A GAS CHROMATOGRAPHY-MASS SPECTROMETRY INVESTIGATION OF THE HIGHEST OPTICALLY ACTIVE DISTILLATE CUT FROM A SHALE OIL

by

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ABSTRACT

A shale oil sample from the Laramie Energy Technical Center 150-Ton aboveground retort, designed to simulate the in-situ retort process, was vacuum distilled in order to obtain narrow distillate fractions. Then, the optical rotation was measured for each distillate cut. The fraction with the highest optical rotation (470-485°C) was subjected to elution chromatography using hexane as eluant. The resulting saturated fraction was investigated by computerised gas chromatography-mass spectrometry. The analysis included generation of chromatographic retention data by co-injection of a standard reference mixture of normal alkanes, selective ion monitoring for compound-type recognition, and mass spectra for individual compound identification. Three steranes, four pentacyclic triterpanes and five normal alkanes were identified, and the partial structures of two other compounds are postulated. The concept of optical rotation is introduced in general terms as well as in the context of fossil fuels. A description of the parameters involved in the generation of shale oil from oil shale is also discussed. Concluding remarks and suggestions for future studies in the subject are finally formulated.

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INTRODUCTION

The importance of oil shale as a new source of energy has increased in recent years because the resource of petroleum, our current main energy supply, is declining. Like most natural deposits, oil shale has been formed in many different ways from many different sources and occurs on every major land area of the world. However, many deposits are too small or too lean to warrant exploitation. Because of its size the oil shale of greatest current interest is that contained in the Green River formation located in southwestern Wyoming, northwestern Colorado, and northeastern Utah. The current energy shortage dictates that the United States government make oil shale a significant factor in its domestic oil supply. However, economical and environmental barriers are enormous.

The Bureau of Mines, and particularly the Laramie Energy Technical Center has as its charter to assist and encourage private industry in the orderly development of oil shale. Their main goal has been to provide technical information on oil shales and their retorting products, such as the composition and properties of oil shales, chemical reactions and conversion techniques involved in producing useful fuels and by-products.

Most investigations into methods of extracting hydrocarbons from oil shale have been based on the underground (in-situ) retort (1). This process will eventually eliminate the mining operation, which accounts for the major share of the cost of producing crude oil from oil shale. As a result of the sharp increase in oil prices, the commercial exploitation of oil shale by the in-situ process may become a reality.

Various in-situ processes, differing primarily in the method of supplying the heat to the retort (2), are under investigation. However, the major disadvantage of these processes results from the difficulty of monitoring the underground conversion changes such as gas flow, heating rate, maximum temperature and control of flame front.

Because of the difficulty in studying the variables involved in an actual in-situ operation, aboveground retorts were built to simulate field in-situ processes. The first of these retorts had a nominal capacity of 10 tons of oil shale. The latest retort has a nominal capacity of 150 tons and is described in detail later in this dissertation.

So far 18 runs on a 150-Ton retort at L.E.T.C. have been made to study variables such as the gas flow and the flame front travel through the broken shale, the grade of shale and the particle size distribution. Other variables,

including the method of obtaining the required permeability, the control of the combustion front movement, and the recovery of the retorting products, can be studied only in actual field experiments. Hence, the Bureau of Mines and the Department of Energy have for several years been conducting field experiments in southwestern Wyoming between the towns of Rock Springs and Green River.

Several approaches to solve the problems of monitoring the in-situ process are being individually investigated. The subject of this thesis deals with the development of a technique based on the possible use of optical rotation of the produced shale oil in monitoring the underground temperature during an in-situ process operation. The foundation for this study is based on the following criteria:

(1) optical rotation of petroleum hydrocarbons decrease with thermal maturity (3).

(2) shale oil hydrocarbons are similar to petroleum hydrocarbons in that they are both pyrolytic products resulting from thermal alteration in the kerogen matrix (4).

The first results from the application of this technique at a laboratory scale (5), (6), (7) were satisfactory, and a relationship between variables such as optical

rotation, heating rate, pour point, oil yield, and cracking was established. However, application of this technique to field experiments has not been as successful (5), primarily because of more severe and variable conditions in an actual field in-situ process. In addition, the lack of knowledge of the optically active compounds in the produced shale oil complicates data correlation. The distribution of these optically active compounds in the relatively very small samples of oil shale investigated in the laboratory is very consistent. However, with larger field in-situ experiments where large blocks of shale are retorted, the possibility of composition differences exists. For example, the composition of a soluble extract (bitumen) from samples taken from the top of the formation differs from that of the bottom. Some of these differences are related to structural transformations resulting from burial temperature, while some are related to source material composition (3). This would imply that a relationship of temperature versus optical rotation would be incomplete without the incorporation of the compositional factor of the retorted oil shale. Such a relationship would hold only if uniformity of the retorted oil shale is established.

