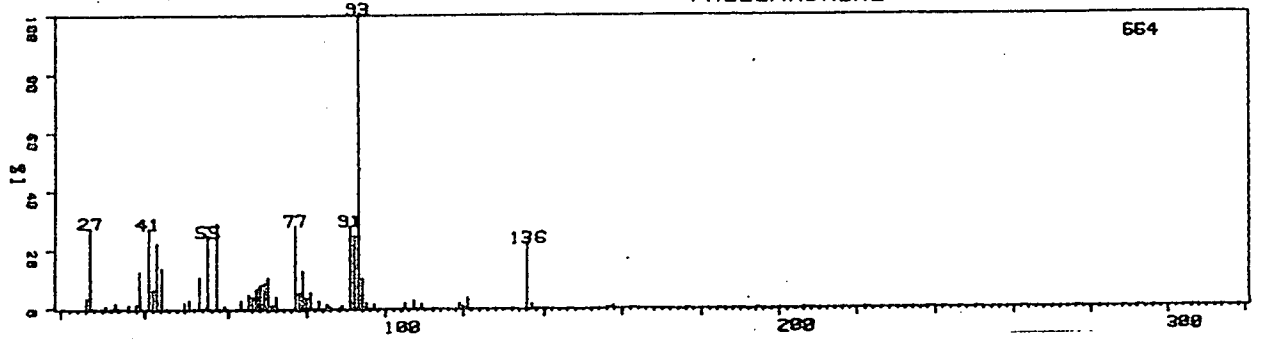
β -PINENE



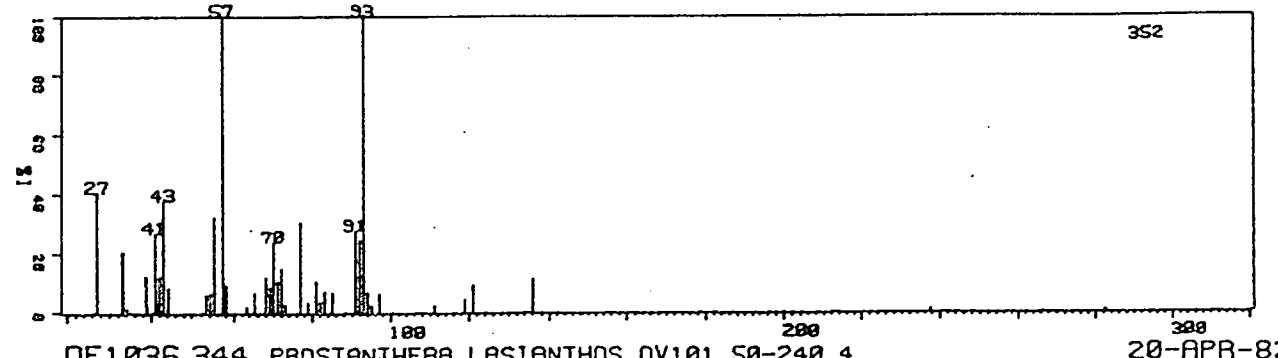
DE1036 309 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 9:44
MYRCENE



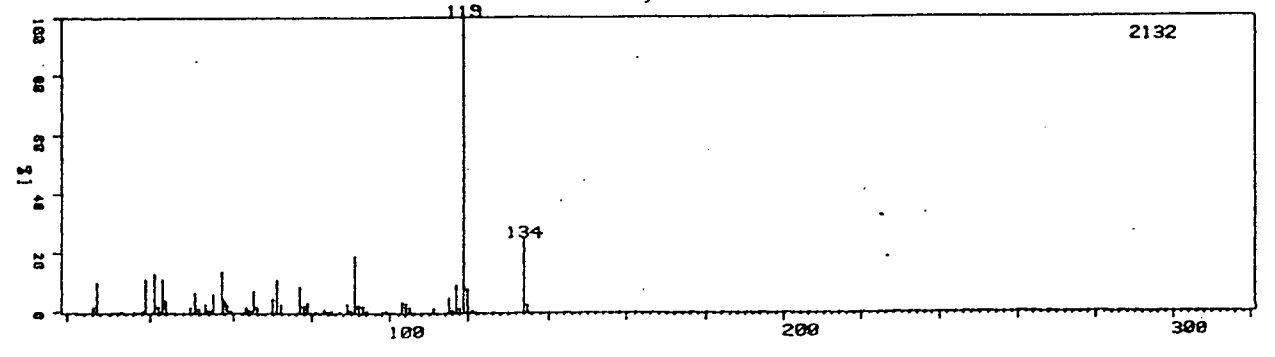
DE1036 327 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 10:18
α -PHELLANDRENE



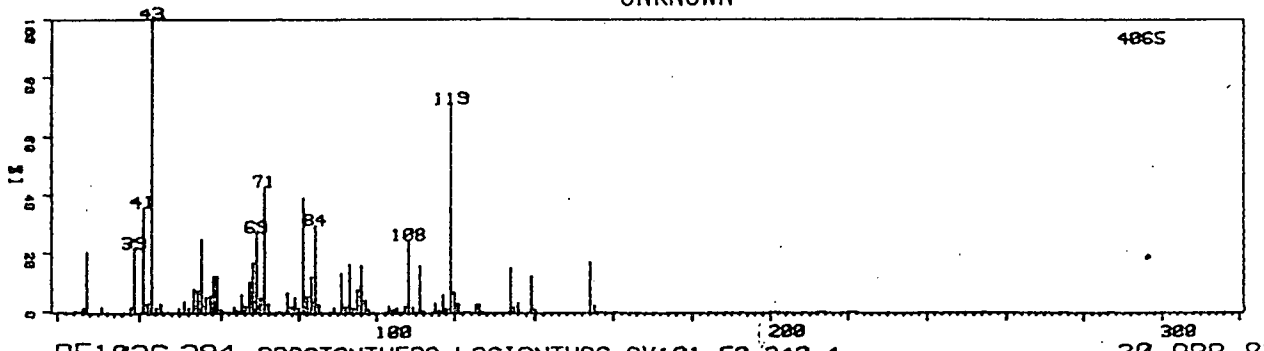
DE1036 331 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 10:26
CYMENE MIXTURE



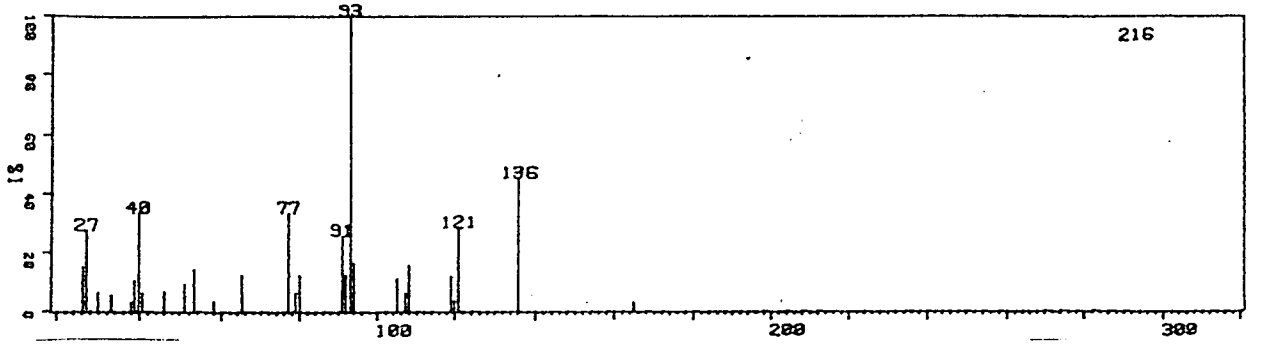
DE1036 344 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 10:50
1,8 CINEOLE + CYMENE



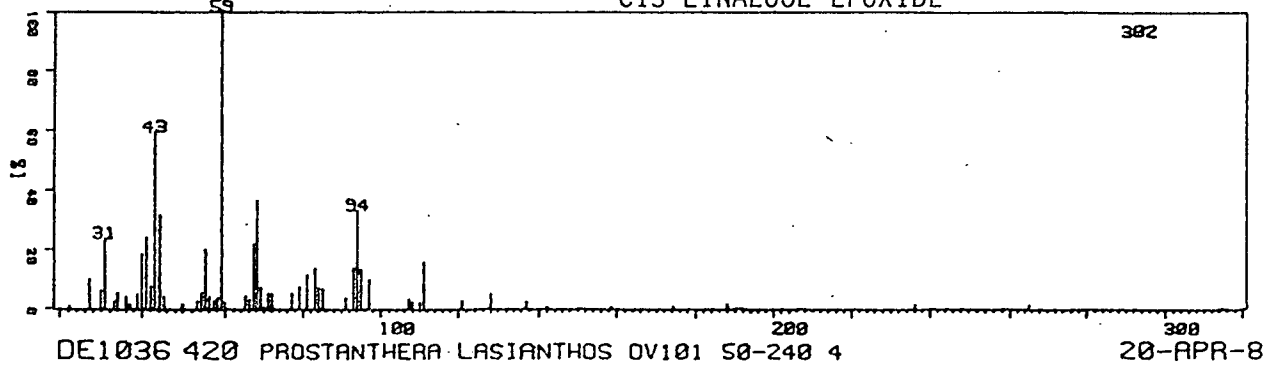
DE1036 355 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 11:11
UNKNOWN



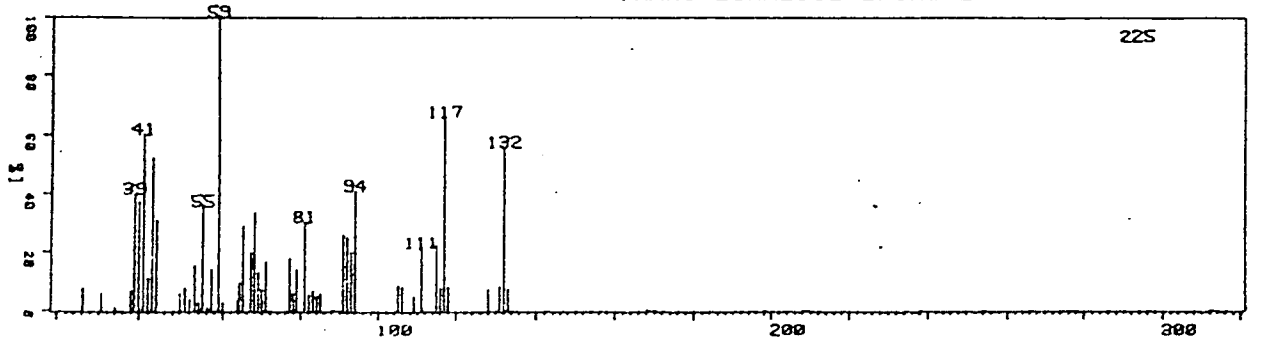
DE1036 394 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 12:24
UNKNOWN MOMOTERPENE



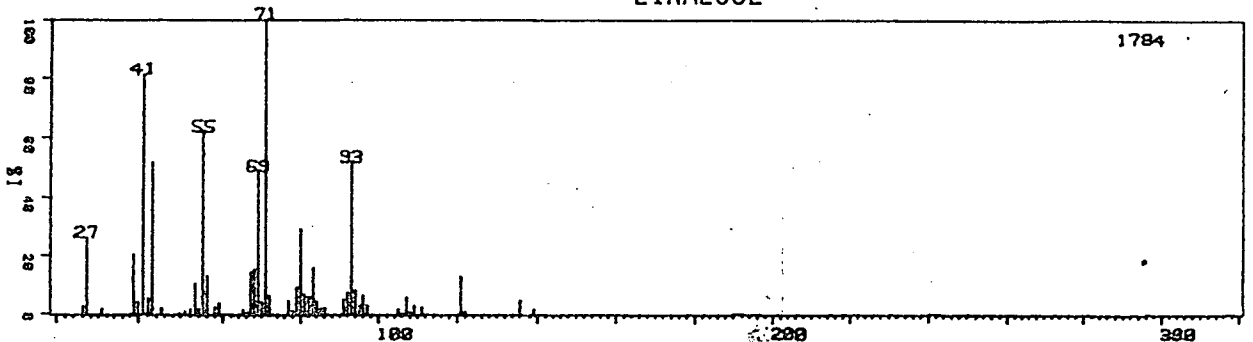
DE1036 404 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 12:43
CIS LINALOOL EPOXIDE



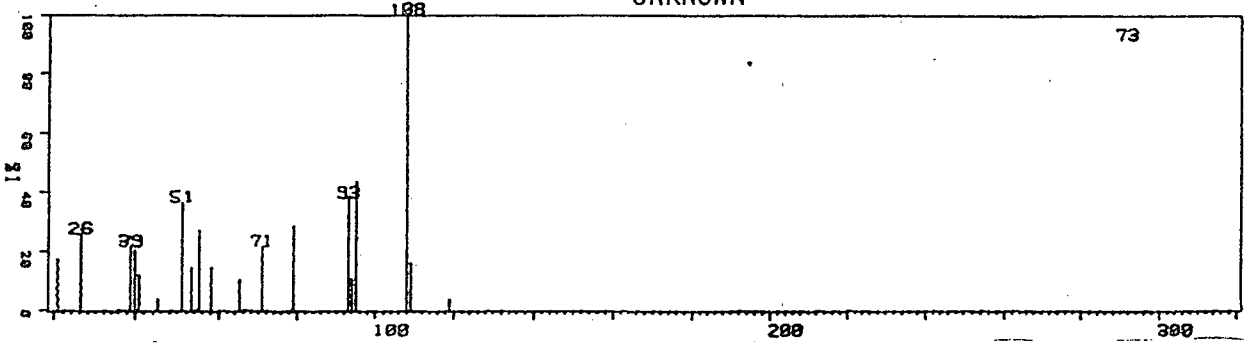
DE1036 420 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 13:14
TRANS LINALOOL EPOXIDE



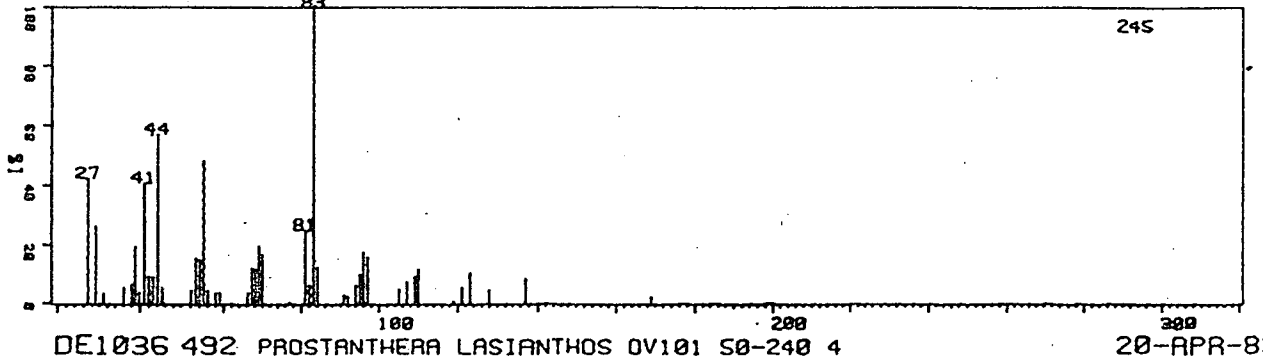
DE1036 437 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 13:46
LINALOOL



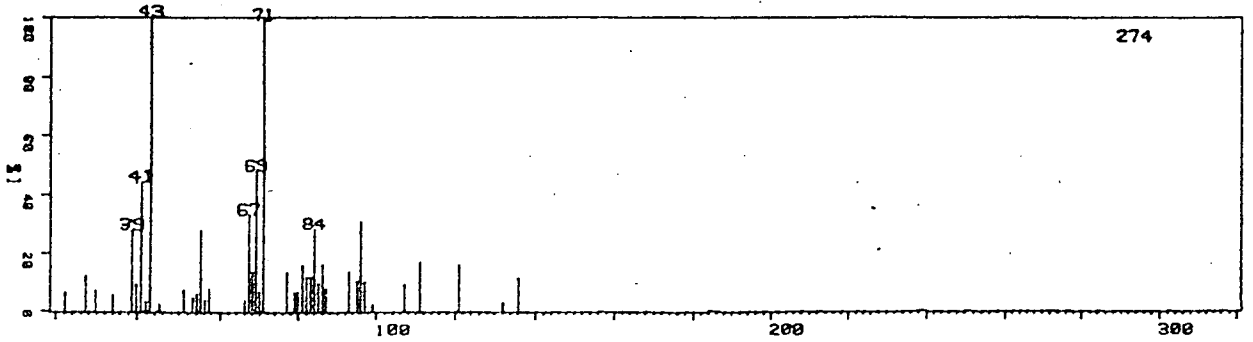
DE1036 458 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 14:25
UNKNOWN



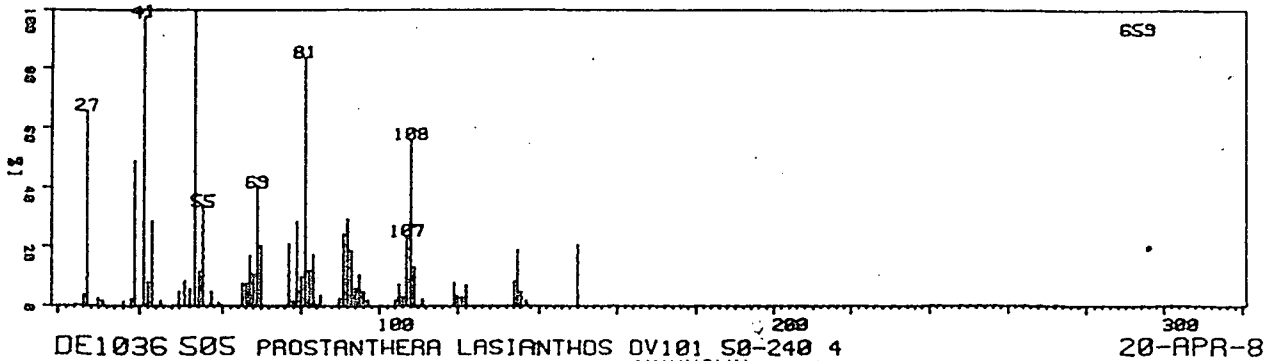
DE1036 460 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 14:29
UNKNOWN



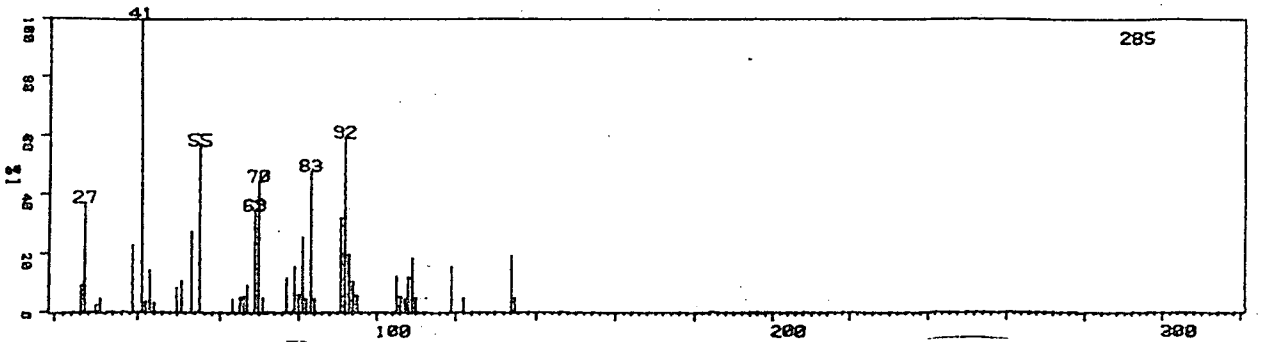
DE1036 492 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 15:29
CAMPHENE HYDRATE



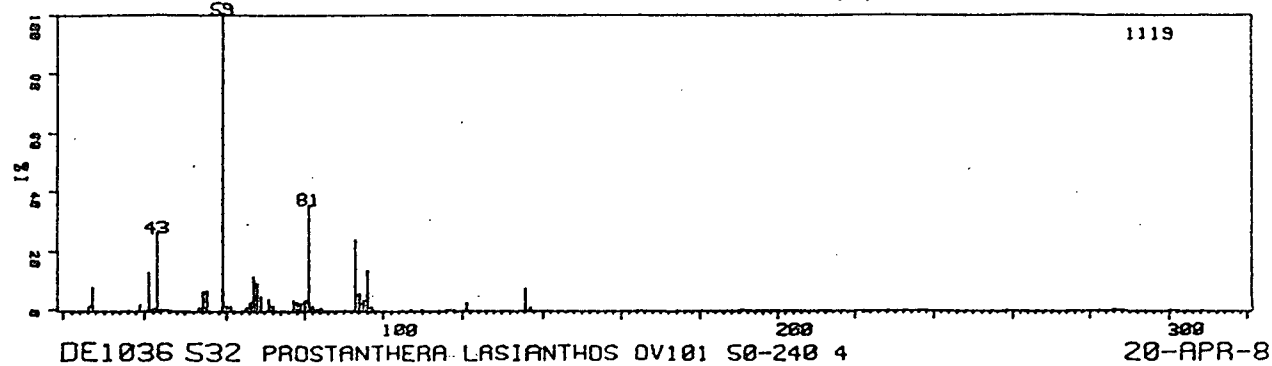
DE1036 499 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 15:43
PINOCARVONE



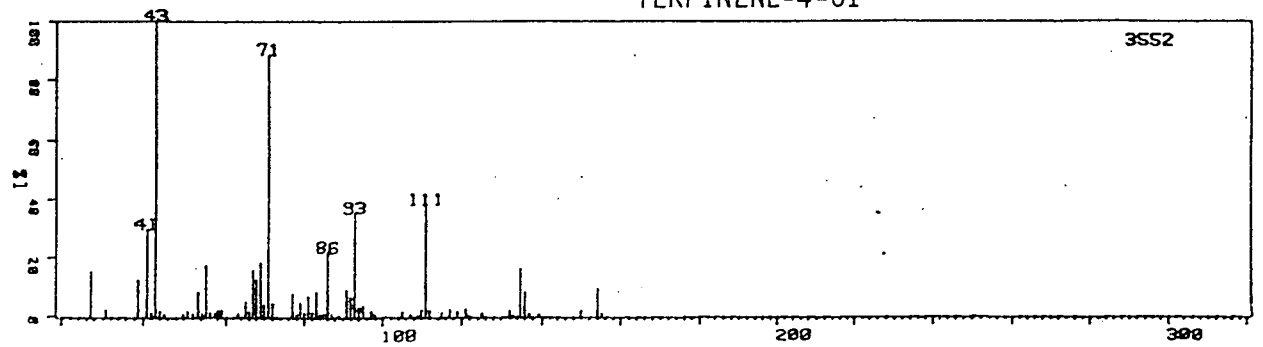
DE1036 S05 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 15:54
UNKNOWN



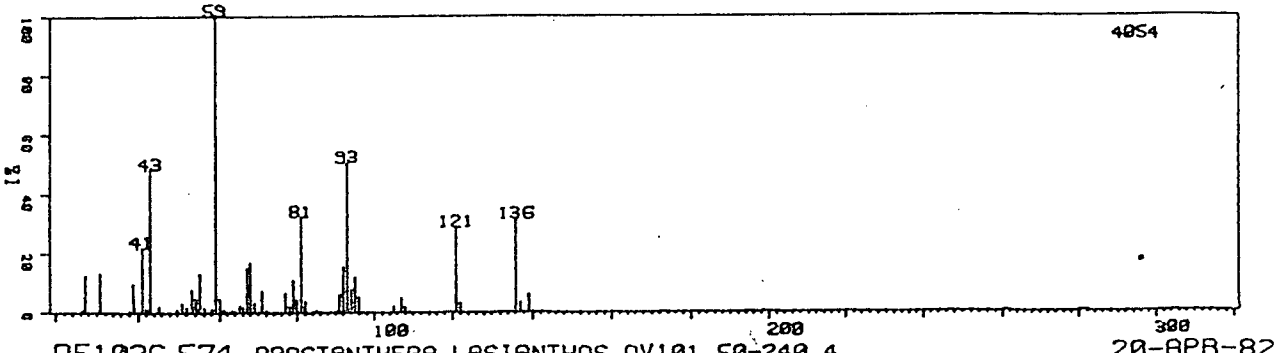
DE1036 S14 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 16:11
ARCHILLINOL (?)