In this investigation, we wish to contribute to the development of in-situ monitoring by optical rotation and

extend its applications to oil recovery by providing information on the compounds responsible for the occurrence of optical activity in Green River oil shale. Combined gas chromatography-mass spectrometry together with computer facilities for data handling and processing is believed to be the most convenient system for such an analysis, and was the analytical tool used in this investigation. Prior to that analysis, a series of experiments, including vacuum distillation, optical rotation measurement and elution chromatography, were carried out in order to prepare the samples.

CHAPTER II

OPTICAL ROTATION

A. THEORETICAL CONSIDERATIONS

Optical rotation has been known since the last century from the work of Aragot, Van't Hoff, Biot, Fresnel and Pasteur. When plane polarized light is passed through an optically active substance, the velocity of one of its components (right and left hand circularly polarized light) is reduced more than the other, depending on the refractive index of the sample. When the two components emerge from the sample, a phase difference has occurred and their resultant vector has rotated its plane of polarization with respect to its angle when it entered the sample. The amount of the angular rotation is a function of the phase difference between the two components and is called optical rotation (optical activity).

The occurrence of optical rotation in a substance is closely related to its molecular dissymmetry. "Dissymetrie moleculaire" was first stated by Pasteur about 130 years ago and means the non-superimposability of an object and its mirror image. Unfortunately, the word "dissymetrie" although

always used correctly in the french literature has been almost universally mistranslated as "asymmetry" in the American, English and German literature.

It took almost fifty years for a percentage of chemists to recognize that in terms of the symmetry elements of the molecule, molecular dissymmetry required the absence of any plane of symmetry ($\sigma = S_1$), a center of symmetry ($i = S_2$), or in the broad sense an improper axis of rotation (S_n). Thus, the use of either asymmetry or symmetry should not be invoked in the condition of optical rotation.

The example in Figure 1 illustrates the correct relationship between symmetry, asymmetry and dissymmetry. The molecule of trans-1,2-dichlorocyclopropane possesses an element of symmetry C_2, therefore is symmetric (non-asymmetric) but is not superimposable on its mirror image (has no improper axis of rotation), therefore is dissymmetric and optically active.

In organic molecules, the molecular dissymmetry is most commonly satisfied by molecules containing one or several chiral carbons (carbons atoms to which four different groups are attached, Figure 2). However it should be emphasized that these chiral carbons are not the necessary condition for optical activity. For example, substituted dihydrophenanthrene (Figure 3) is devoid of chiral carbon atoms but

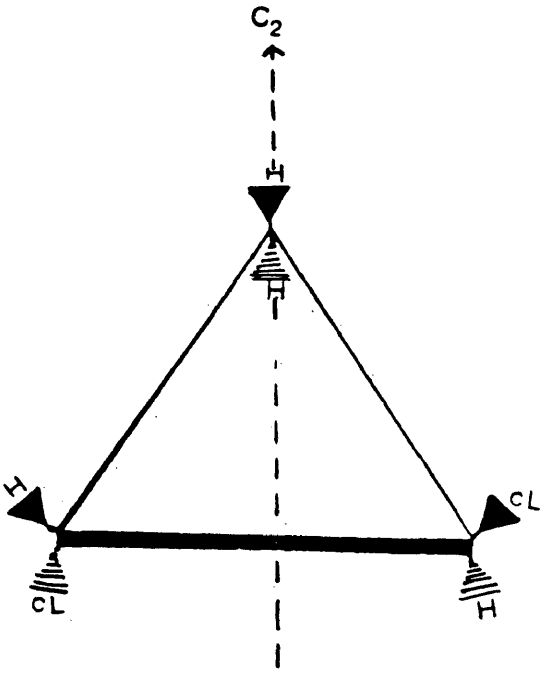


Figure 1. Trans-1,2-dichlorocyclopropane (8)

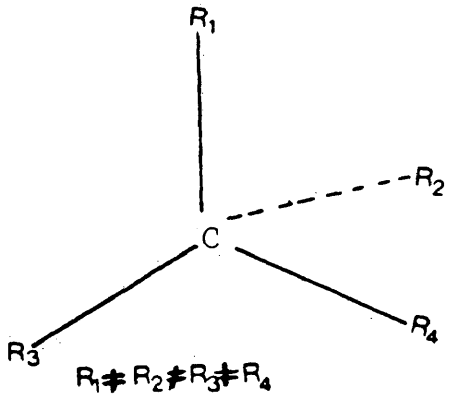


Figure 2. Chiral Carbon Center in Organic Molecules

has no plane or center of symmetry, and therefore is optically active.