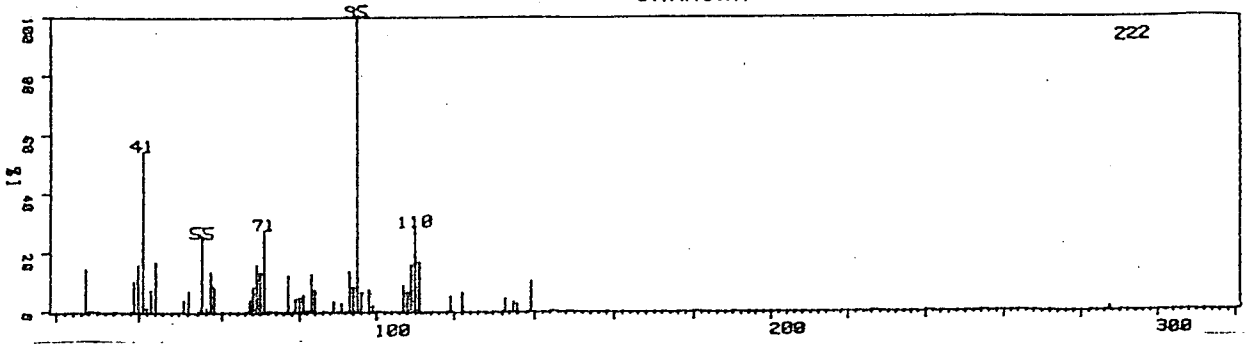
DE1036 S32 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 16:45
TERPINENE-4-01



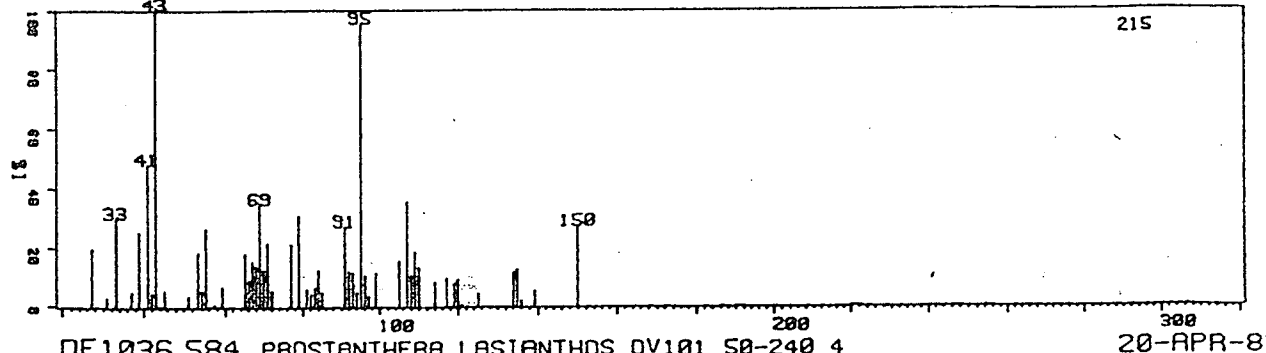
DE1036 S48 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. α-TERPINEOL 17:15



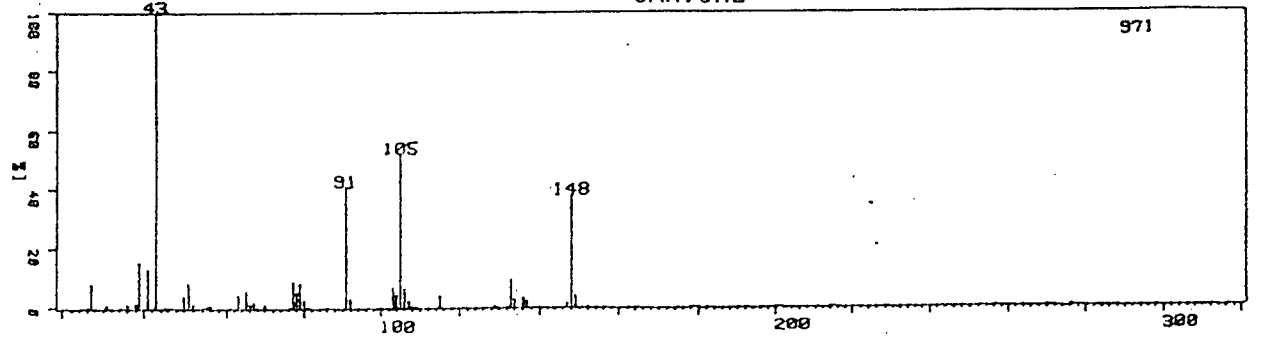
DE1036 S74 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 18:4



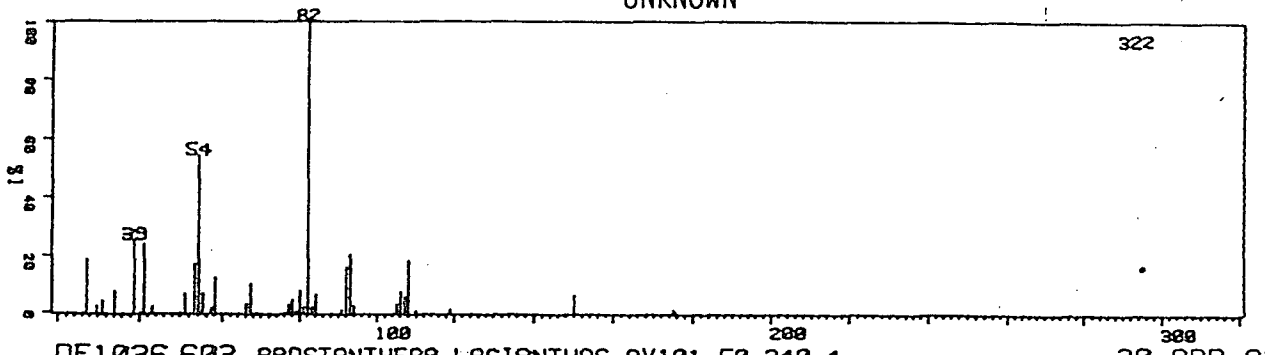
DE1036 S77 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 18:10



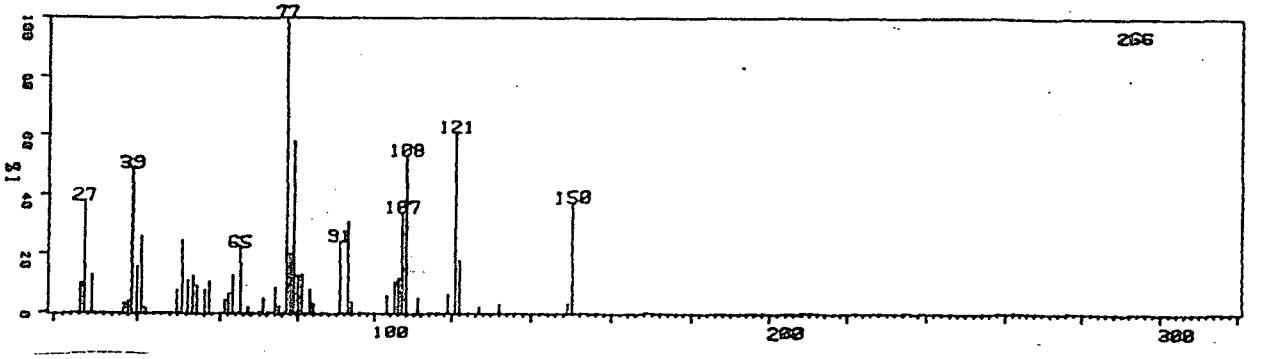
DE1036 S84 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. CARVONE 18:23



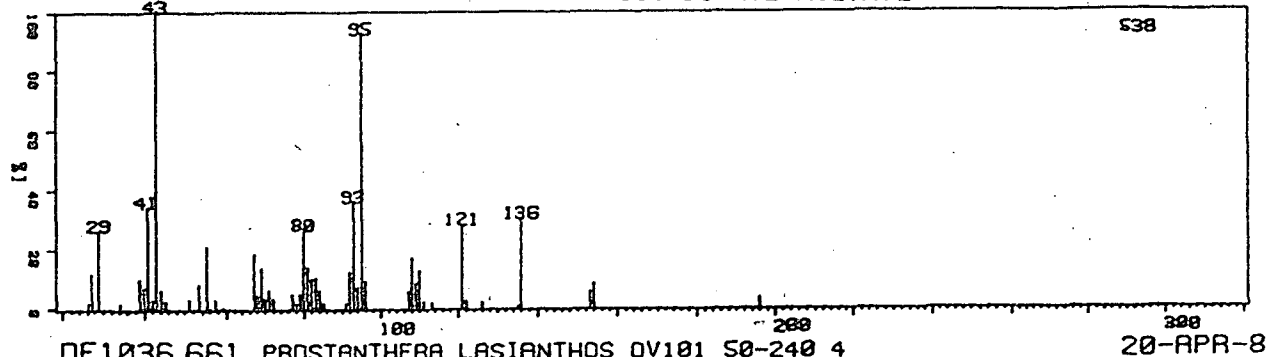
DE1036 592 PROSTANTHERA LASIANTHOS OV101 50-240 4 20-APR-82
CAL:1D400 STA:E. 18:38
UNKNOWN



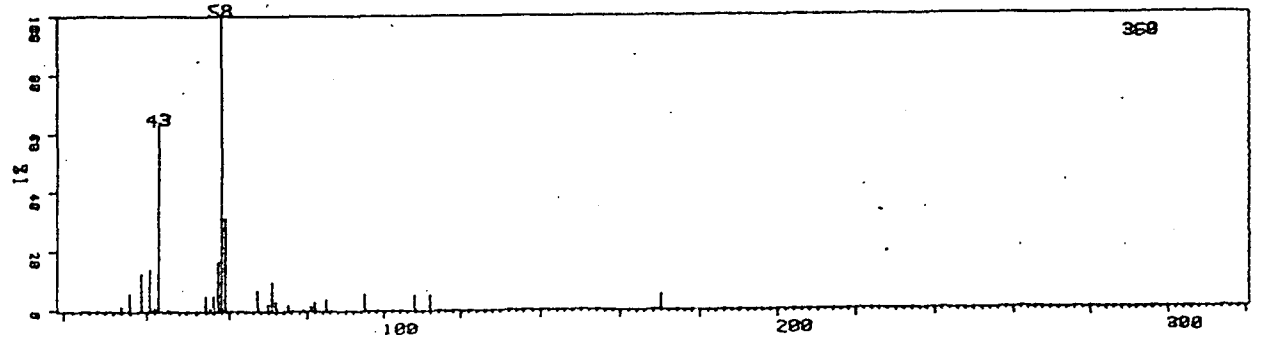
DE1036 603 PROSTANTHERA LASIANTHOS OV101 50-240 4 20-APR-82
CAL:1D400 STA:E. 18:59
UNKNOWN



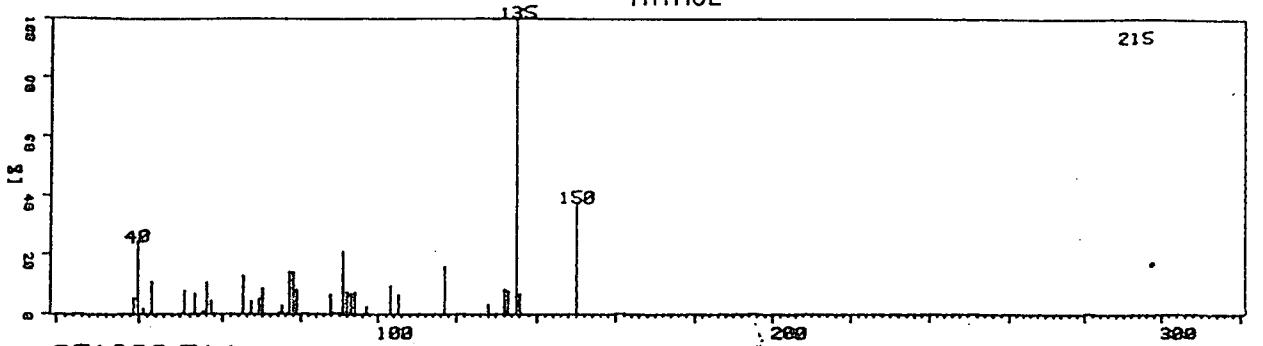
DE1036 655 PROSTANTHERA LASIANTHOS OV101 50-240 4 20-APR-82
CAL:1D400 STA:E. 20:37
ISO-BORNYL ACETATE



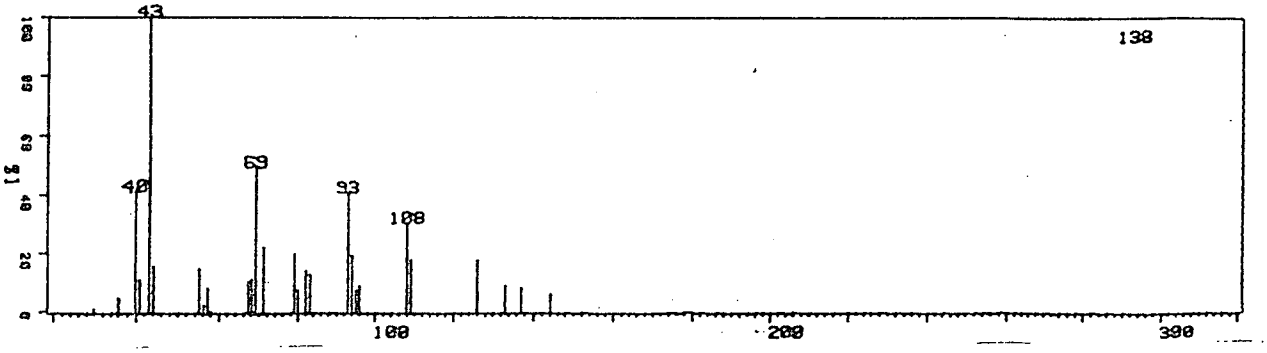
DE1036 661 PROSTANTHERA LASIANTHOS OV101 50-240 4 20-APR-82
CAL:1D400 STA:E. 20:48
UNKNOWN



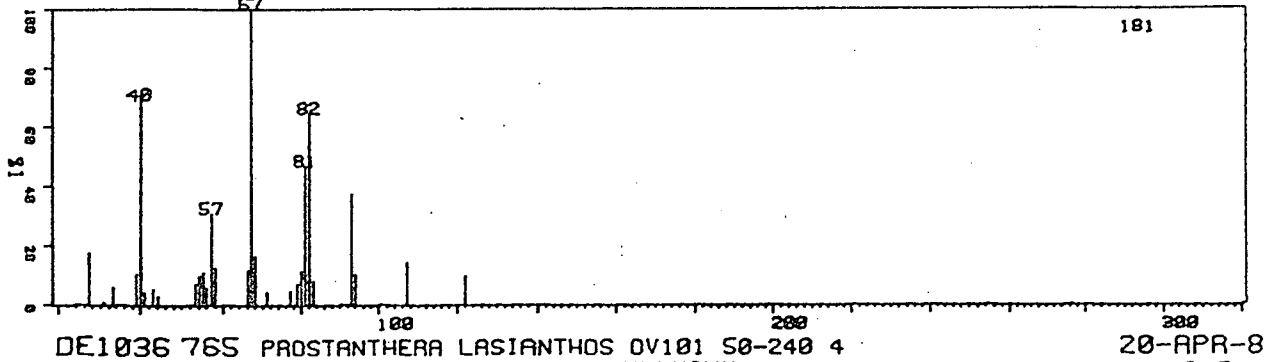
DE1036 670 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 21:5
THYMOL



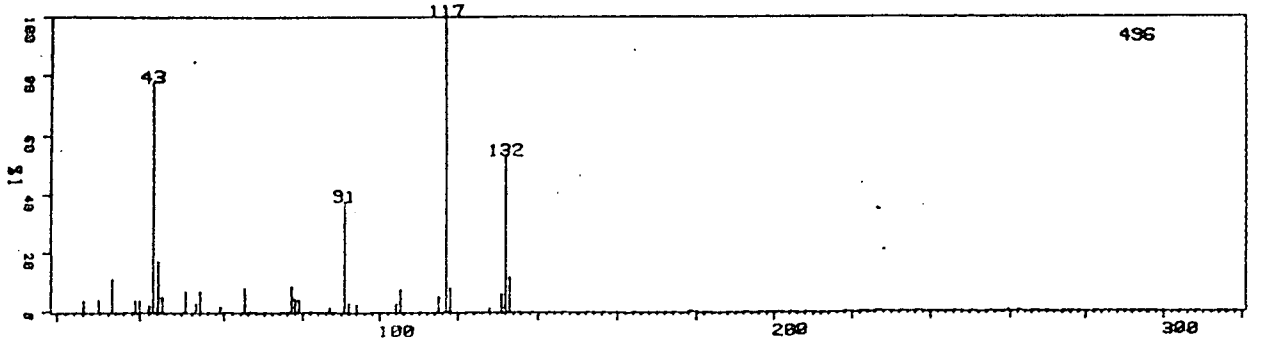
DE1036 714 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 22:29
UNKNOWN

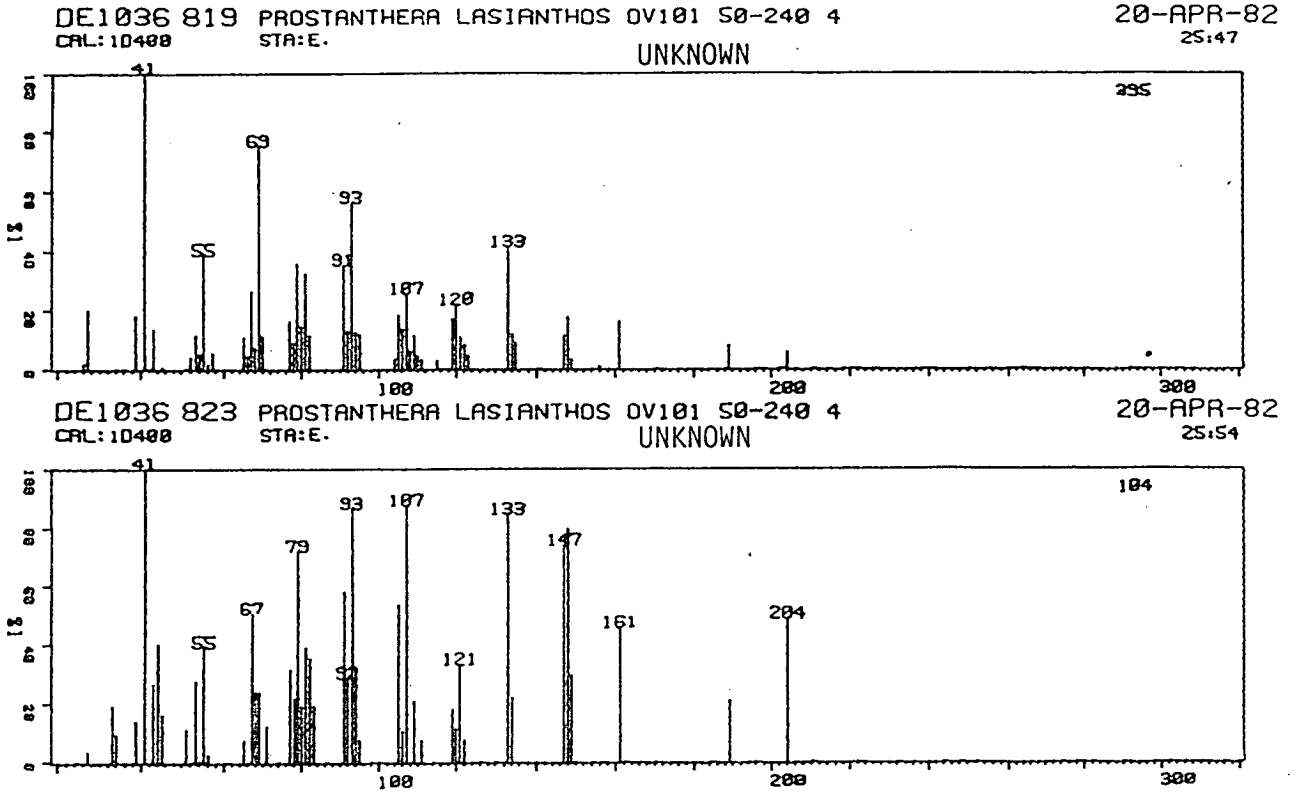


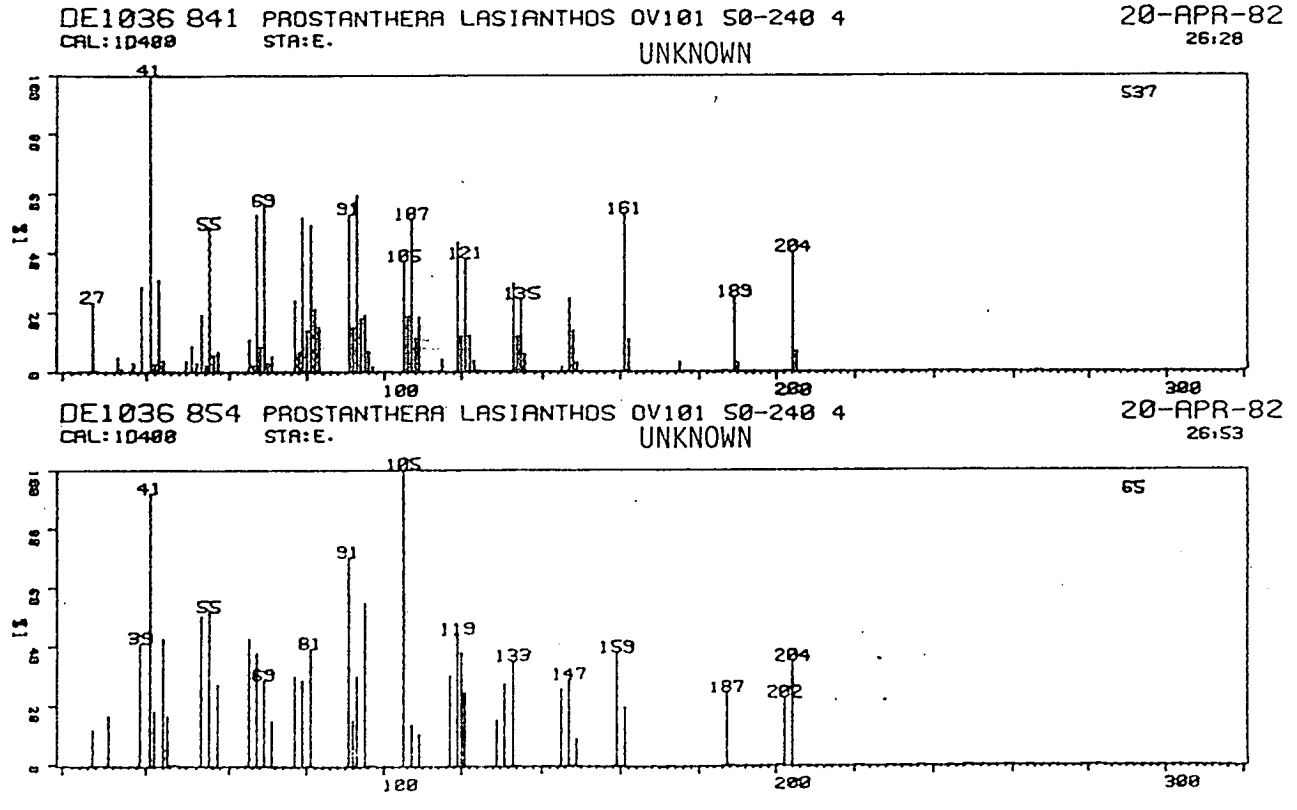
DE1036 719 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 22:38
UNKNOWN