Finally in 1965 Wynberg, in an attempt to study the effect of chain length on optical activity (10), carefully synthesized butylethylhexylpropylmethane (Figure 4). The molecule did not show any detectable optical rotation between 280 and 580 nm, probably because the electronic interactions of the four alkyl groups with polarized light were sufficiently similar, such that no rotation was observable.

The Wynberg molecule is in good agreement with what has been reported by Jaeger, more than half century ago (11). He pointed out that optical activity is primarily associated with electronic distribution and secondarily with atomic configuration. However, most chemists think that the optical activity of butylethylhexylpropylmethane was probably too small to be detected and accept asymmetric (chiral) carbons as a sufficient condition for the occurrence of optical rotation in organic molecules.

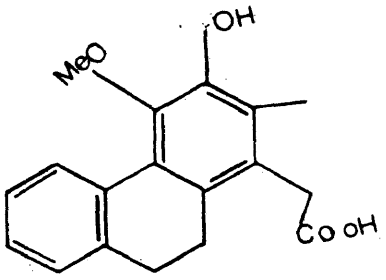


Figure 3. Substituted Dehydrophenanthrene (9)

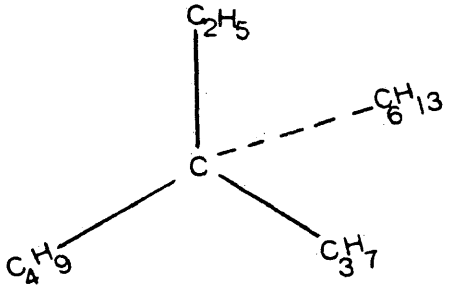


Figure 4. Butylethylhexylpropylmethane (10)

The optical activity of an individual molecule can be deduced from its dissymmetry. However, the rotation of a given molecule is cancelled in the presence of its non-superimposable mirror image (enantiomer), which rotates the light in the opposite direction to the same extent. A mixture of equal amounts of enantiomers is optically inactive and is called a "racemic modification". This is the main reason for the failure of laboratory synthesis of optically active substances. Living organisms are uniquely capable of synthesizing organic compounds which possess optical rotation. This is accomplished through enzymatically catalyzed processes in living cells. Thus, the optical activity is commonly used as an argument of biological origin.

The above discussion on optical rotation is concerned with small organic molecules in the liquid phase, of interest in this investigation. The concept of optical rotation in crystals and polymers is beyond the scope of this dissertation.

B. OPTICALLY ACTIVE CHROMOPHORES

According to Moscowitz (12), optically active chromophores can be classified into two extreme types:

1) Inherently dissymmetric chromophores

This situation arises in molecules containing delocalized electrons, in which the nuclear framework of the electronic system is dissymmetric. An example of this is hexahelicene (Figure 5). This molecule is helicoidal and possesses no improper axis to prohibit optical activity, nor is there any chiral carbon to provide optical rotation. The entire molecule acts as a single chromophore. The dissymmetry necessary for optical rotation is built into the chromophore itself. Optically active organic substances in this category are rare and are usually characterized by a relatively high optical activity.

2) Inherently symmetric chromophores which are dissymmetrically perturbed

In this case the individual parts or groups of the molecule are considered to possess elements of symmetry, which are usually known in advance from structural chemistry. In an optically active molecule, these symmetric groups are juxtaposed to form a dissymmetric ensemble. Figure 6 shows that the incorporation of a methyl group in the

cyclohexanone nucleus creates a chiral carbon which induces a dissymmetric molecular environment and causes the observed optical activity in 2-methylcyclohexanone.

It is also necessary to consider the fact that in a molecule, the atoms are not limited to a single arrangement, but are free to rotate around single bonds. Therefore, the extent of symmetry or asymmetry may vary considerably from one conformation to another. In addition, chirality and consequently optical rotation can be induced by isotopic substitution (14).

C. SPECIFIC AND MOLECULAR ROTATION

Optical activity is often reported in the literature as specific rotation [α] or molecular rotation [M]. They are defined as :

$$\text{SPECIFIC ROTATION} = \frac{\text{MEASURED ROTATION (DEGREE)}}{\text{CONCENTRATION(g/ml)} \times \text{CELL LENGTH(decim)}}$$

$$\text{MOLECULAR ROTATION} = \frac{\text{SPECIFIC ROTATION} \times \text{MOLECULAR WEIGHT}}{100}$$

The expression of the optical rotation as specific rotation or molecular rotation, rather than the observed rotation is very advantageous. The specific and molecular