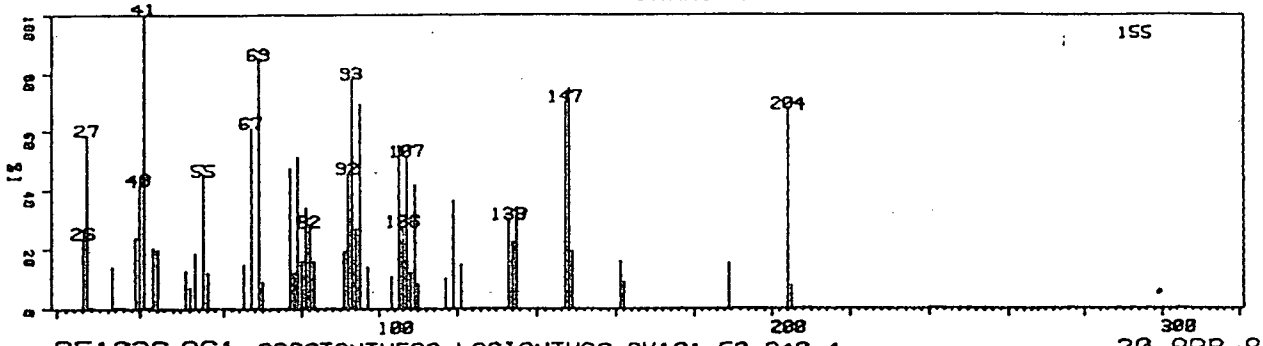
DE1036 765 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. 24:5
UNKNOWN



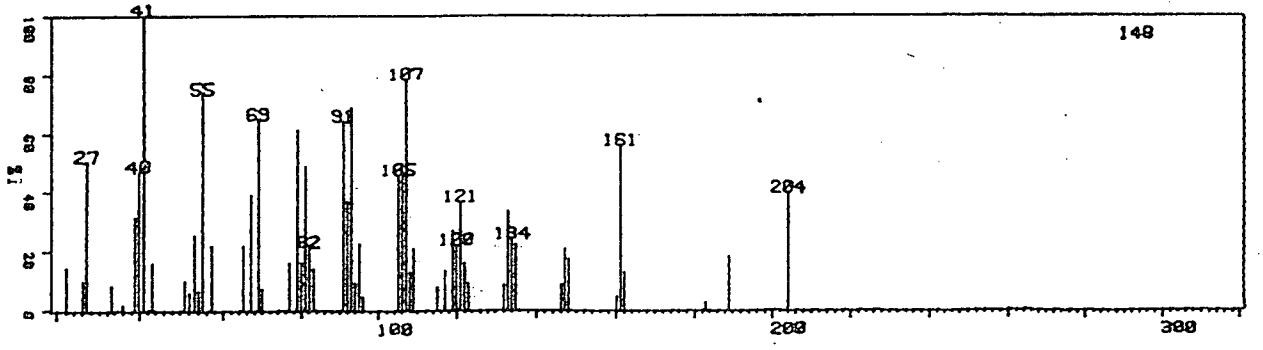

DE1036 819 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
UNKNOWN
20-APR-82
25:47
DE1036 823 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
UNKNOWN
20-APR-82
25:54


DE1036 841 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
UNKNOWN
20-APR-82
26:28
DE1036 854 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
UNKNOWN
20-APR-82
26:53

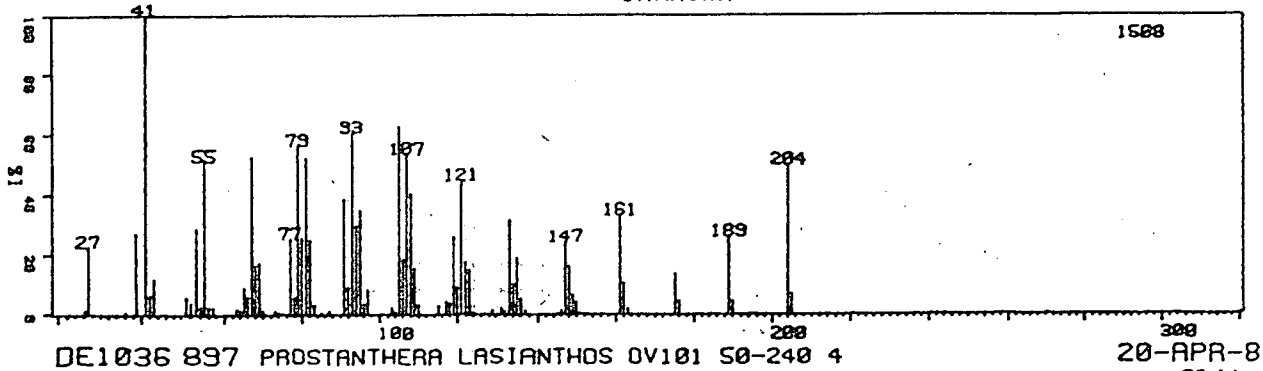
DE1036 857 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 26:58



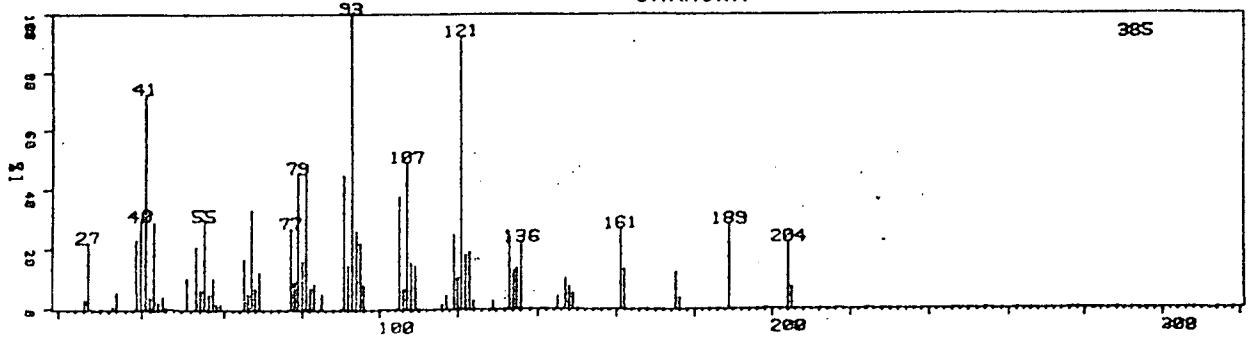
DE1036 861 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 27:6

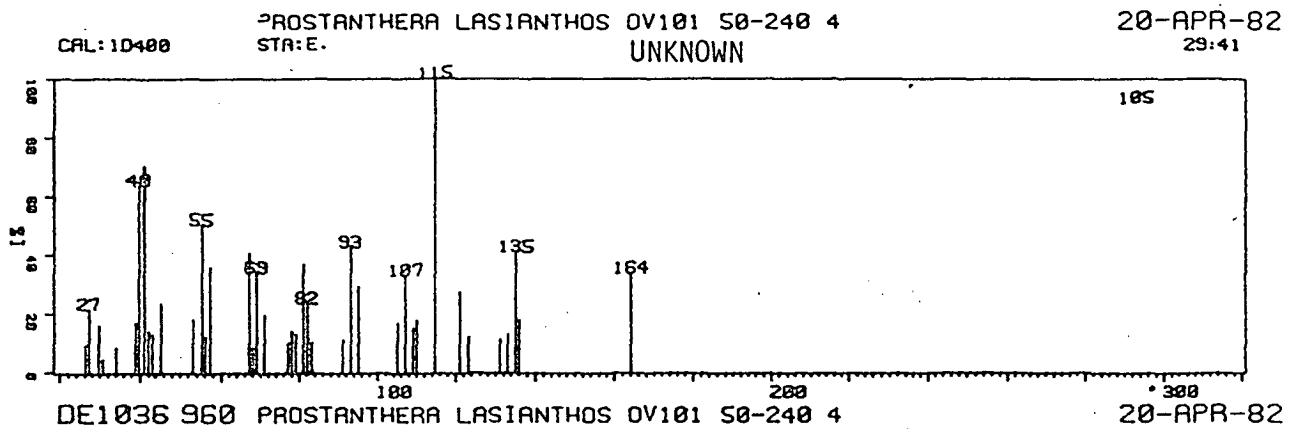


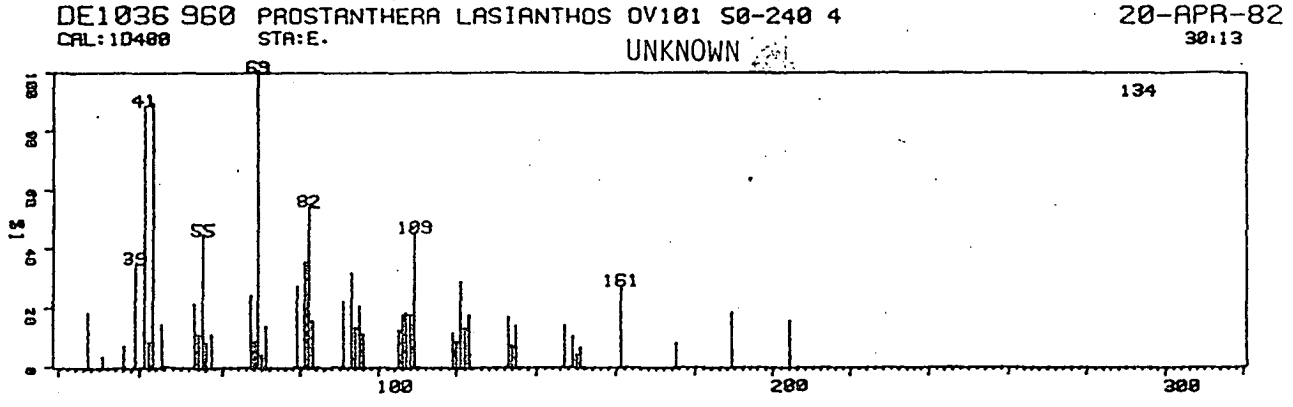
DE1036 890 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 28:1

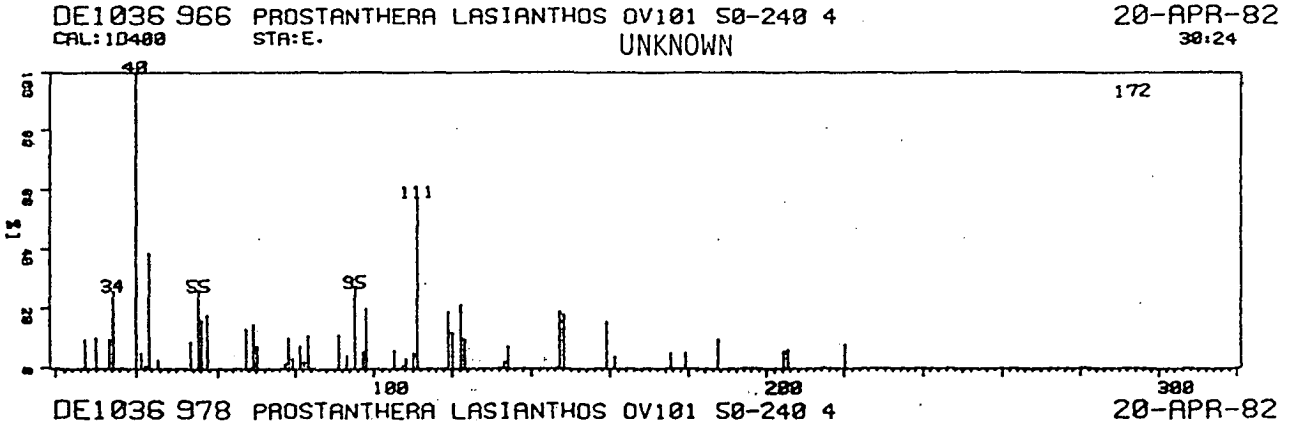


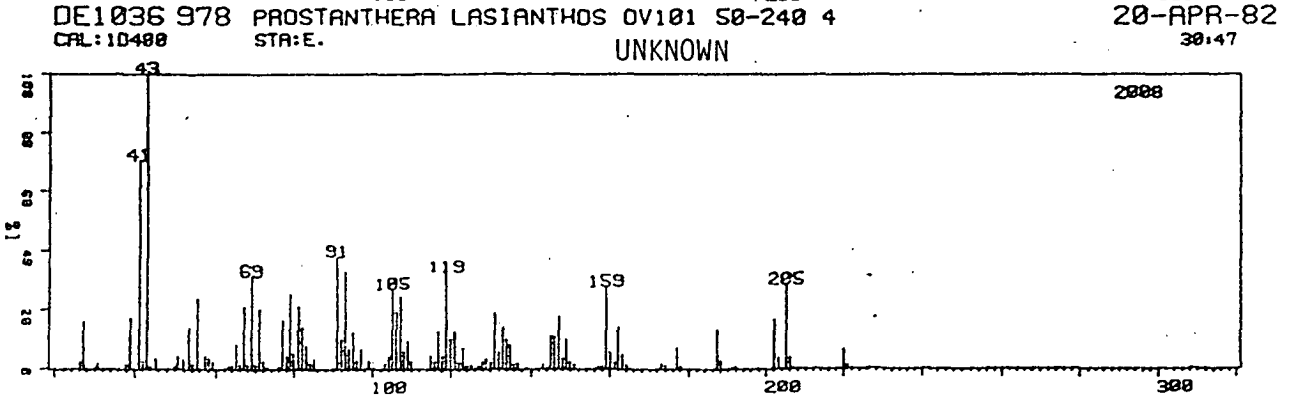
DE1036 897 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 28:14



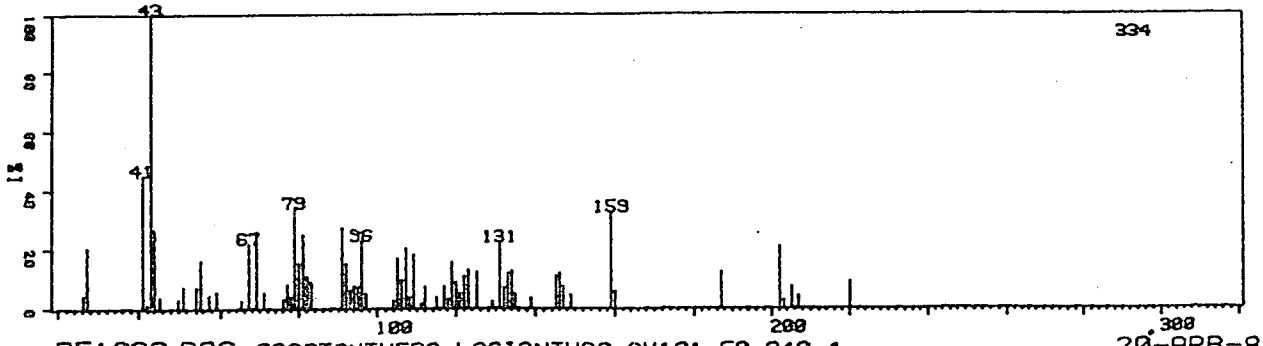

PROSTANTHERA LASIANTHOS OV101 S0-240 4
20-APR-82
CAL:1D400
STA:E.
UNKNOWN
29:41
115
105
43
55
93
135
69
107
164
27
82
100
200
300


DE1036 960 PROSTANTHERA LASIANTHOS OV101 S0-240 4
20-APR-82
CAL:1D400
STA:E.
UNKNOWN
30:13
69
134
41
82
55
109
39
161
100
200
300

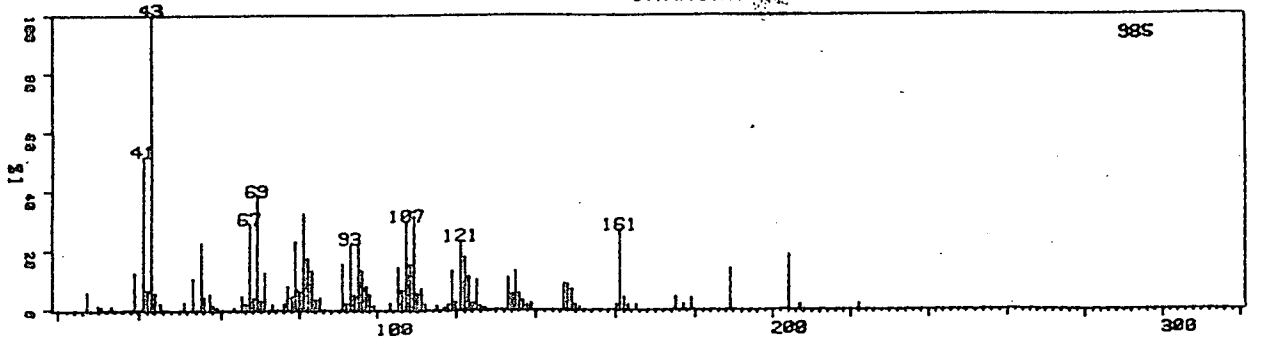

DE1036 966 PROSTANTHERA LASIANTHOS OV101 S0-240 4
20-APR-82
CAL:1D400
STA:E.
UNKNOWN
30:24
43
172
111
34
55
95
100
200
300


DE1036 978 PROSTANTHERA LASIANTHOS OV101 S0-240 4
20-APR-82
CAL:1D400
STA:E.
UNKNOWN
30:47
43
2000
41
91
69
119
105
159
205
100
200
300

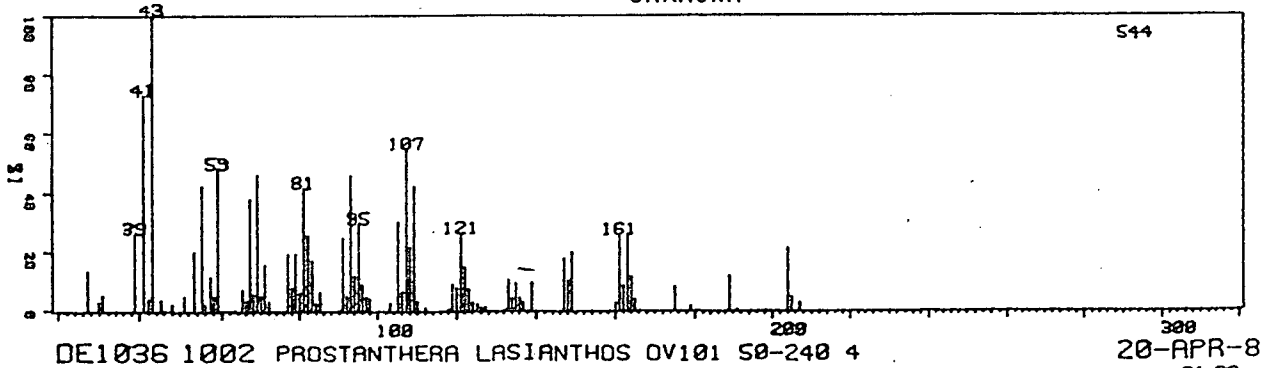
DE1036 981 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 30:53



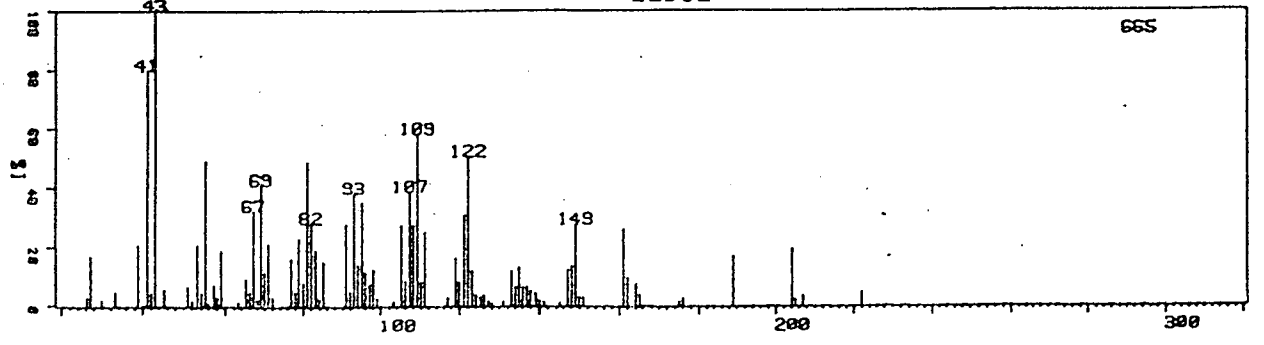
DE1036 986 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 31:2

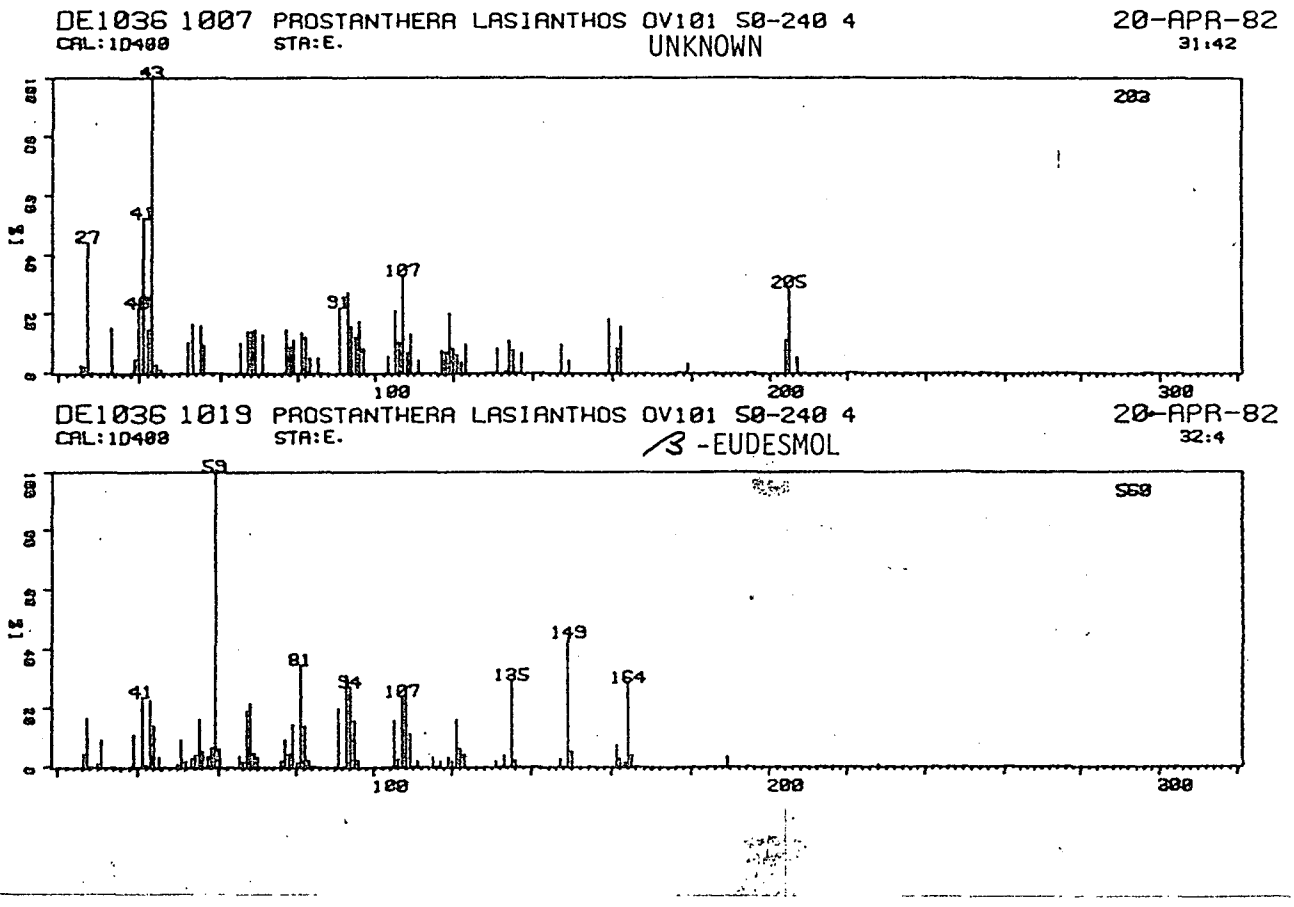


DE1036 993 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. UNKNOWN 31:15

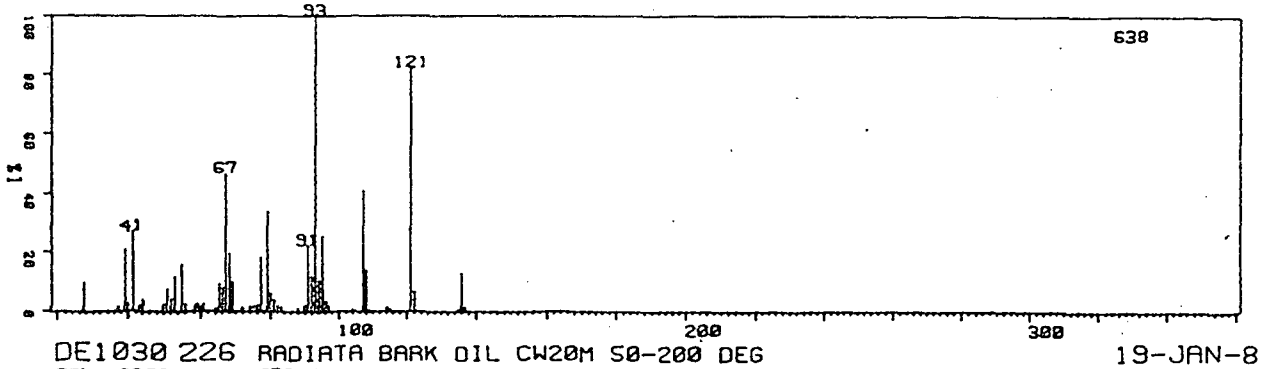


DE1036 1002 PROSTANTHERA LASIANTHOS OV101 S0-240 4 20-APR-82
CAL:1D400 STA:E. LEDOL 31:32

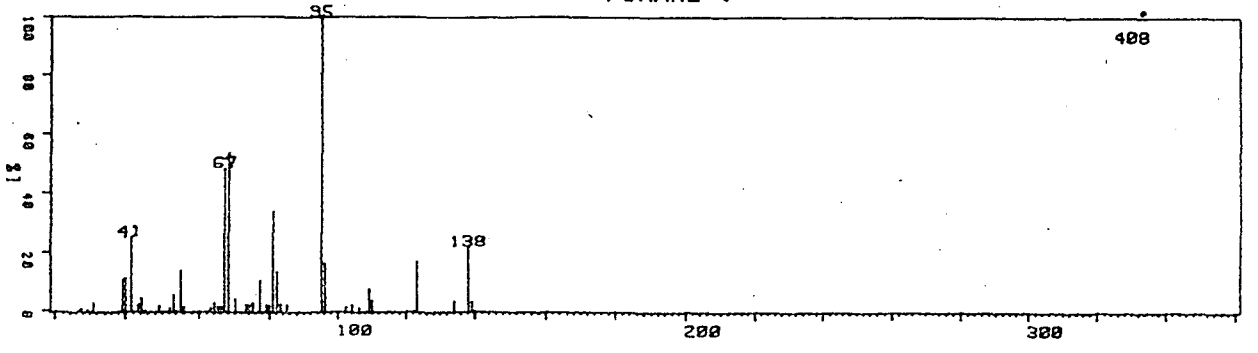



DE1036 1007 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
UNKNOWN
20-APR-82
31:42
43
41
27
48
91
107
205
203
100
200
300
DE1036 1019 PROSTANTHERA LASIANTHOS OV101 S0-240 4
CAL:1D400 STA:E.
β-EUDESMOL
20-APR-82
32:4
59
81
94
107
135
149
164
41
560
100
200
300

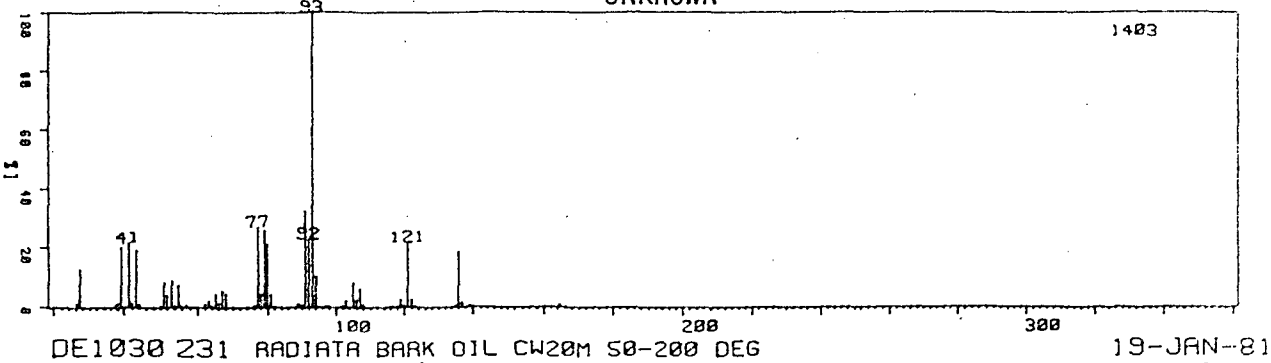
DE1030 176 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. CAMPHENE 6:5



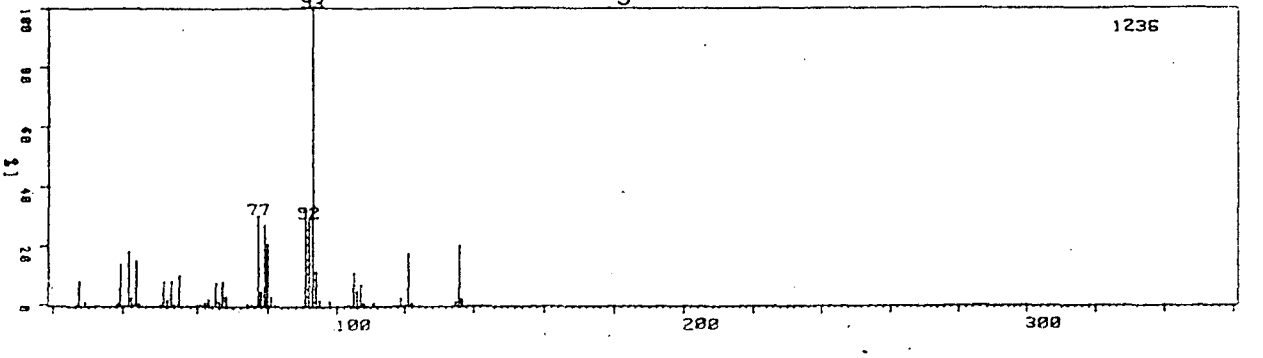
DE1030 226 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. PINANE ? 7:48



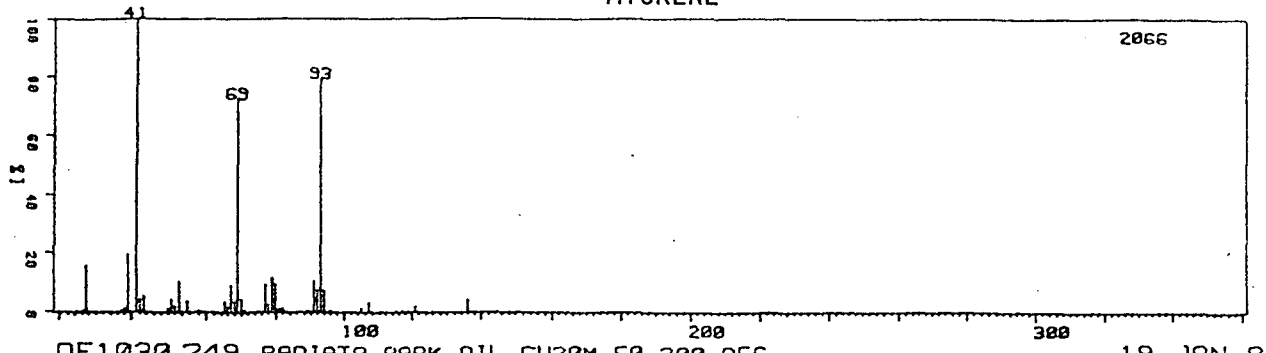
DE1030 228 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 7:52



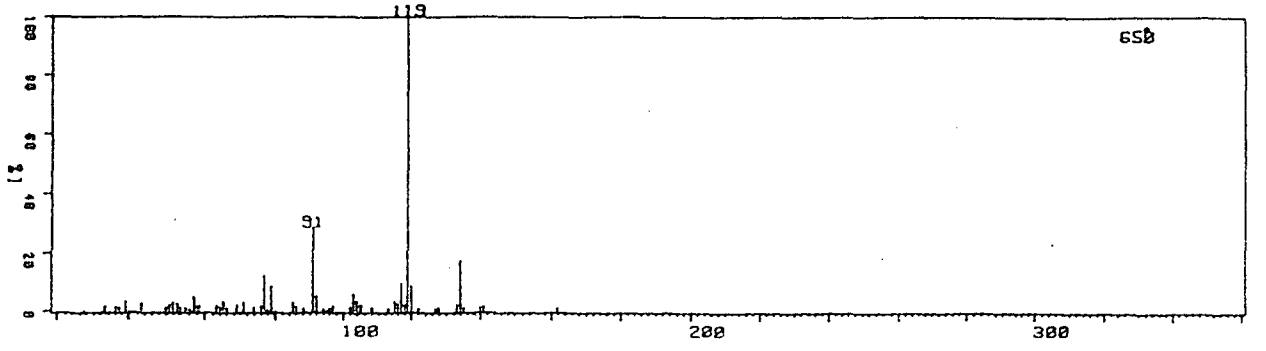
DE1030 231 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. Δ_3 CARENE 7:58



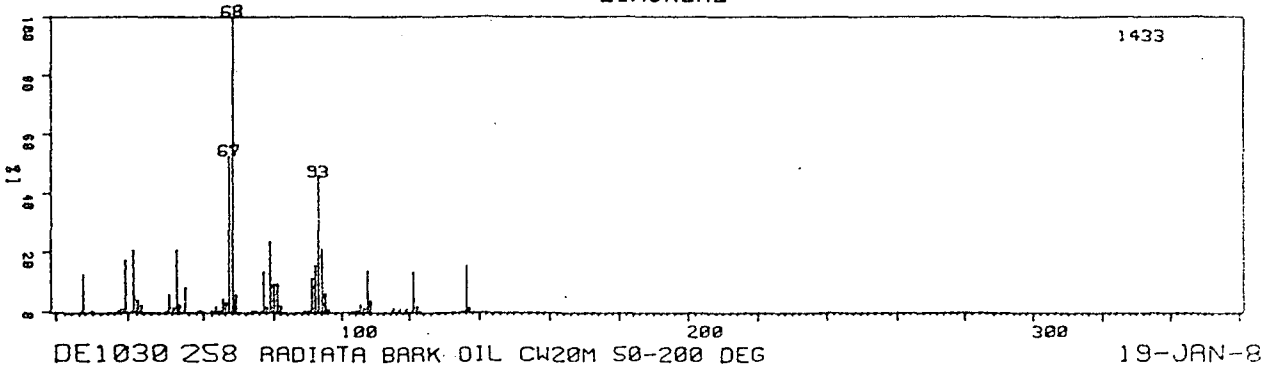
DE1030 240 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. MYCRENE 8:17



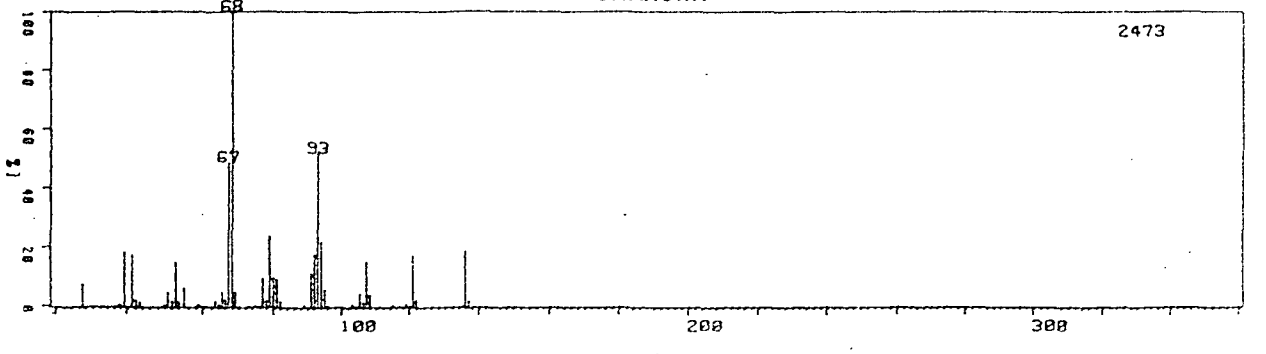
DE1030 249 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. CYMENE (TYPE) 8:35

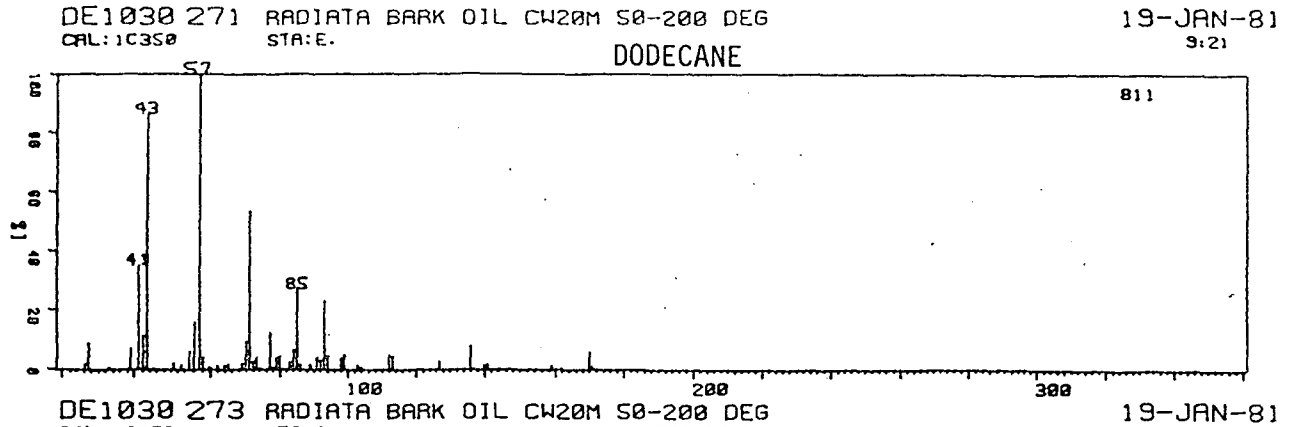


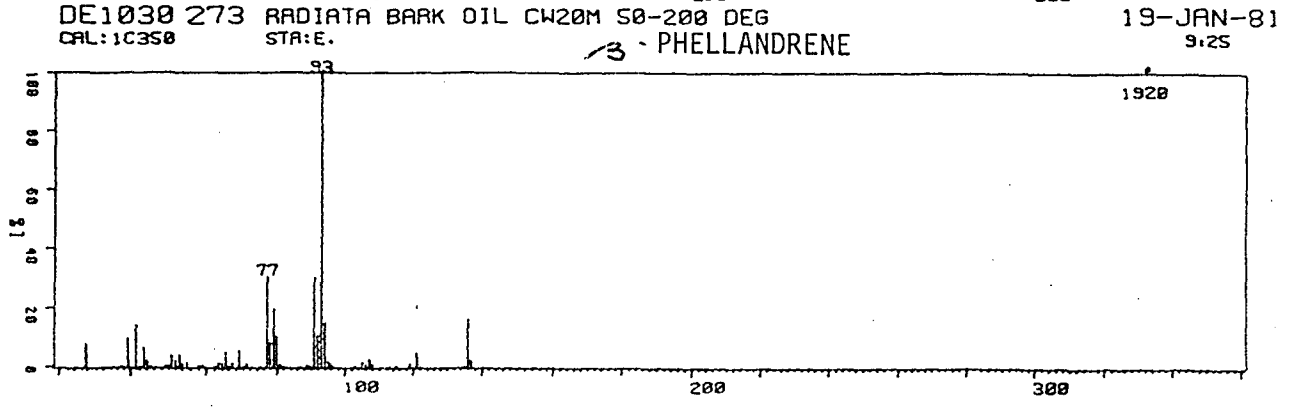
DE1030 257 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. LIMONENE 8:52

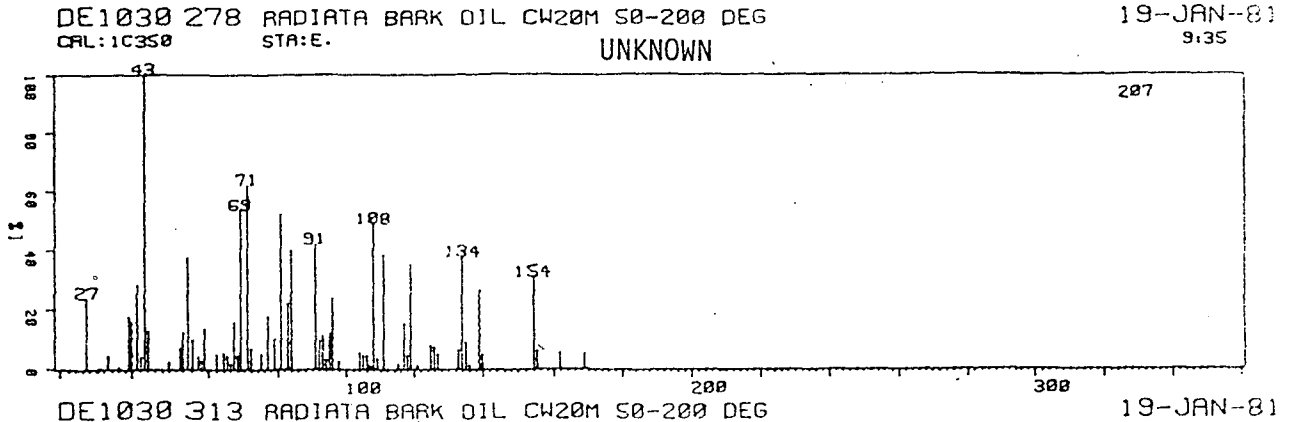


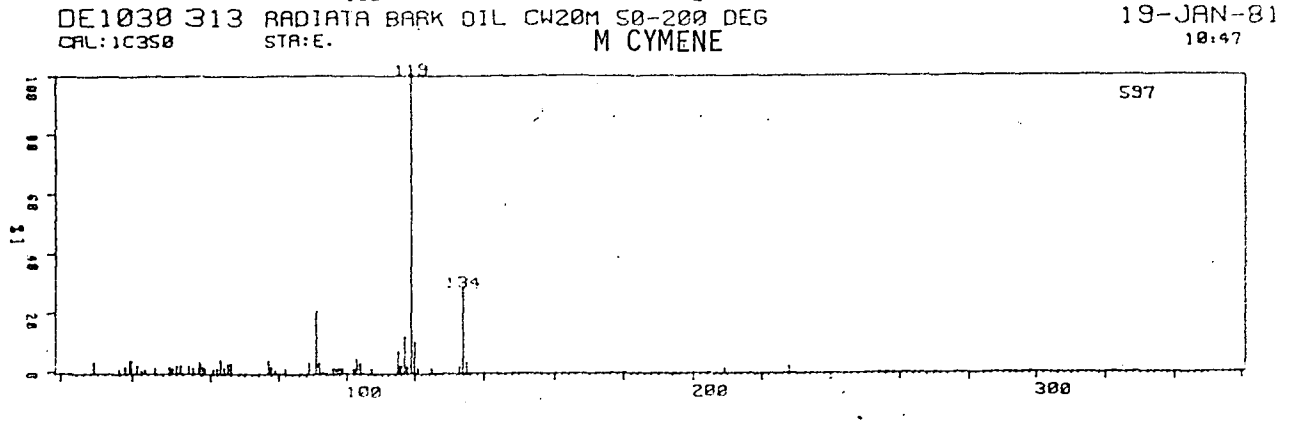
DE1030 258 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 8:54




DE1030 271 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
9:21
DODECANE
811
57
43
41
85
100
200
300

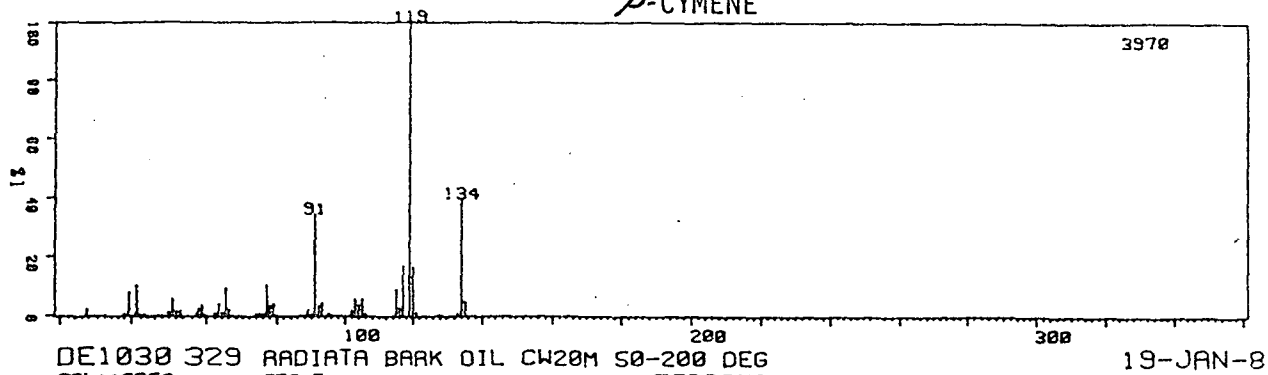

DE1030 273 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
9:25
3 - PHELLANDRENE
1920
93
77
100
200
300


DE1030 278 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
9:35
UNKNOWN
207
93
71
69
91
108
134
154
27
100
200
300


DE1030 313 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
10:47
M CYMENE
597
119
134
100
200
300