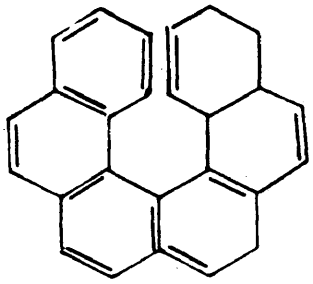
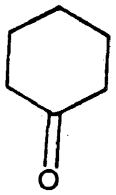
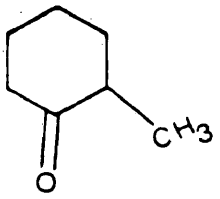


Figure 5. Hexahelicene



optically inactive



optically active

Figure 6. Cyclohexanone and 2-methylcyclohexanone

rotation represent physical constants, as well as being more suitable for comparison purposes. In the present investigation, only specific rotation will be considered because the sample consists of a complex mixture of compounds of unknown molecular weights.

The specific rotation is usually given for the strongest yellow band called the D-line, corresponding to 589 nm. A variation of optical rotation with the wavelength gives an optical rotatory dispersion (ORD) curve, which provides multiple points of comparison. This approach is particularly useful in structural elucidation.

D. OPTICAL ROTATION CONCEPT IN FOSSIL FUELS

Although the optical rotation of petroleum has been known for many years and has been widely used in the field of petroleum geochemistry, the optical rotation of shale oil has not been given any considerable attention in the past. Shale oil should be optically active, because the kerogen of oil shale is not distinct from the kerogen of petroleum source rock. Both are thought to be derived from the remains of some form of life existing during their deposition.

Bradley (15) was one of the early investigators to propose that the organic material in Green River oil shale was of biological origin. The exact precursors are not known. However, it is believed that a variety of organisms contributed to the organic debris and a variety of reactions produced the resulting carbonaceous material.

As it was stated in a previous section, the common feature between shale oil and petroleum is that they are both pyrolytic products of a common source of organic matter (kerogen). It is well known that the optical rotation of petroleum has been in the past correlated to its thermal maturity. This optical rotatory power reflects the extent to which the petroleum compounds have been transformed by slow thermal decay as a consequence of burial temperature. The

retorting of oil shale to products accelerates this thermal decay process and new insights into the retorting may be realized by following changes in the optical rotation of the shale oil produced.

The organic matrix (kerogen) of rocks contains practically the entire suite of organic structures identified in living organisms. This includes terpenoids, steroids, porphyrins, amino acids, ketones, sugars, alcohols, carboxylic acids and ethers (16).

Steroids and triterpenoids represent ubiquitous cyclic constituents of living organisms. These are usually found in living systems as oxygenated substances. The "fossil molecules", however, seldom appear as such, but are present as fully reduced (steranes and terpanes) or, to a lesser extent, as partially (or completely) aromatized structures (17), (18). These reduced forms are responsible for most of the optical activity exhibited by many common fossil fuels such as petroleum (19) and coal (20).

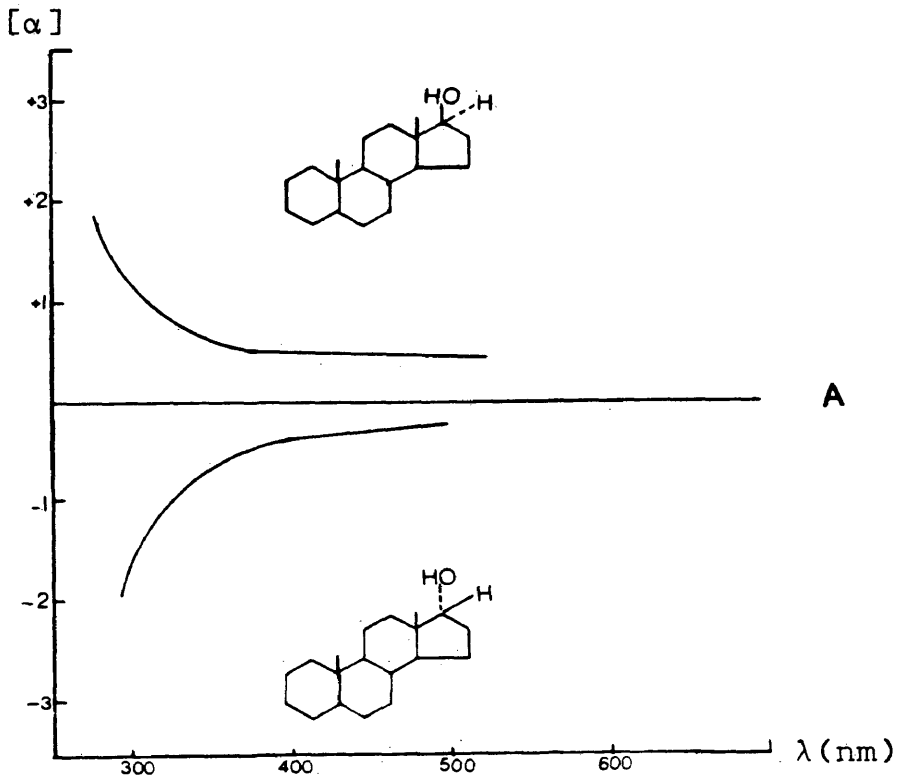
The transformation of the original optically active structures, synthesized by living organisms into fossil fuel hydrocarbons causes parallel changes in optical rotation. These changes are mainly caused by thermal alteration and dilution of the optically active compounds with newly formed optically inactive hydrocarbons (3).