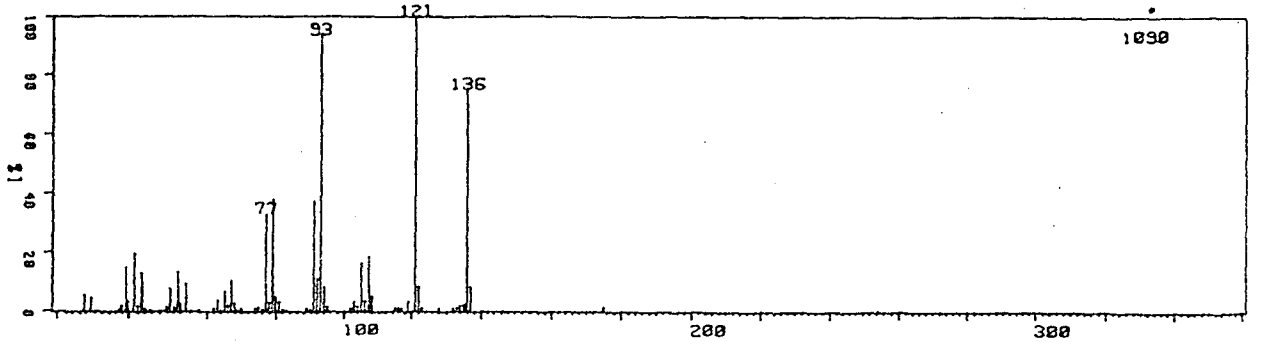
DE1030 321 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 11:3

p-CYMENE



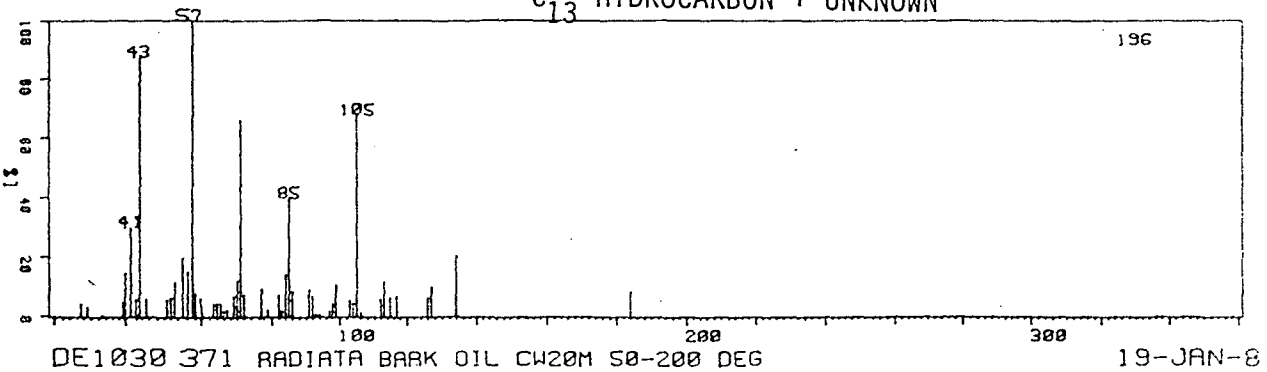
DE1030 329 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 11:20

α-TERPINOLENE



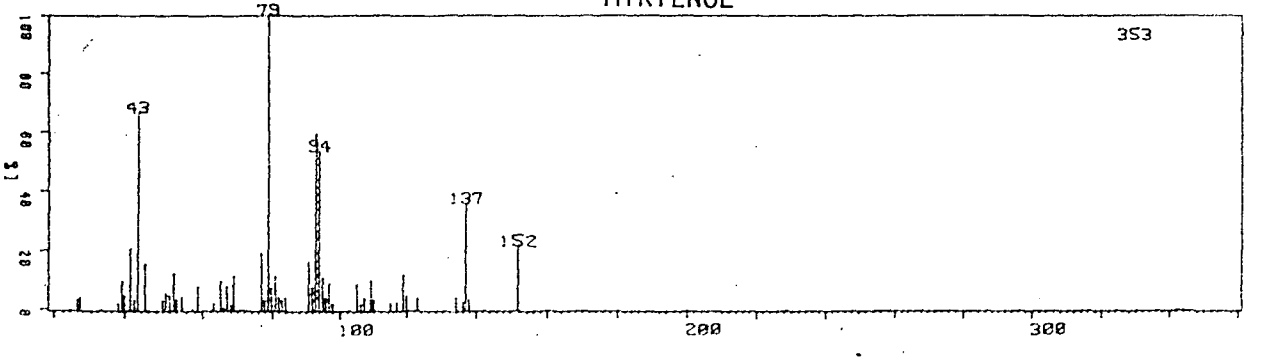
DE1030 349 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 12:1

C_{13} HYDROCARBON + UNKNOWN

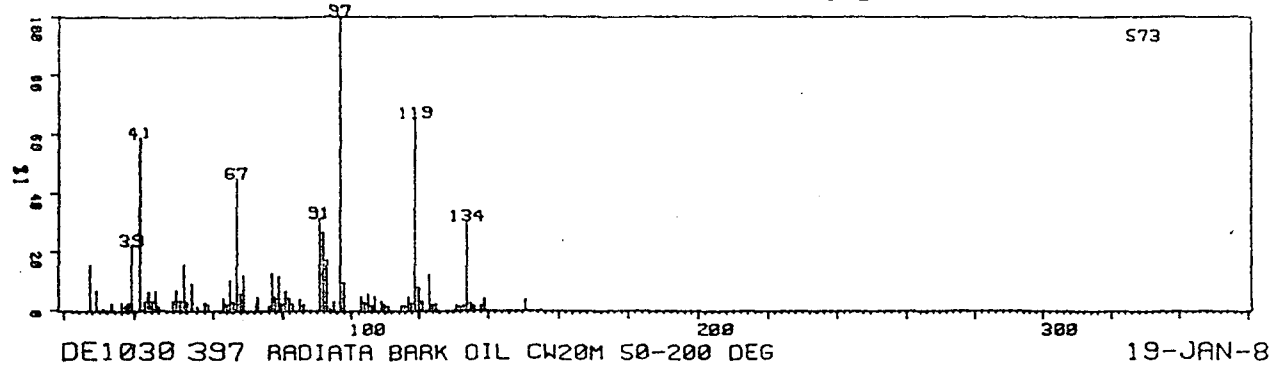


DE1030 371 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 12:46

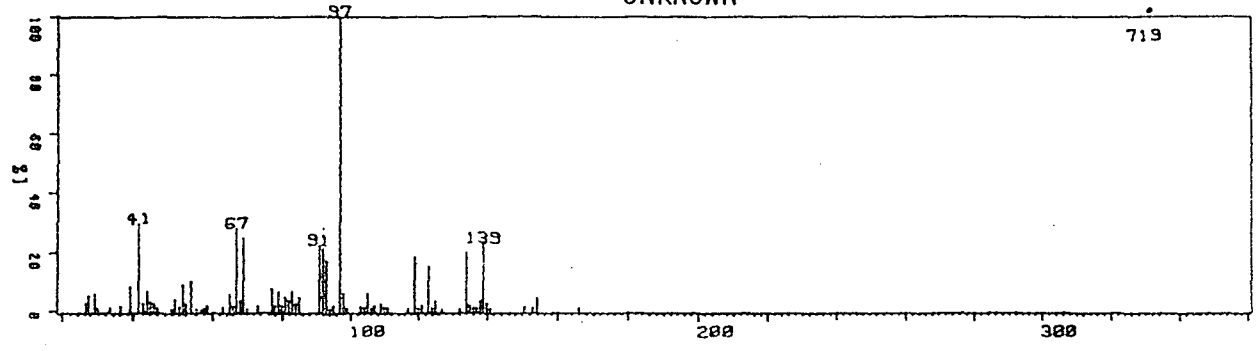
MYRTENOL



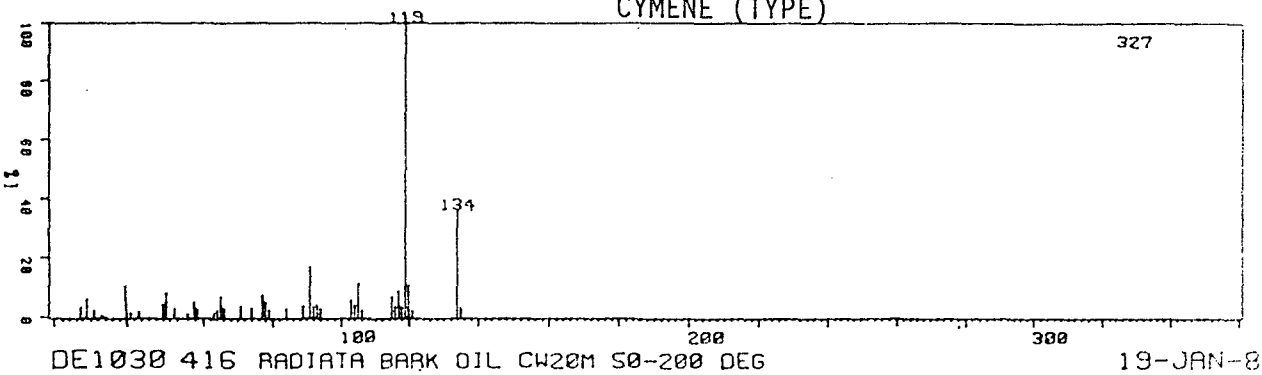
DE1030 396 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 13:37
UNKNOWN MIXTURE



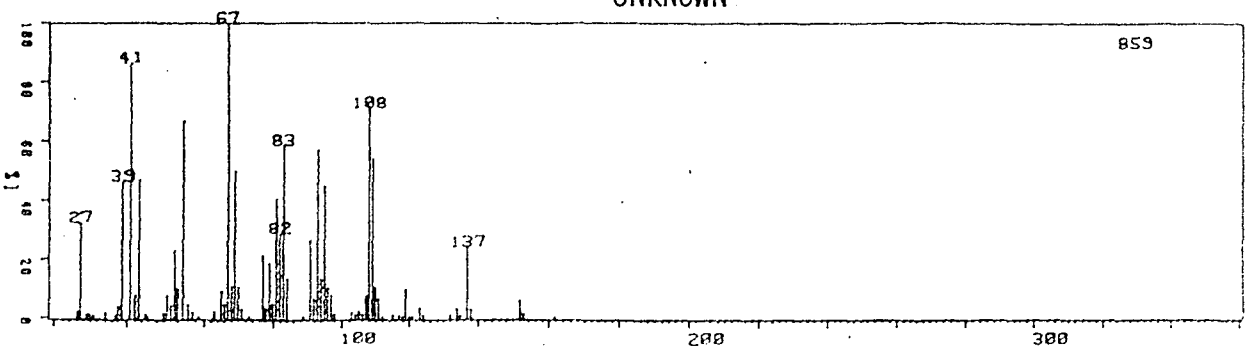
DE1030 397 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 13:40
UNKNOWN

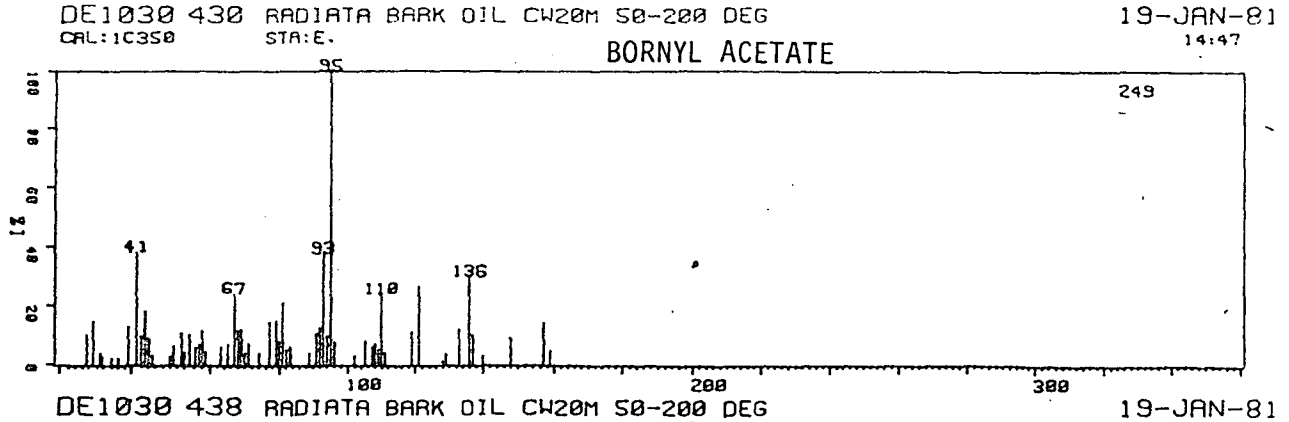


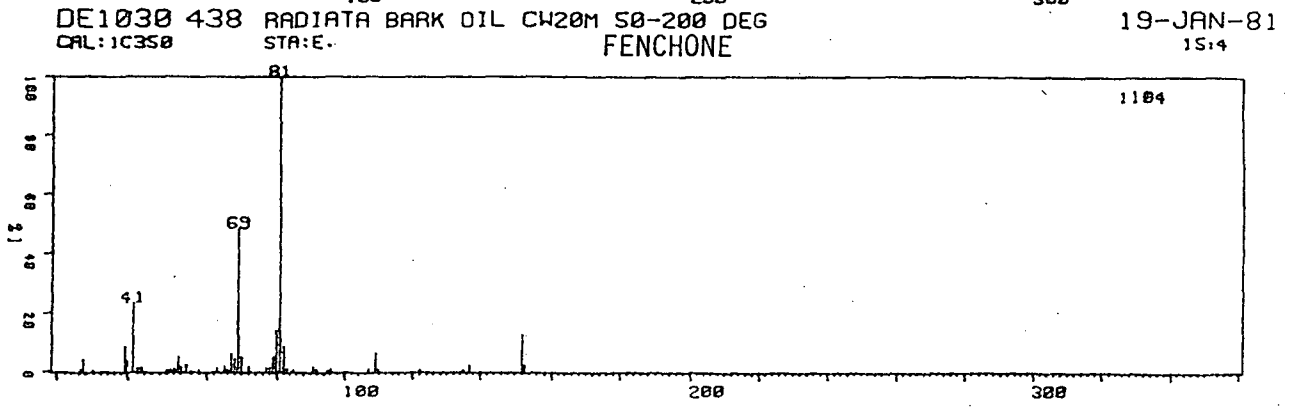
DE1030 403 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 13:52
CYMENE (TYPE)

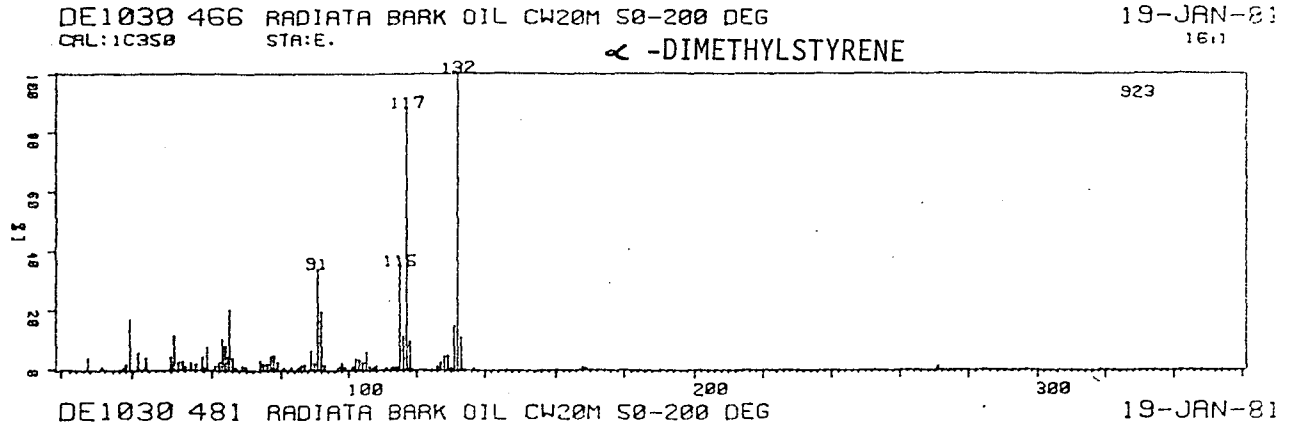


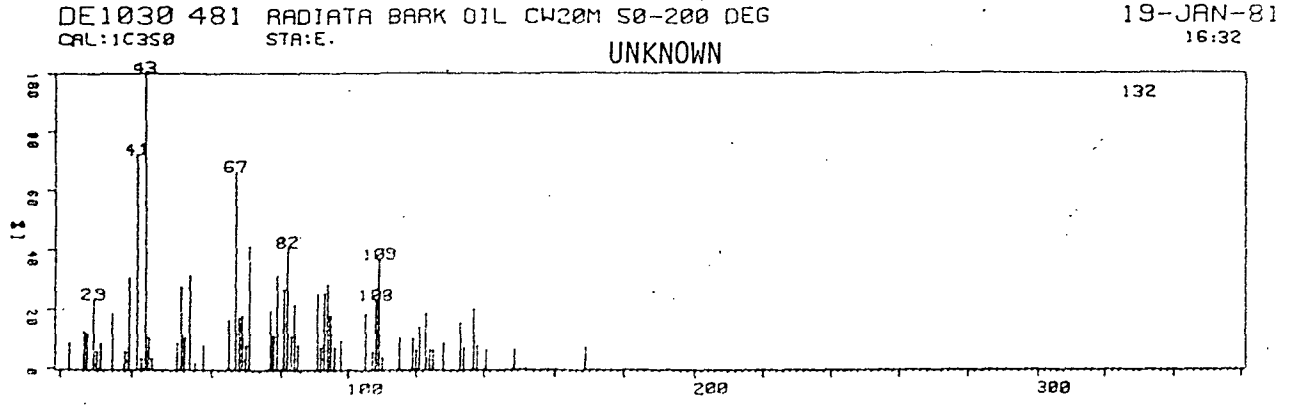
DE1030 416 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 14:19
UNKNOWN



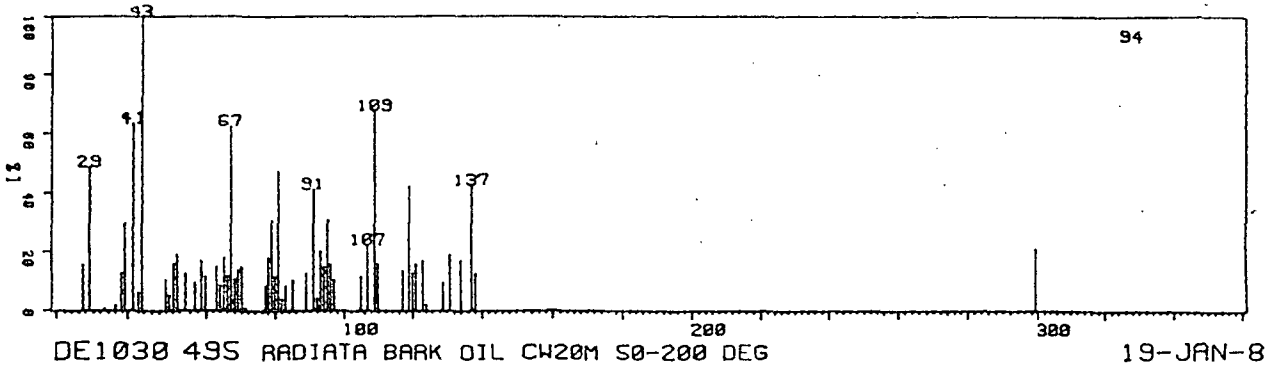

DE1030 430 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
14:47
BORNYL ACETATE
95
249
41
93
67
110
136
100
200
300


DE1030 438 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
15:4
FENCHONE
81
1184
69
41
100
200
300

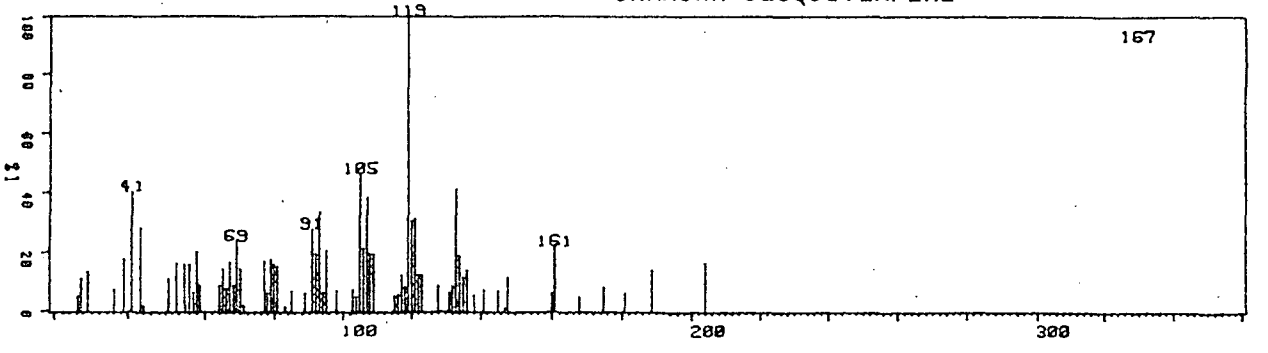

DE1030 466 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
16:1
∝ -DIMETHYLSTYRENE
132
117
923
91
115
100
200
300


DE1030 481 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
19-JAN-81
16:32
UNKNOWN
93
132
41
67
82
109
23
100
200
300

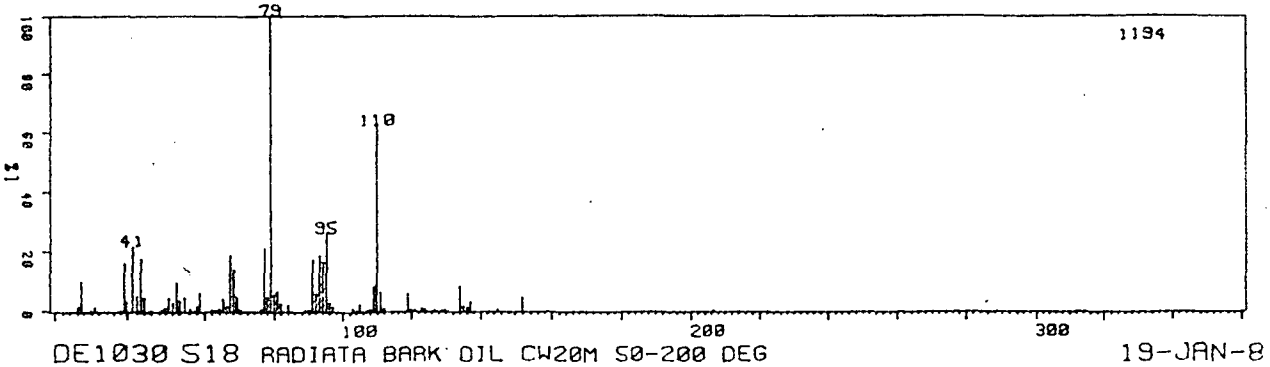
DE1030 484 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 16:38



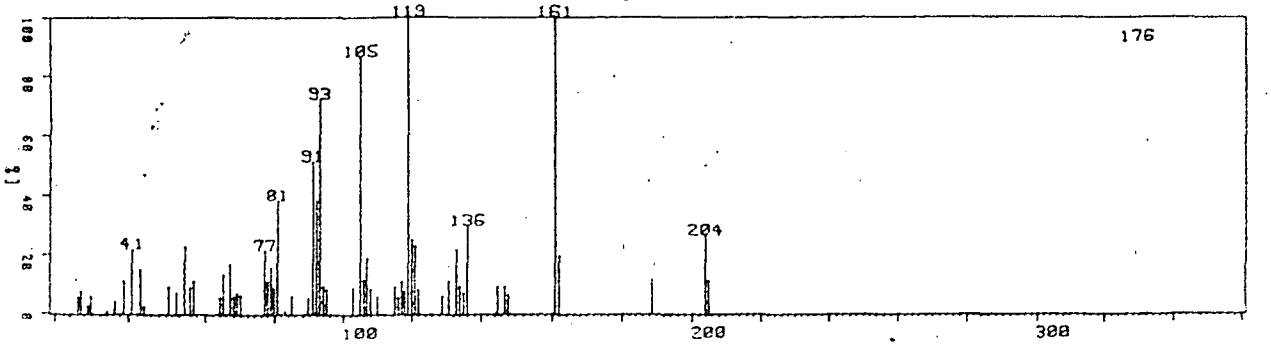
DE1030 49S RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN SESQUITERPENE 17:1