1. THERMAL ALTERATION

Hydrocarbons heated by earth temperature undergo slow but continuous changes in structures and molecular weights. These reactions usually proceed in the direction of lower free energy and mainly involves dehydration, cyclization, cracking, aromatization, hydrogenation, dehydrogenation, epimerization, demethylation and modification of side chain and functional groups. The most important reactions, believed to contribute significantly to changes in optical rotation during thermal alteration, will be discussed.

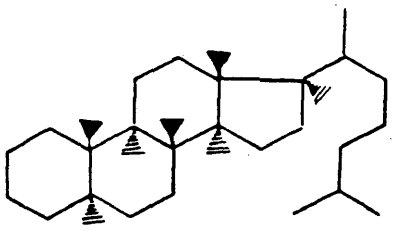
a) Epimerization

Epimerization usually occurs in saturated hydrocarbons at an asymmetric carbon center having an attached hydrogen atom. The process occurs when the hydrogen is removed from the ring juncture, then later returned to a planar site (the original asymmetric carbon center) from the opposite side. This can occur through the formation of a carbonium ion, carbanion or free radical. All three intermediates can be induced by active sites present in clay minerals (21). The ease of epimerization depends on the lability of the attached hydrogen and the stability of the intermediate species. Epimerization may result in either enantiomerism or non-enantiomerism (Figure 7). The conditions which cause



5α-CHOLESTANE

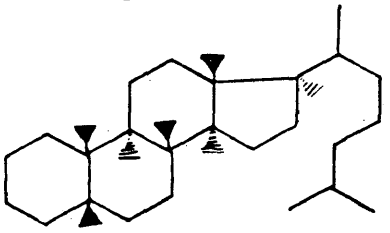
$[M_R^1]_{589}$ = 100



B

5β-CHOLESTANE

$[M_R]_{589}$ = 102



[1]Relative Molecular Rotation, 0/0

Figure 7. Epimerization

A - Enantiomers (9)

B - Non-enantiomers (22)

the occurrence of epimerization in geochemical processes are not totally understood.

b) Loss of the side chain

The loss of optical rotation occurs often by a dealkylation process, which usually causes the elimination of asymmetric carbons centers. Figure 8 shows how the presence of the side chain in 5 -cholestane causes a hundred fold increase in its optical rotation, as compared to that of 5 -androstane which is devoid of side chain.

c) Hydrogenation

The phenomenon of hydrogenation to produce various fossil fuel hydrocarbons is not well understood. It is evident that hydrogenation of a double bond in steroids and triterpenoids will eventually create new asymmetric centers and a subsequent increase in optical rotation is expected (racemization excluded), as illustrated in the catalytic hydrogenation (Figure 9). The hydrogenation process requires a source of hydrogen. Free hydrogen usually is not available. Therefore hydrogen is obtained from accompanying reactions, such as cyclization, aromatization and polycondensation of aromatic rings.