DE1030 S02 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 17:15

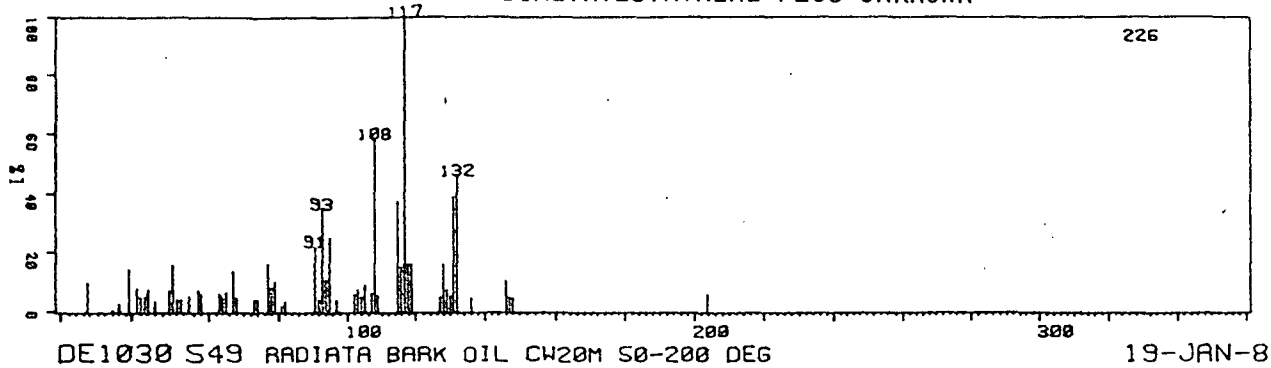


DE1030 S18 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. ∝- COPAENE 17:48



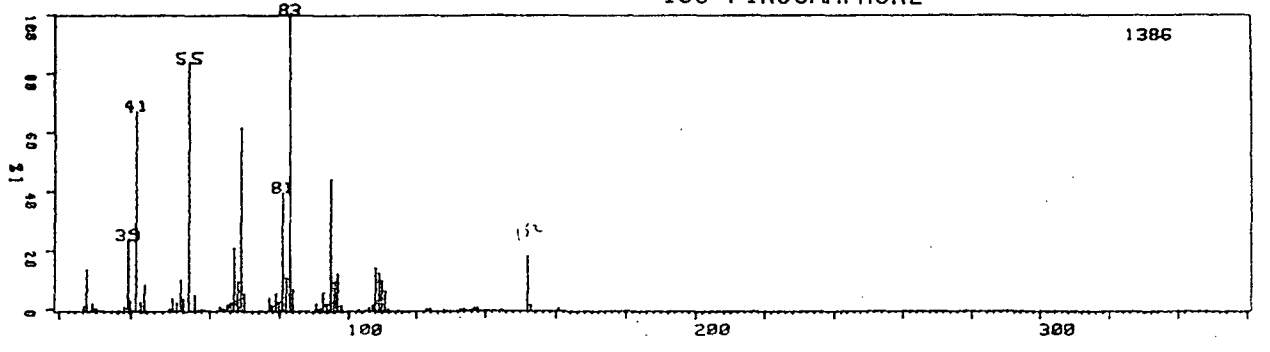
DE1030 S23 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 17:58

DIMETHYLSTRYRENE PLUS UNKNOWN



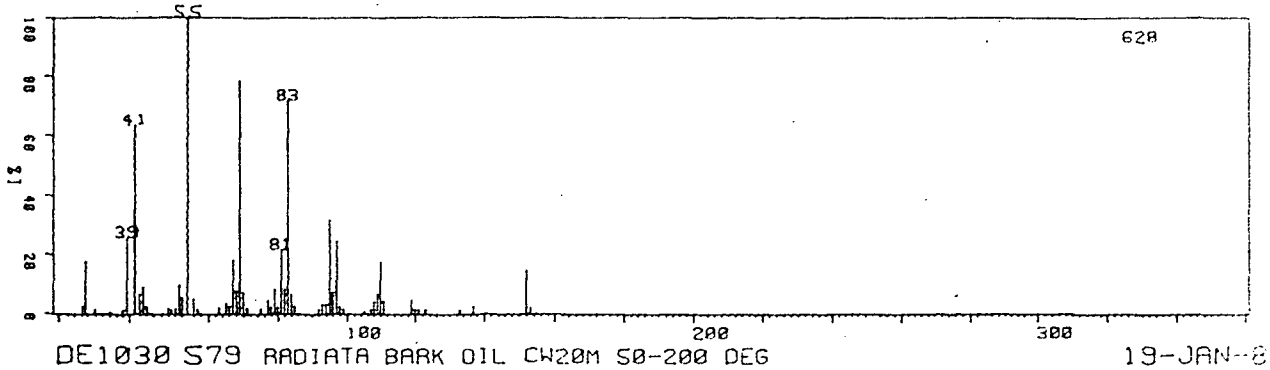
DE1030 S49 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 18:52

ISO PINOCAMPHONE



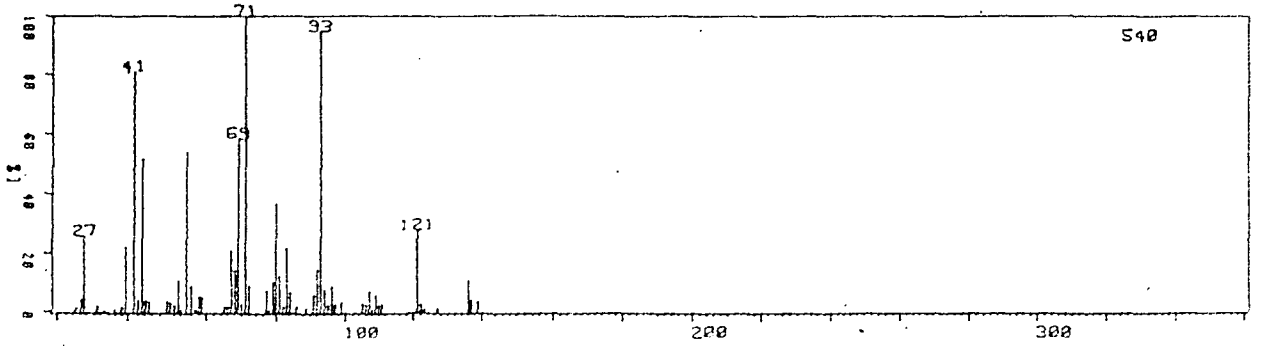
DE1030 S75 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 19:45

PINOCAMPHONE

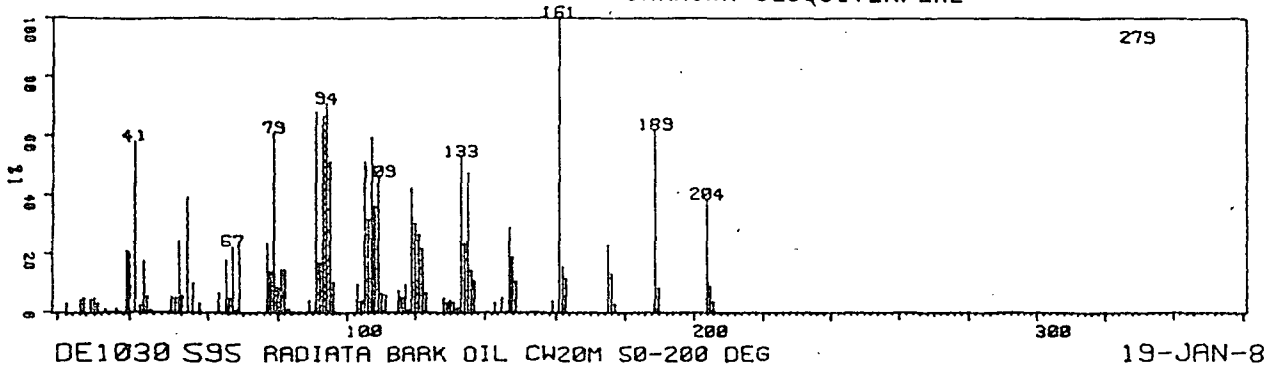


DE1030 S79 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 19:53

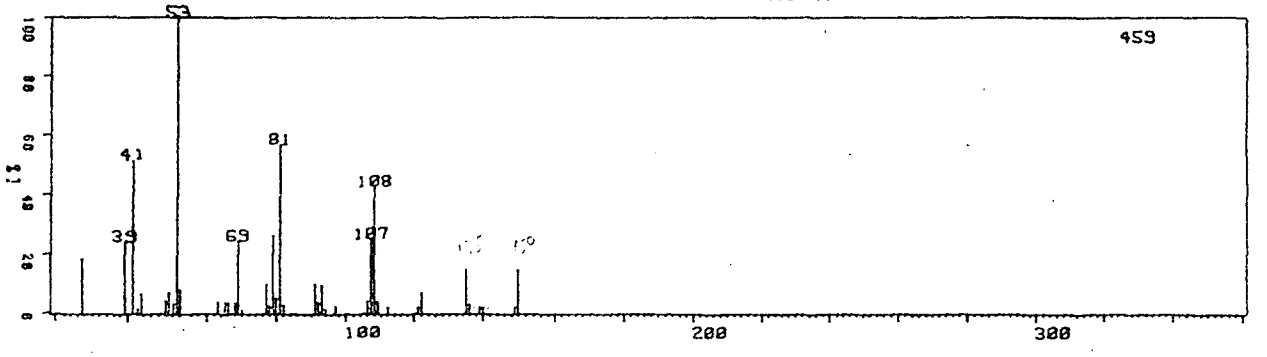
LINALOOL



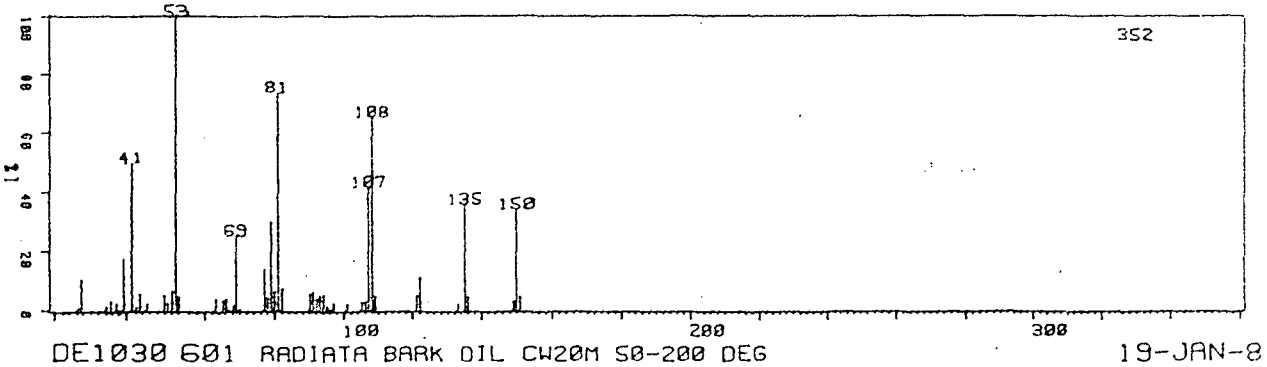
DE1030 S88 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN SESQUITERPENE 20:12



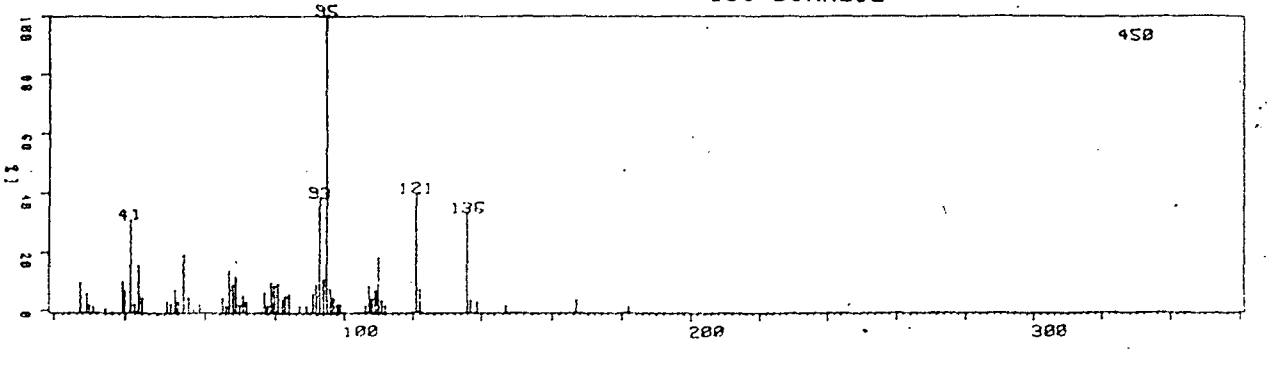
DE1030 S95 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 20:26



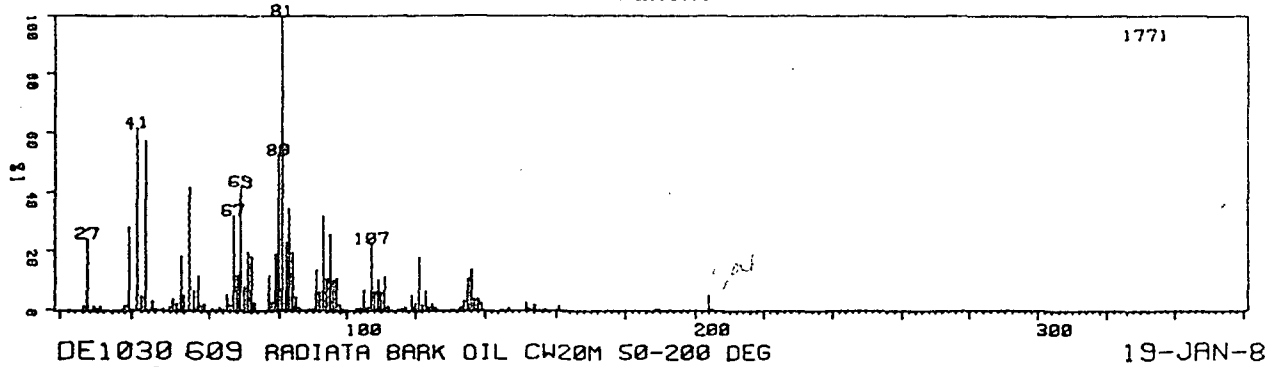
DE1030 S96 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 20:28



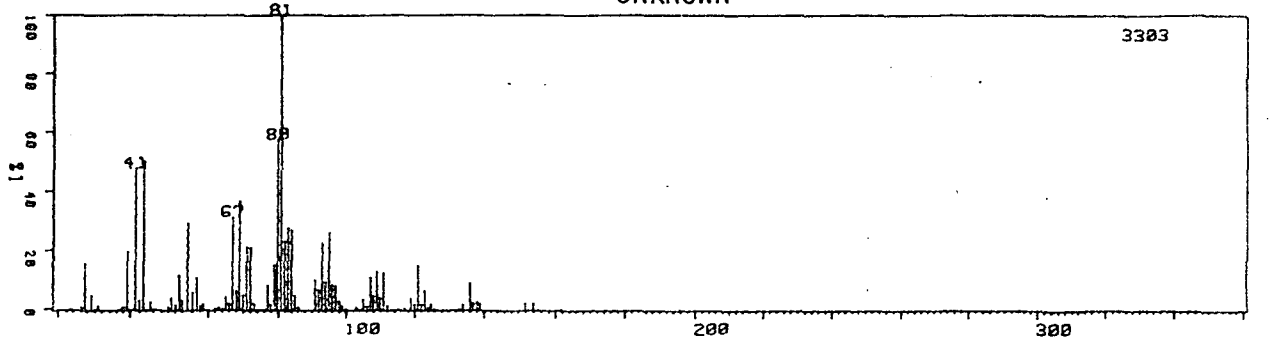
DE1030 601 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. ISO BORNEOL 20:38



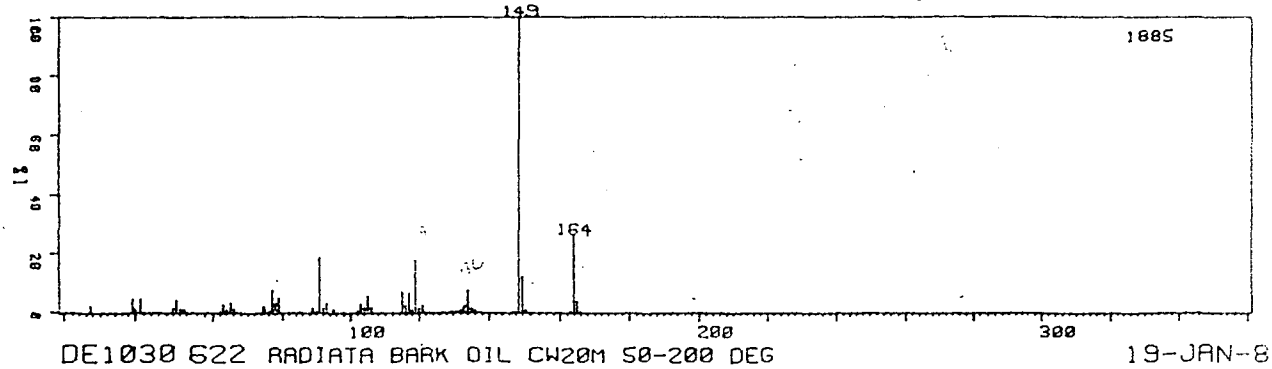
DE1030 608 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. FENCHOL 20:53



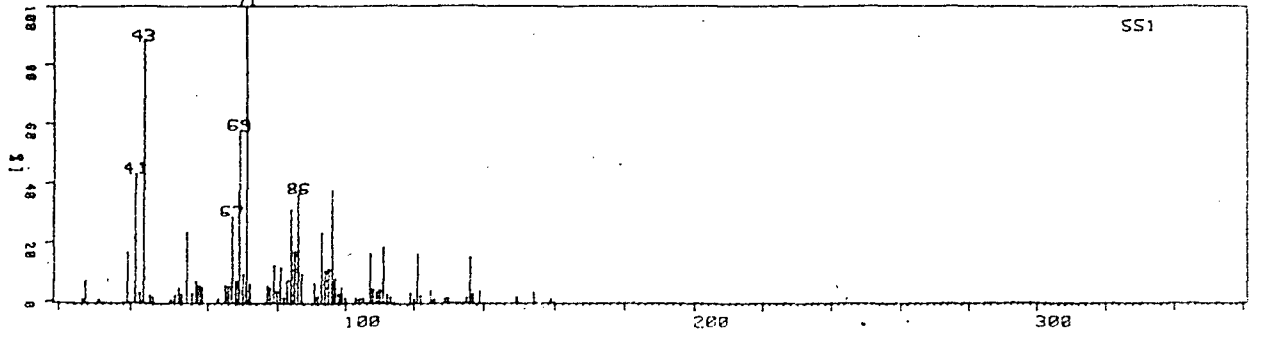
DE1030 609 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 20:55



DE1030 614 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 6 TERT. BUTYL CRESOL 21:5

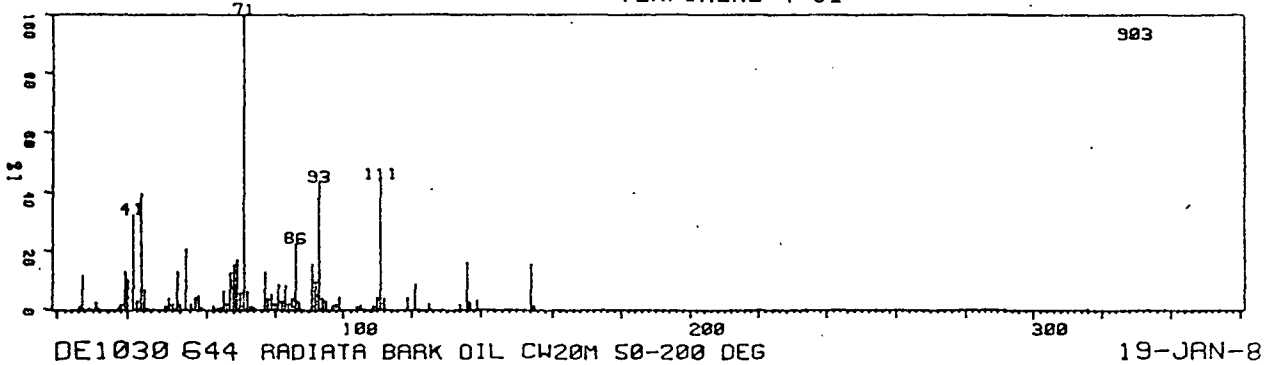


DE1030 622 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. UNKNOWN 21:22



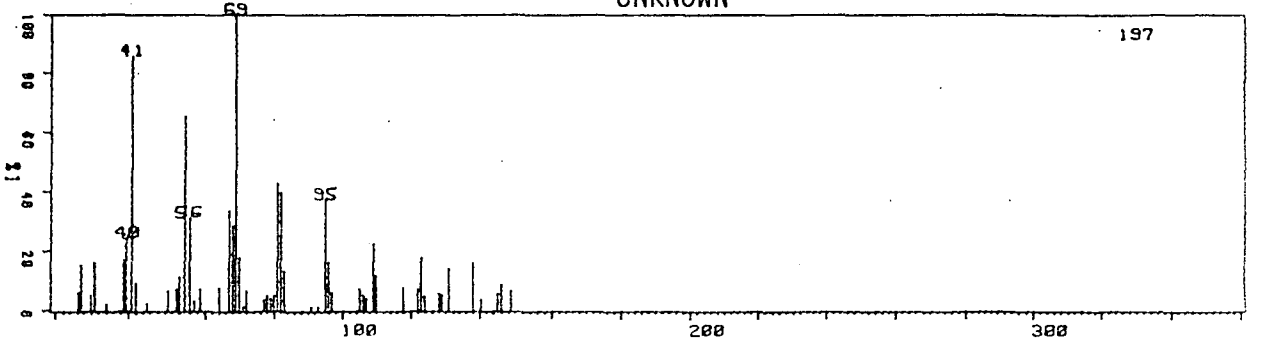
DE1030 628 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 21:34

TERPINENE-4-o1



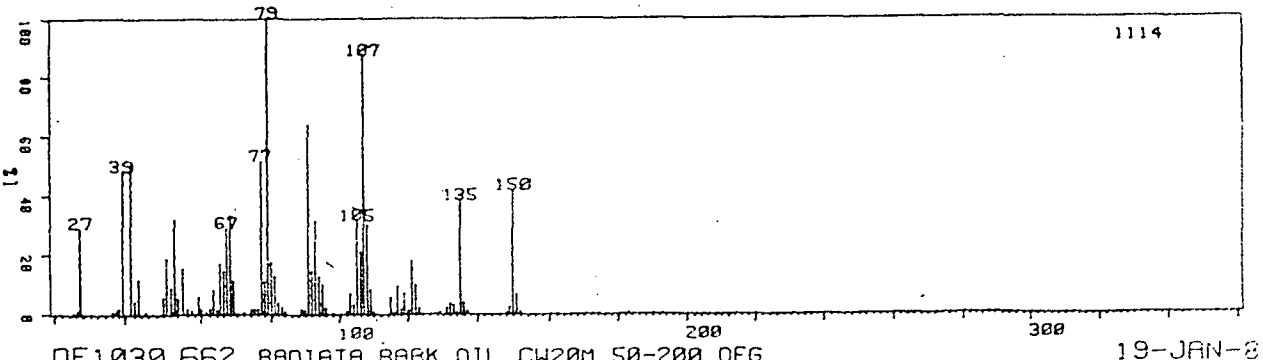
DE1030 644 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 22:7