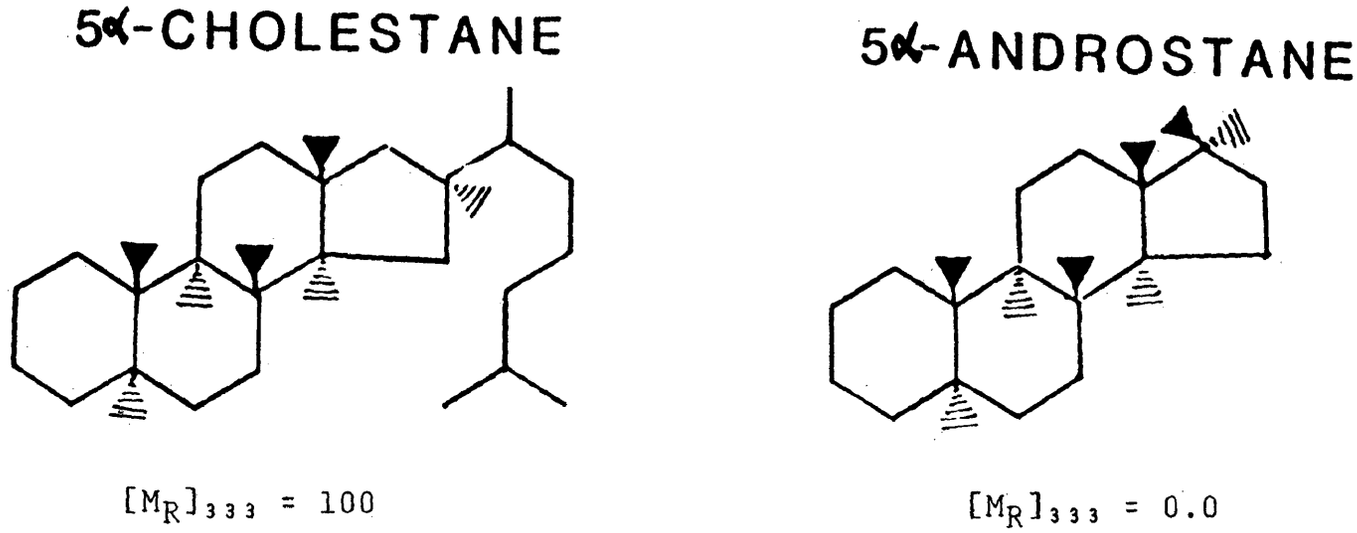


Figure 8. Effect of Side Chain on Optical Rotation (22)

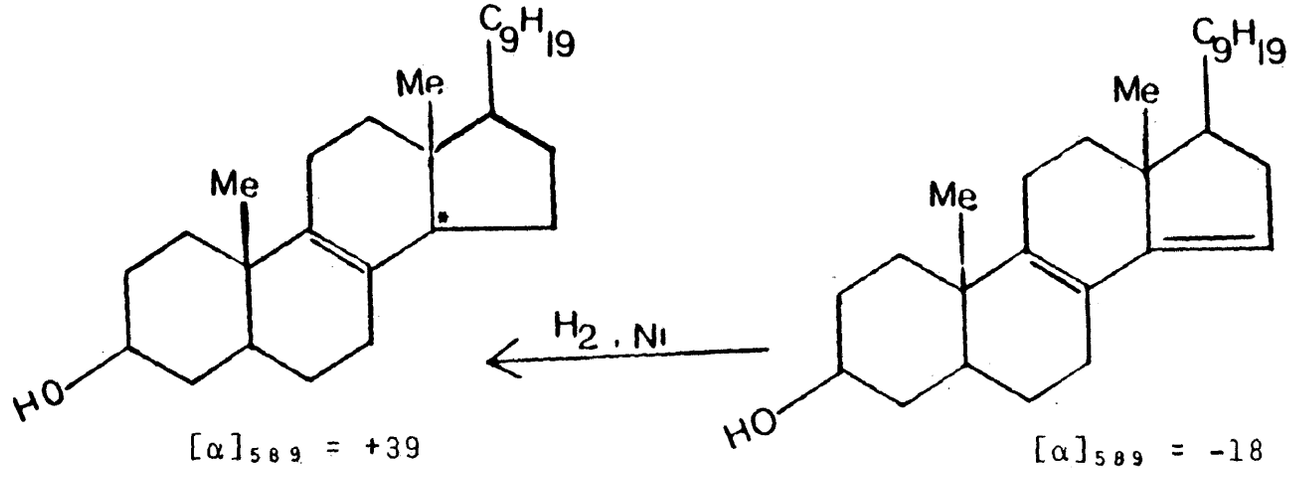


Figure 9. Catalytic Hydrogenation of Dehydroergostenol (13)

d) Aromatization

Finally, the example in Figure 10 shows the remaining major mechanisms by which optical rotation changes can occur during the thermal alteration process. Using cholesterol, a typical sterol formed by living organisms as an example, a series of elimination reactions can occur (loss of OH, side chain, H), followed by carbon-carbon cleavage. These losses create double bonds that can destroy asymmetric centers. Cholesterol can also be converted to a fully aromatic structure which is totally void of optical rotation. Douglas & Mair (24) reported in 1965 the possible role of sulfur in producing such aromatic structures from steroids and triterpenoids. The reaction of cholesterol with sulfur at 150°C over a 30 day period in a laboratory experiment resulted in the evolution of hydrogen sulfide and the formation of benzene, naphtalene and phenanthrene ring system hydrocarbons.

2. DILUTION OF THE OPTICALLY ACTIVE COMPOUNDS BY NEWLY FORMED HYDROCARBONS

This factor results as a direct consequence of thermal alteration and accounts for the majority of the decrease in optical rotation observed in crudes. As the temperature increases, the extent of transformation of the original

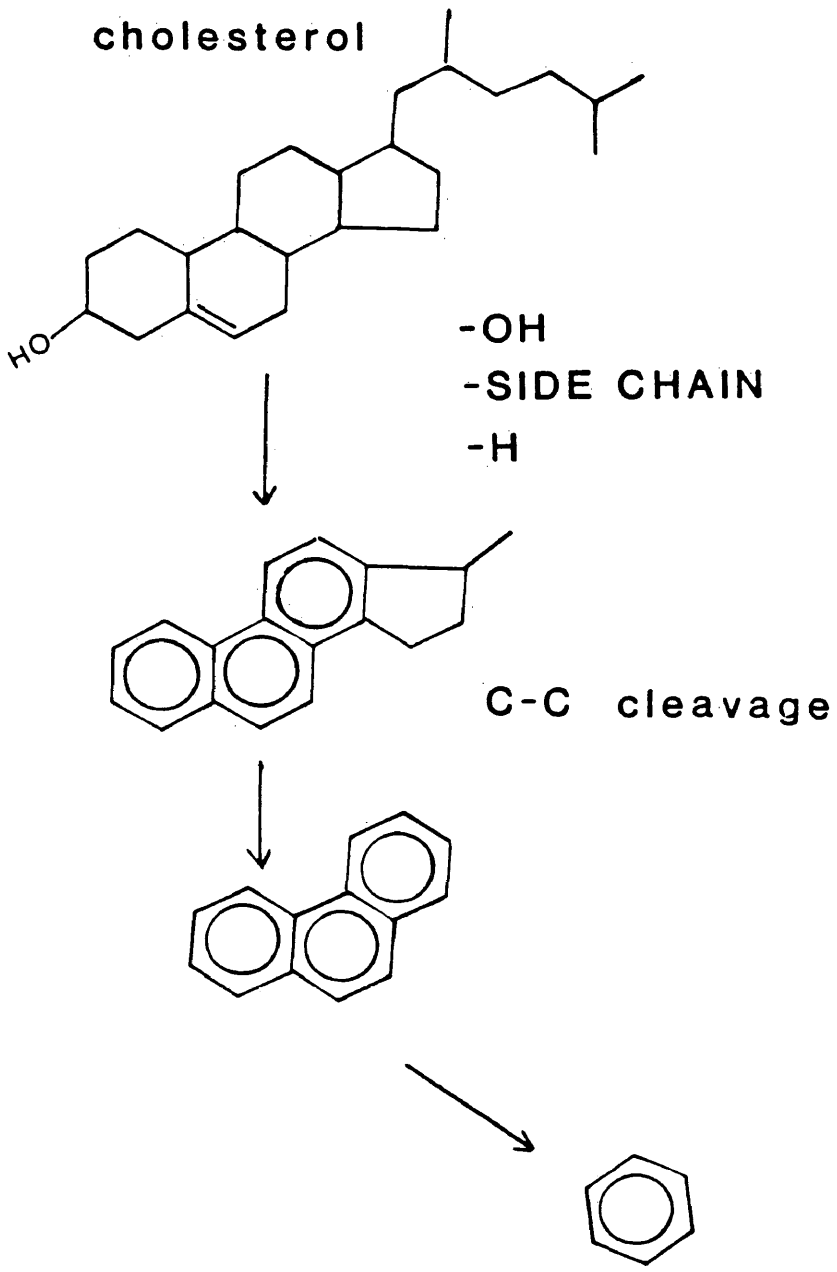


Figure 10. Possible Elimination and Aromatization Reactions of Cholesterol (16)

hydrocarbons increases and the surviving optically active structures are continuously diluted by the newly formed optically inactive compounds (e.g., n-paraffins).

It is worthwhile to add that a small variation in optical rotation may be introduced by microrganisms, which are known to consume optical enantiomers of a racemic mixture at different rates, thus creating optical activity originally cancelled by racemization (25). In addition they may cause normal alkane depletion and consequently a net increase in the overall optical rotation.

CHAPTER III

GENERATION OF SHALE OIL FROM OIL SHALE

Shale oil is produced from oil shale, by simply providing enough thermal energy to cleave bonds of the organic constituents of the oil shale. The resulting fragments are allowed to volatilize and later condense as shale oil. To get a better understanding of the above mechanism, a description of the parameters involved in the process of shale oil generation will be given in this section.