UNKNOWN



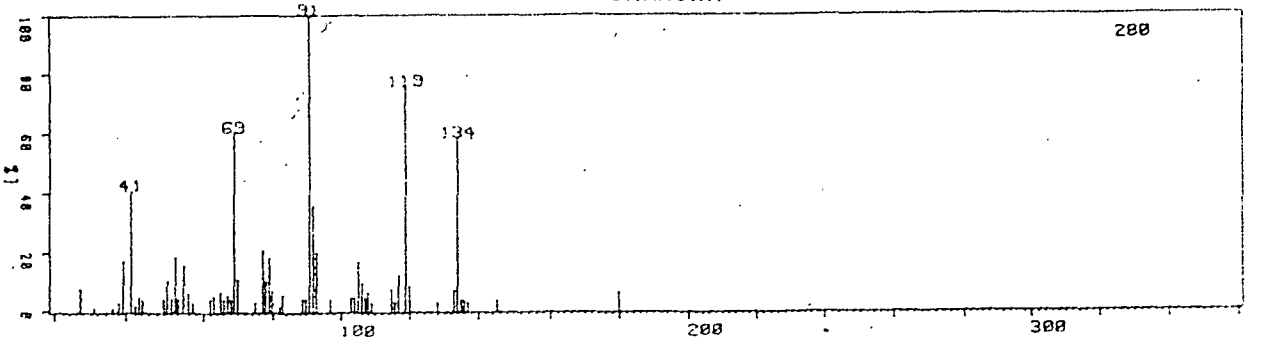
DE1030 651 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 22:21

MYRTENAL

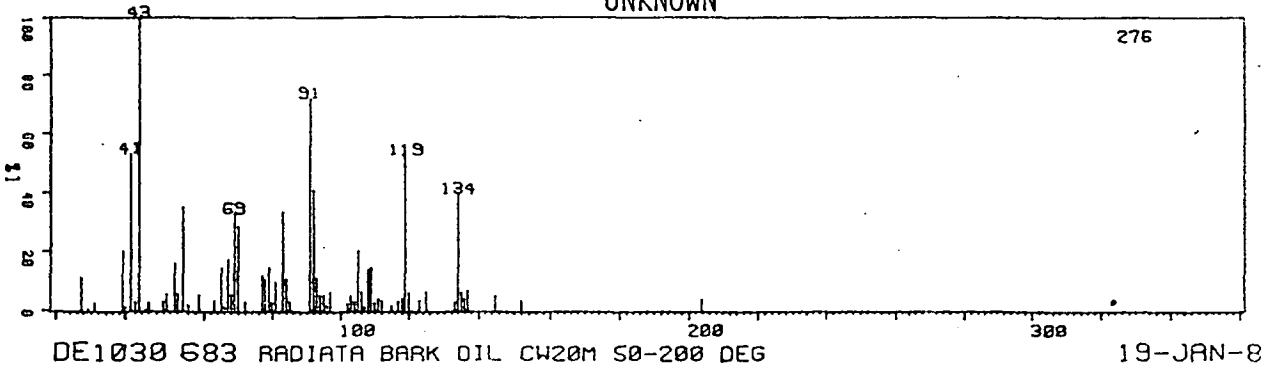


DE1030 662 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 22:44

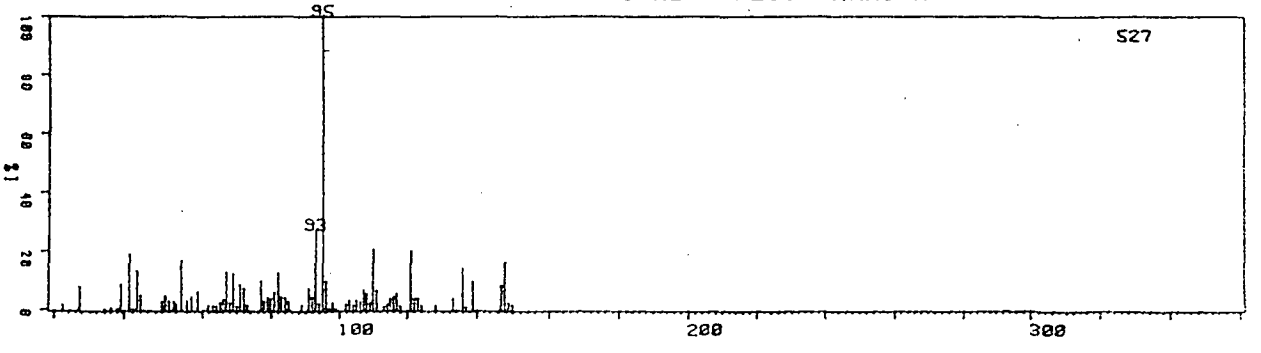
UNKNOWN



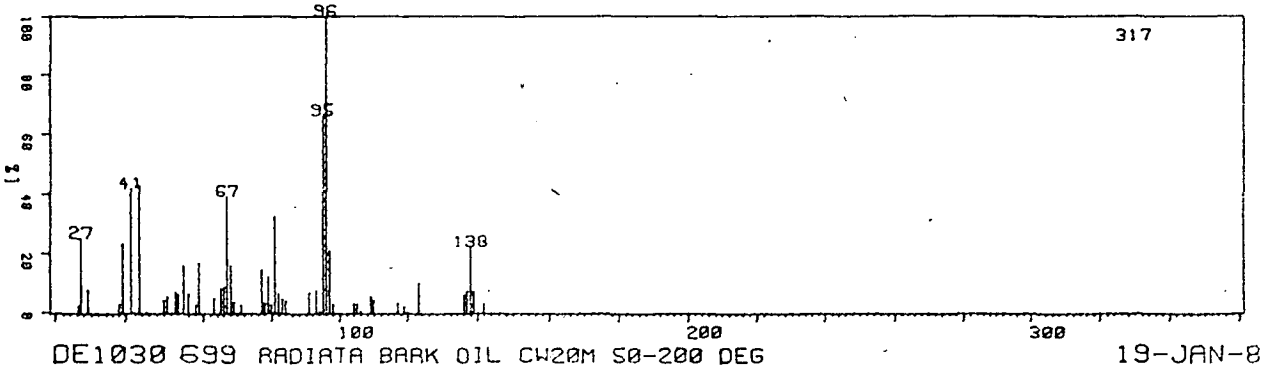
DE1030 672 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 23:4
UNKNOWN



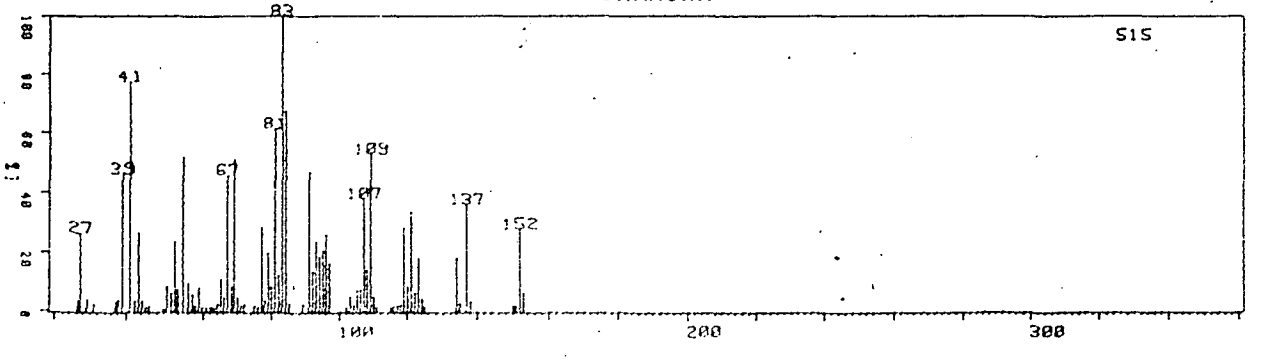
DE1030 683 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 23:27
BORNEAL PLUS UNKNOWN

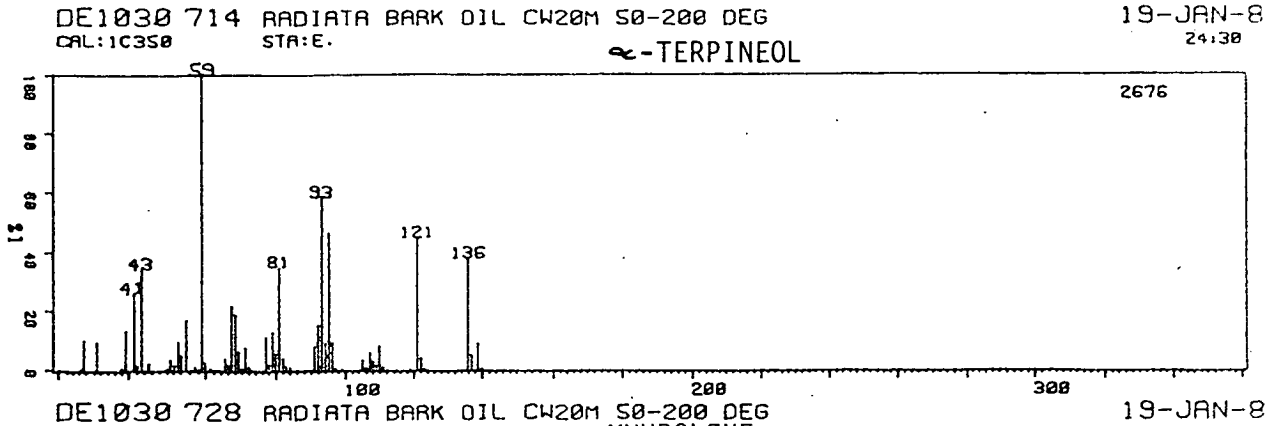


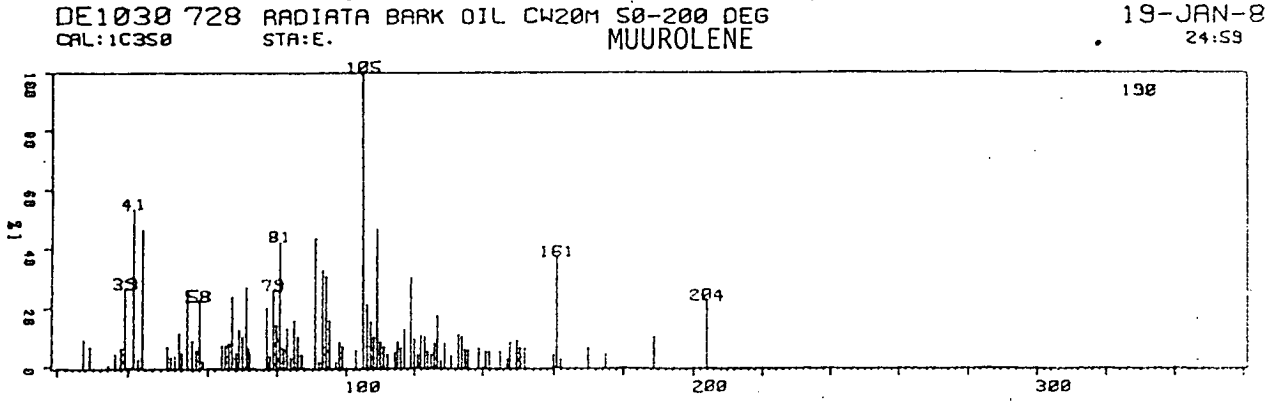
DE1030 691 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 23:43
UNKNOWN

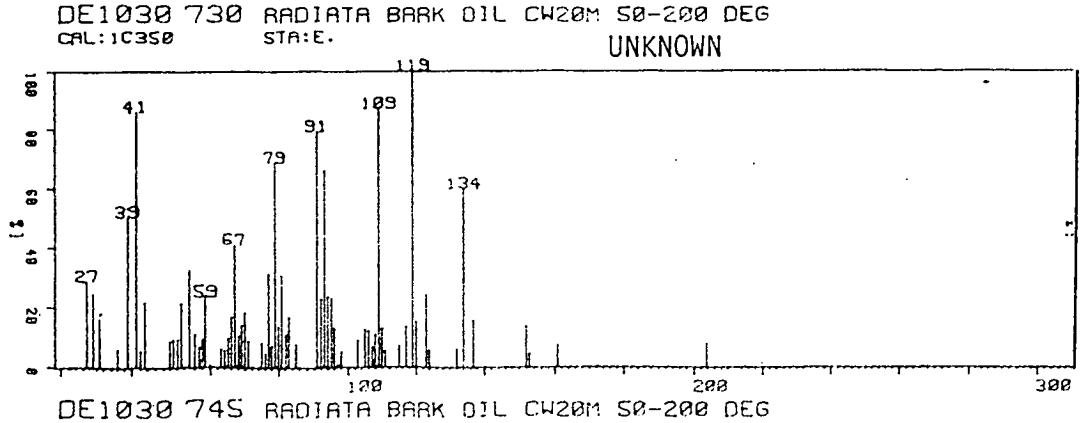


DE1030 699 RADIATA BARK OIL CW20M S0-200 DEG 19-JAN-81
CAL:1C3S0 STA:E. 24:0
UNKNOWN




DE1030 714 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
α-TERPINEOL
19-JAN-81
24:30
2676
59
93
121
136
81
43
41
100
200
300


DE1030 728 RADIATA BARK OIL CW20M S0-200 DEG
CAL:1C3S0 STA:E.
MUUROLENE
19-JAN-81
24:59
190
105
41
81
161
39
58
79
204
100
200
300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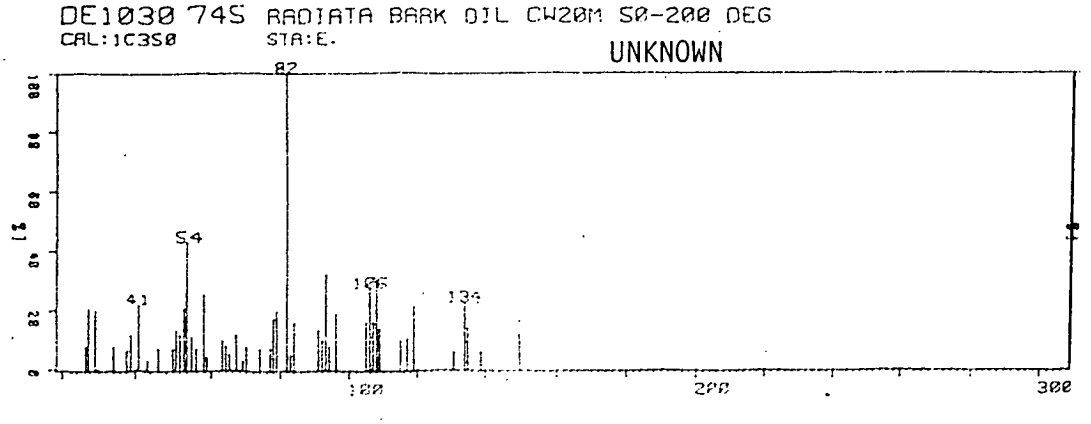
39
67
27
59
100
200
300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41
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200
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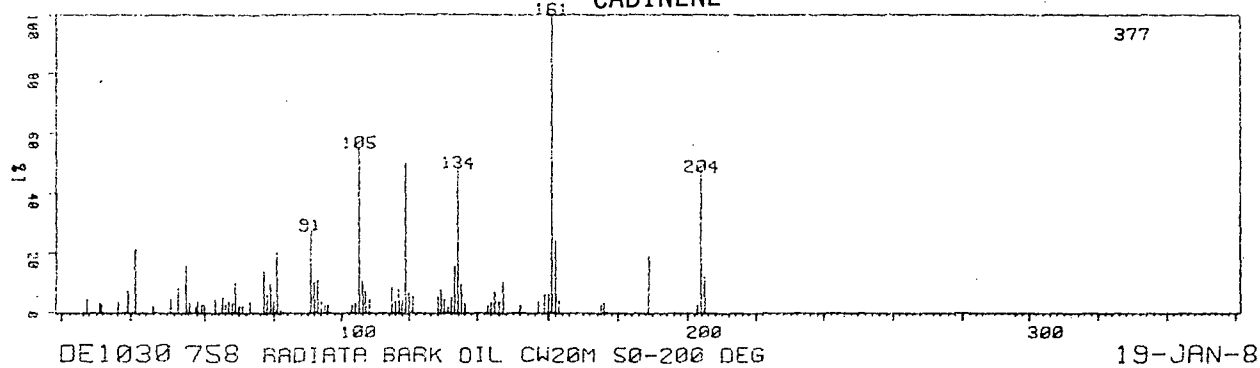

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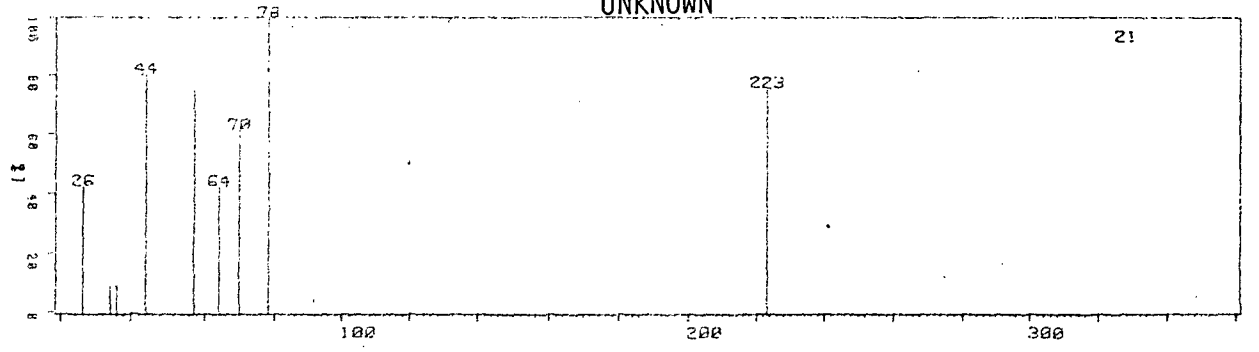

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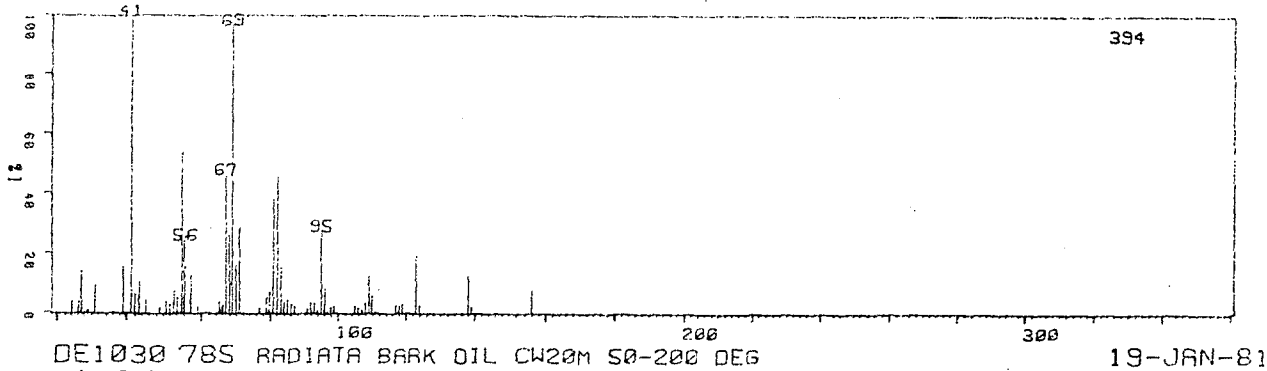

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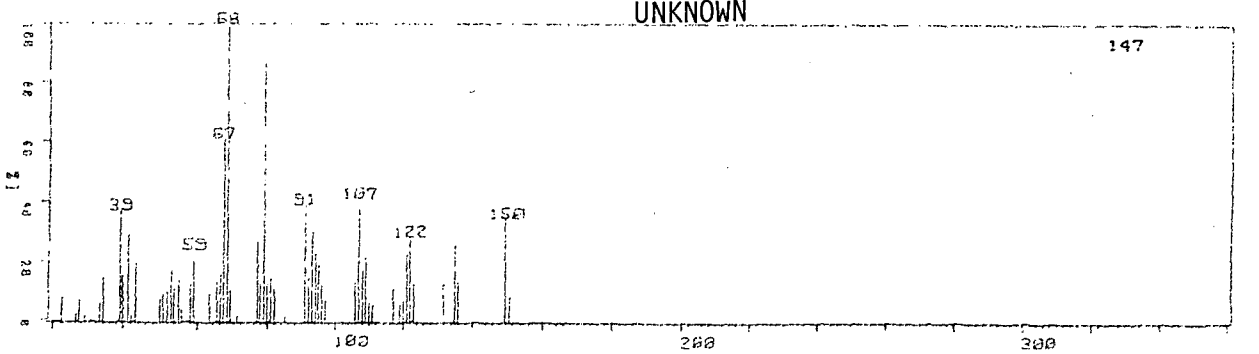
UNKNOWN



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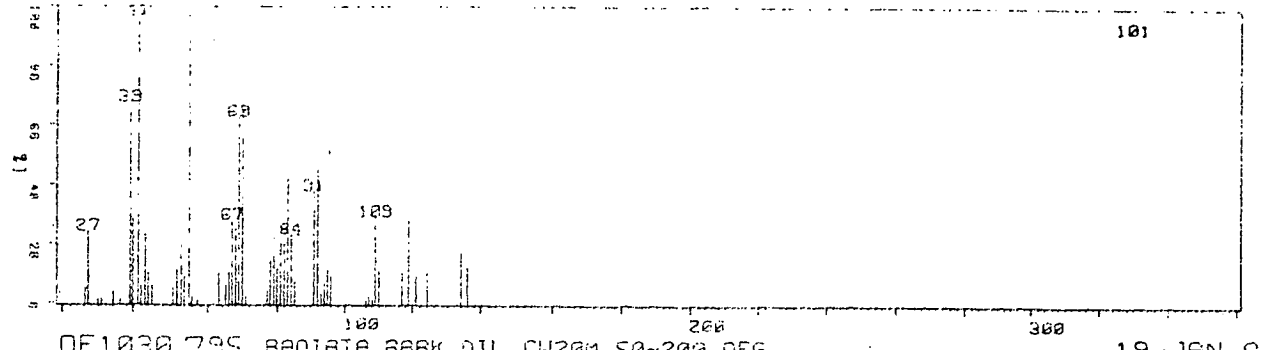
UNKNOWN



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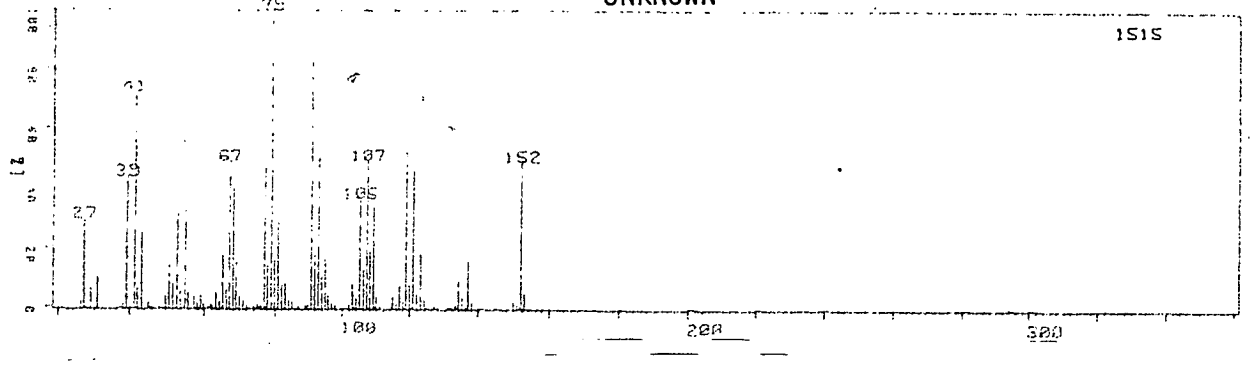

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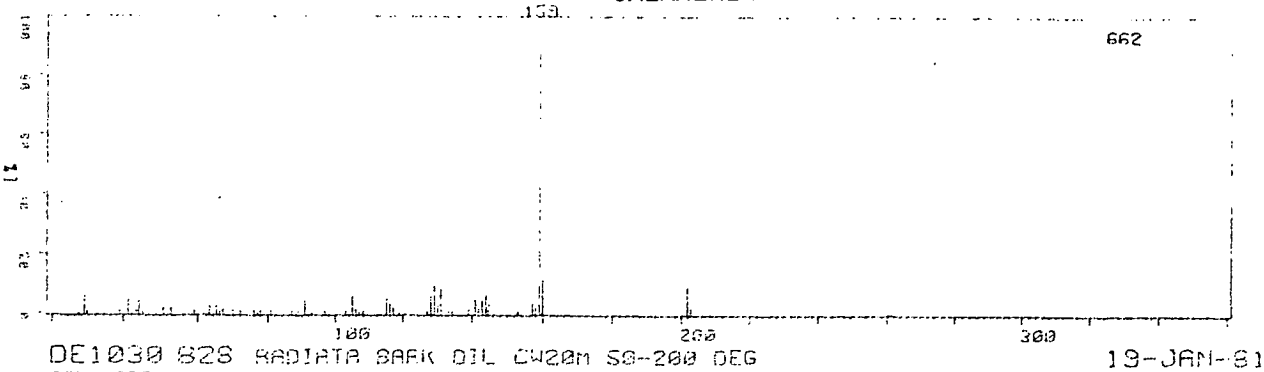
CALAMENENE



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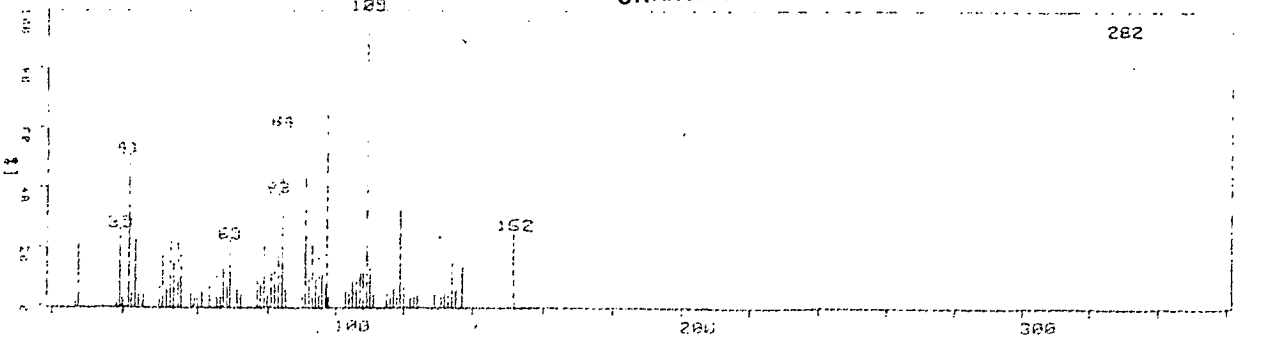
UNKNOWN



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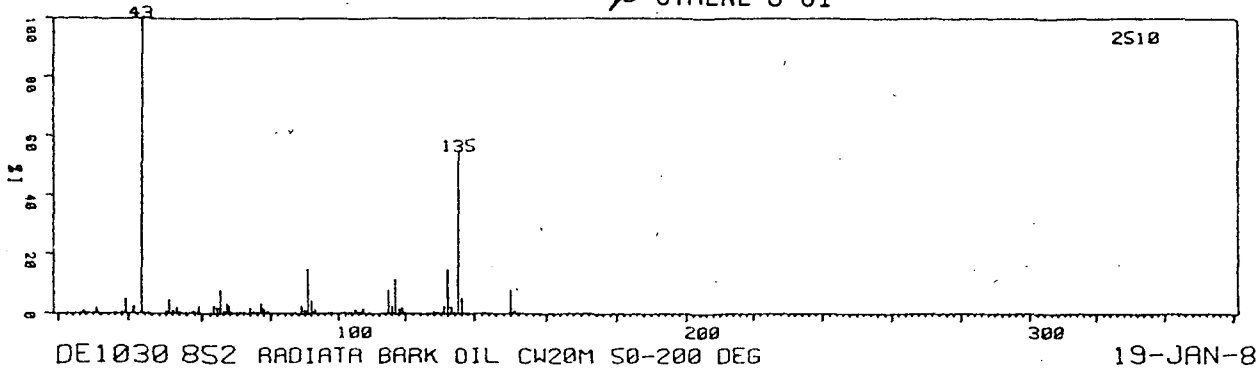

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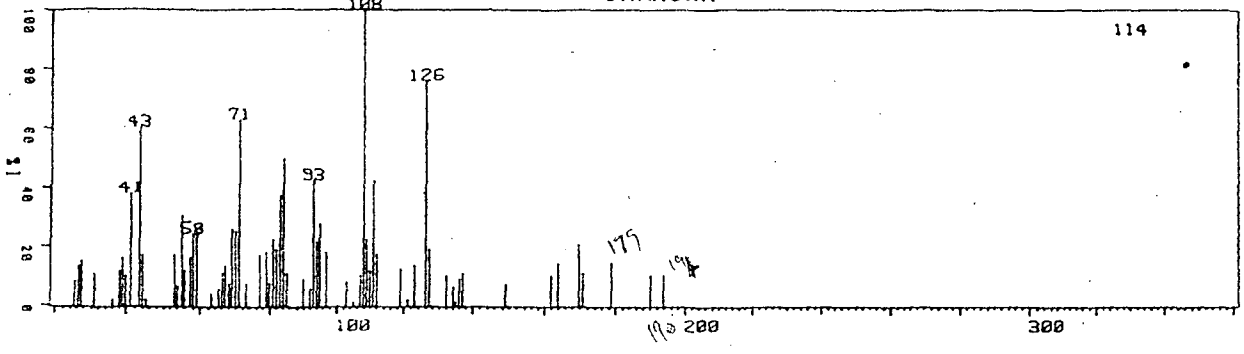

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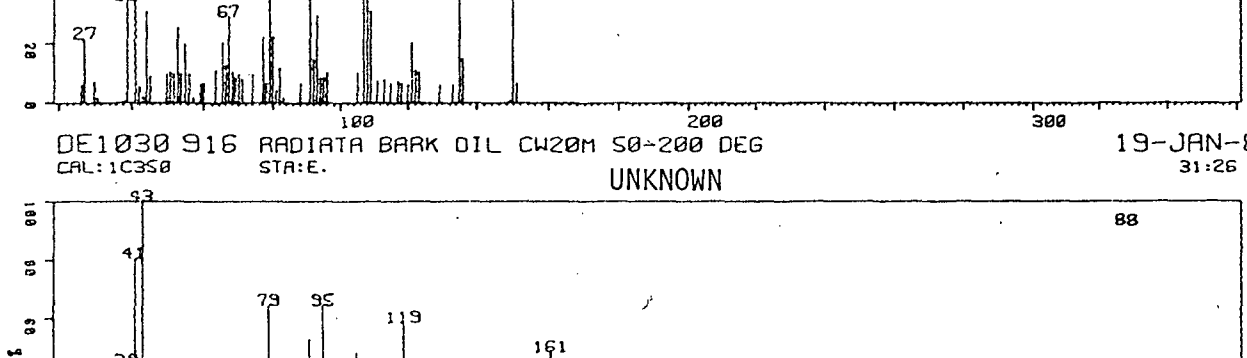

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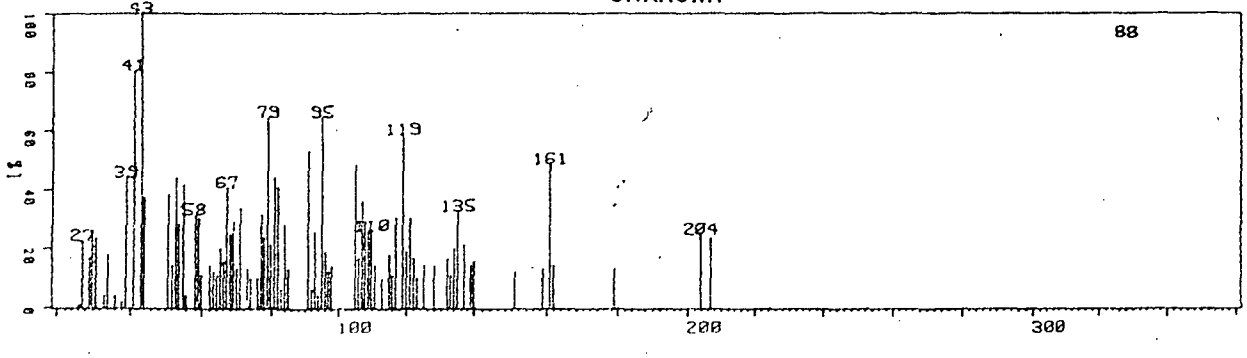

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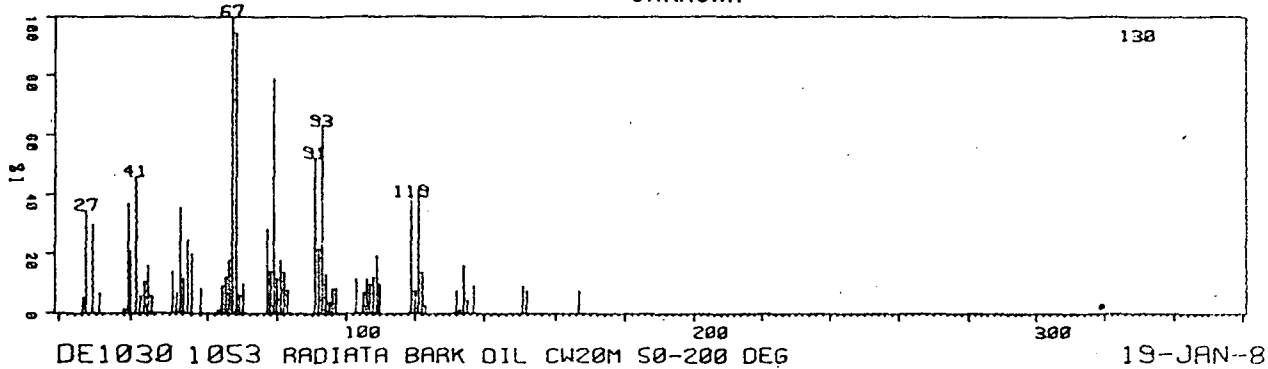

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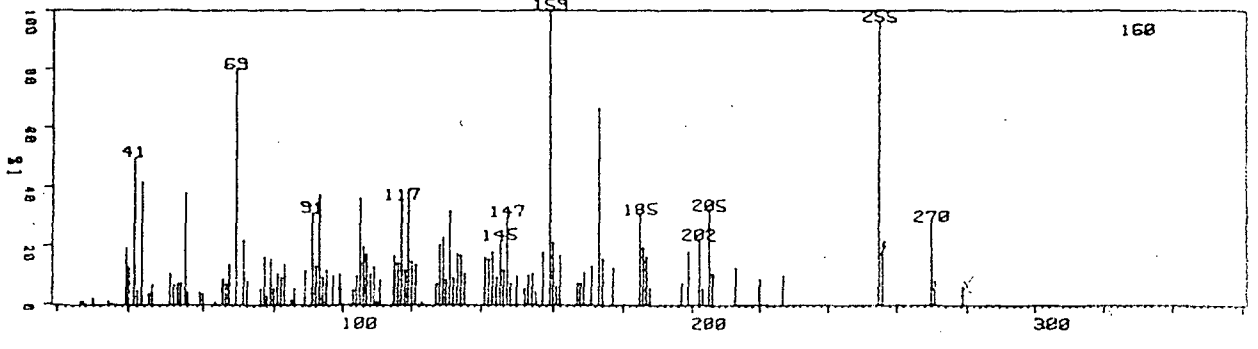

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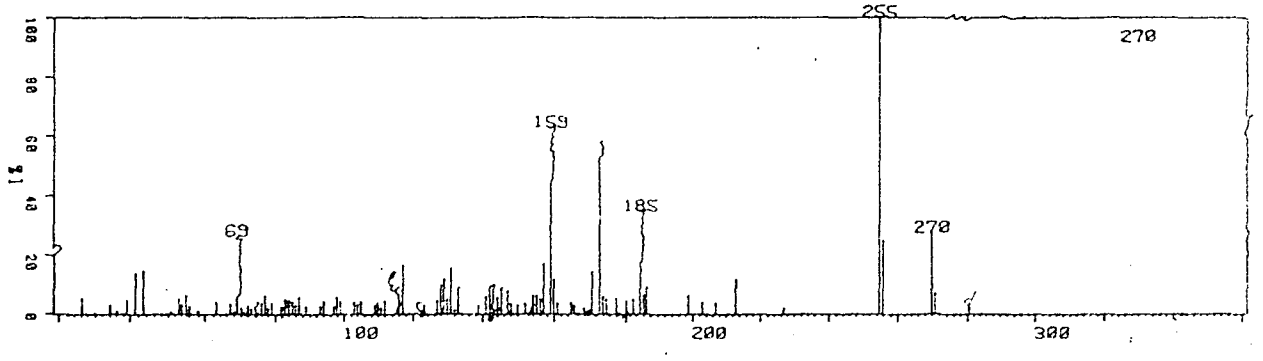

A TECHNIQUE FOR THE SAMPLING OF VOLATILE ORGANIC COMPOUNDS

R. B. (Bob) Chesterman

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INTRODUCTION The sampling of volatile organic compounds has been undertaken using a wide variety of techniques such as cryogenic trapping[1], liquid adsorption[2], solid adsorption[3] and chemical reaction. Each technique has inherent problems associated with either the collection of unwanted material, such as moisture, or the quantitative desorption of components of interest. Tenax GC has proved one of the most effective trapping mediums and has been widely used for the collection of volatile organic compounds from air[4], water[5] and complex matrices including biological material.[6,7]

The sampling system described has been used successfully to study volatile material from diverse sources including plant material, industrial furnaces, working environment atmospheres, and for ambient air monitoring. Extensive development of systems outlined in the literature has resulted in a versatile sample collection/elution system for routine use in the field or industrial workplace. An outline of a similar system is given by Versino[8] in which he describes the use of 2.5 g Tenax sample tube to record recovery checks on a series of standard compounds. The capacity of Tenax to adsorb and desorb a range of organic components was reported in detail by Brown and Purnell[9], and Butler and Burke.[10]

Practical details of the sampling and desorption system used by this laboratory are given, and an example of the collection and analysis of volatiles from a wood burning stove is used to illustrate the technique.

EXPERIMENTAL PROCEDURES

Sample collection tubes consist of 170 mm lengths of glass lined stainless steel tubing 6 mm O.D., 4 mm I.D., previously baked at 500°C and packed with Tenax-GC (0.4 g) and held by silanised glass wool. New packing was pre-conditioned at 325°C for 25 hours in a stream of high purity nitrogen, and the sample collection tubes were re-conditioned at 300°C for 2 hours prior to use in the field. The tubes were held individually in stoppered glass containers, with a small amount of dried silica gel, for storage and transport to and from the sampling area.

Collection of the volatile organic components of the flue gas was accomplished by inserting the Tenax sample tube into a water cooled jacket (Figure 1) and drawing gases through the sample tube from the flue of the wood burning stove. The sample collection point was 4 m above the grate. A calibrated flow control valve was used to maintain the gas flow rate to the gas pump at 40 mL per minute for 2 hours.

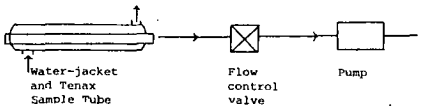

Figure 1. Sample Collection System.

Desorption of the collected volatile organic components was controlled by heating of the sample tube in a stream of carrier gas to "inject" the trapped components into the inlet of a gas chromatograph or gas chromatograph/mass spectrometer system (GC/MS) for characterisation.

The heating block consisted of a 25 x 150 mm cylindrical stainless steel rod with two holes drilled longitudinally. The central hole accepts the stainless steel Tenax sample tube held in position by a ¼' Swagelock fitting at one end, and a 1/16' Swagelock fitting for the carrier gas inlet at the other. The second drilled hole contained a thermocouple junction to monitor the temperature of the block. The heating element consisted of a single layer of No. 20 gauge B. and S. resistance wire of 1.779 Ohm/metre. The total length of wire wound over a sheet mica base was 7.2 m. A voltage of 50 V from a variable voltage transformer provided sufficient power to heat the block to 300°C in approximately 10 minutes. Figure 2 is a half scale drawing of the elution equipment.

The eluted organic components are carried by the gas stream to a length of 2 mm x 230 mm glass lined stainless steel tubing (C) bent to form a U shaped trap. Coupling of the sample collection tube to the U trap was accomplished using stainless steel Swagelock fittings silver soldered to the 2 mm tube and employing graphite ferrules to form a compression seal at the heating block end. At each end of the 2 mm tubing (points A and B) a brass lug was silver soldered onto the fitting to provide electrical contact. Fitting A consists of a Luer syringe needle coupling or, an additional length of glass lined tubing, for coupling directly to a capillary GC column.

Immersion of the U shaped section of tubing into a liquid nitrogen bath condensed the organics eluted from the heated sample trap. A 10 minute time interval at the pre-selected elution temperature ensured efficient displacement of the organics from the Tenax. After removal of the liquid nitrogen bath, the 2 mm glass lined tubing was rapidly heated by the passage of an electric current (40A from a welding transformer) between points A and B. The current was applied for 30 seconds and the maximum temperature reached was 300°C. The organics were vaporised and carried to the injector system of the GC or GC/MS. Resistance heating of the glass lined tubing at this current setting is sufficient to ensure that breakage of the tubing does not occur.

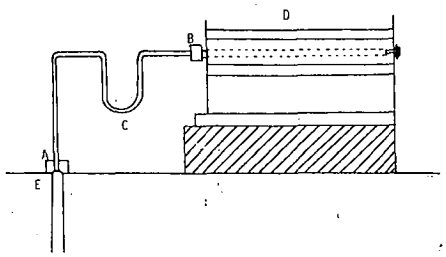

Figure 2. Sample Elution — Injection Apparatus.

technique described could be accomplished on a routine basis using a number of sample tubes and despatching them to a central laboratory for analysis.

SUMMARY AND CONCLUSIONS

An effective method for trapping volatile organic compounds from air and gas streams is presented. Construction details are provided and an example of the collection and an analysis of the flue volatiles from a wood burning stove is used to illustrate technique. Quantitative measurements of volatile components may be made by incorporation of a suitable bleed of a known concentration of a specific component into the gas stream. Possible applications of the technique include ambient air monitoring, forensic and customs search assistance, odour location and analysis.

Monitoring of volatile trace organic components in working and residential areas will become increasingly important as city populations increase. (There were 11 cities of over 1 million people in 1900, by the end of the century the number is expected to be over 500.) Trends in the lowering of ambient air quality and the health effects resulting need to be carefully documented at an early stage to avoid serious long term problems.

ACKNOWLEDGEMENTS The assistance of Mr. C. Richards in the construction of the equipment and the preliminary prototypes is gratefully acknowledged. The help of the staff and the use of the equipment of the Central Science Laboratory of the University of Tasmania is also acknowledged.

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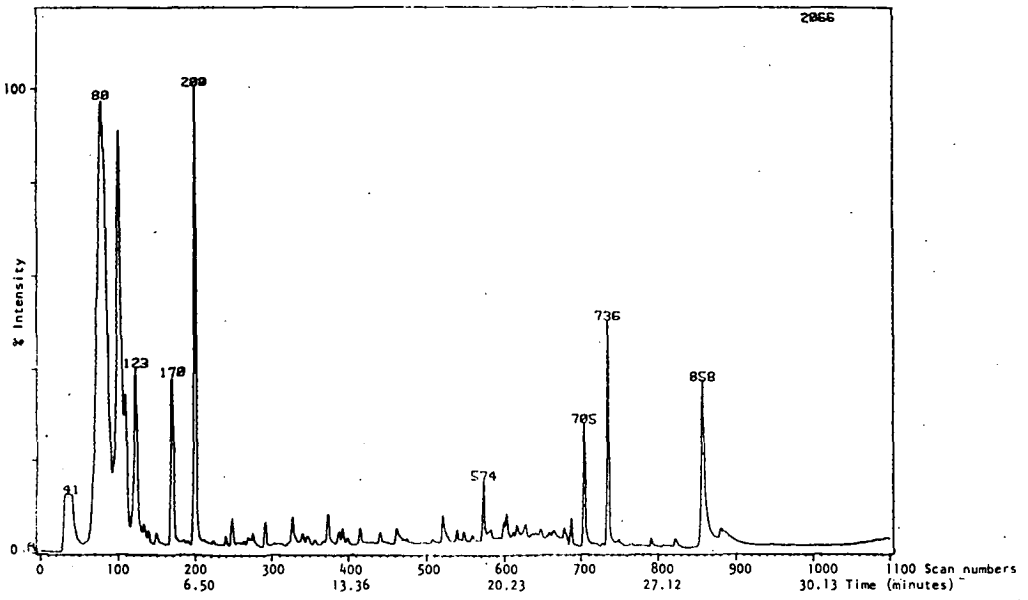

Figure 4. Total Ion Current Trace Boronia Volatiles Scan Number and Time.

Table 1. Volatile Components from a Wood Burning Stove.

Component	Boiling Point °C	Scan No.
1, 2-pentadiene	45	50
2, 3-pentadiene	48	55
acetone	56.5	57
hexane	70	63
benzene	80	74
2, 5-dimethylfuran	94	85
toluene	110	106
2-furyl methyl ketone		121
ethylbenzene	136	159
phenylacetylene	142	168
styrene	145-146	180
2-furaldehyde	162	218
benzaldehyde	179	236
dimethylphenol (6 isomers)	210-225	247-248
p-methylbenzylalcohol		249
trimethylbenzene (3 isomers)	164-170	253
benzofuran	173-175	287
naphthalene	217	573
azulene	270	574
dimethylbiphenyl (5 isomers)	256-295	789
heptadecene	300	814
heptadecane	302	817

Table 2. Threshold Limit Values (TLV) for some Volatile Components

Component	TLV (ppm)	TLV (mg/m^3)
hexane	100	360
benzene	10	32
acetone	1000	2400
toluene	100	375
ethylbenzene	100	435
xylenes	100	435
furfural	5	20
styrene	100	420
cresols	5	22

Table 3. Volatile Components of Boronia Headspace

Scan No.	Identity
41	Carbon dioxide
80	Methylene chloride
101	Chloroform
110	Methylcyclopentane
123	Cyclohexane
140	Heptane
151	Methylcyclohexane
170	Toluene
200	Tetrachloroethylene
241	Xylene
293	Nonane
342	Monoterpene (unknown)
349	Isopropylbenzene
371	α-pinene
386	Camphene
392	β-pinene
400	Myrcene
416	Limonene
442	Linalool
522	Unknown
574	Menthone
600	Naphthalene
604	Ethylbenzene
705	Methylnaphthalene
736	Methyldecanoate
858	β-ionone
882	Dihydroactinidiolide