A. Green River oil shale

Gavin (26) defined oil shale as a compacted laminated rock of sedimentary origin, yielding over 33 percent ash and containing organic matter that yields oil when destructively distilled, but not appreciably when extracted with ordinary organic solvents. The Green River oil shale of Eocene age was deposited in a lacustrine environment in a subtropical climate (27). The formation is found in four distinct areas: the Uinta basin of Utah, the Piceance basin of Colorado and the Green River and Washakie basins of Wyoming. This formation exists from outcroppings to layers buried

under hundreds of feet of overburden, from very rich to very lean in organic components and in beds of hundreds of feet thickness to thin seams.

Green River shale usually contains organic matter, minerals and small amounts of moisture. The organic content varies from less than one percent to as much as 40 percent. The inorganic constituents, which consist mainly of dolomite and calcite, are an outstanding characteristic of shale oil as compared to petroleum, and are of no interest in this investigation.

B. Organic matter of Green River oil shale

The organic matter of Green River formation is thought to be the world's largest known hydrocarbon deposit and consists mainly of algal remains with significant amounts of pollen and waxy spores (27), (28). The burial temperature of Green River shale has not exceeded 74°C (29), (30). Therefore, the organic material has undergone very little thermal alteration.

The organic matter contained in Green River oil shale consists mainly of a solid material (kerogen), insoluble in common organic solvents. This material shows a great homogeneity and contains predominantly aliphatic chains, with relatively few polyaromatic entities and heterocycles (31). Detailed compositional studies on the organic matter of

Green River shale have shown that the normal paraffins range in size up to C_{38} and cycloparaffins contain up to six rings, with two and three rings dominant (32), (33). Many steranes and triterpanes are present, and about half of the monoaromatics are fused to saturated cyclopentyl or cyclohexyl rings (34), (35), (36).

Attempts on the elucidation of the Green River kerogen structure have been carried out by several workers (37), (38). However, it should be emphasized that it is nearly impossible with the use of present day capabilities to obtain a detailed structure containing the locations of all atoms with stereoconfigurations. Hence, the kerogen structure is still for the most part unknown.

The soluble organic material (bitumen) found in oil shale has a wide range of molecular weights, usually below 500, and generally contains the same groups of compounds as petroleum, but in different proportions. The bitumen content of the shale is a function of the thermal maturity of the shale and therefore contributes only a small amount to the overall organic matter in the immature Green River oil shale.

C. Thermal decomposition of oil shale

Oil shale undergoes phase transformations, desorption of moisture, chemical reactions and decomposition when

heated. Therefore, to generate usable organic products from the shale, the most common process is a simple thermal decomposition of the initial organic fraction in the oil shale.

The heat supplied causes breaking of the various bonds of the kerogen macromolecules, liberating smaller molecules of liquid and gaseous hydrocarbons, and also nitrogen, oxygen and sulfur compounds. When the primary objective of retorting oil shale is to produce liquid products, excessive temperature and time are undesirable, as they may cause considerable coking, gasification and carbonate decomposition.

During the short period of the development of oil shale, countless retort designs have been suggested and very often tried, but in general may be separated into two broad categories :

1) those which mine, then retort the shale (aboveground)
2) those which retort the shale in place (in-situ). This also includes modified in-situ processes (MIS) which require minor mining.

There are significant problems in aboveground retorting, including the high cost of the mining operation, environmental problems and the necessity of disposal of large quantities of spent shale. For these reasons and others, the L.E.T.C. concentrated most of the work in the past

on the development of the in-situ oil shale recovery. This process requires 3 major steps

1) fracturing to obtain permeability
2) injection to achieve communication
3) fluid migration

Fracturing can be achieved through the use of explosive power, both conventional and nuclear. Communication can be provided by injection of hot gases, water and other fluids. Fluid migration to recovery systems is accomplished by the combining effect of gravity and the sweeping motion of the retorting gases.

The objective of L.E.T.C. is to identify, understand, measure and control the principal technical determinants of the feasibility of the in-situ process. There are a number of ways in which the in-situ process might be accomplished. The sample investigated in this report was obtained from the L.E.T.C. 150-Ton retort, which is of the vertical forward combustion type (39), and is described in the following section.

D. 150 - Ton Retort

An aboveground retort was designed to simulate conditions likely to be encountered in modified field in-situ processes. The actual L.E.T.C. retort is located one mile

north of Laramie, Wyoming. It is 45 feet high, has an inside diameter of 11 feet and is supported by a 92-foot superstructure (Figure 11). This retort is very similar to a large kiln or oven. It is charged by an opening at the top, followed by a careful packing of the shale to simulate an underground column that has been fractured by explosives.

Once the filled retort is sealed, retorting is started by igniting the shale at the top of the retort with a natural gas burner for several hours. This process ignites the shale and establishes a combustion zone or "flame front". External blowers provide a flow of air which moves the combustion zone downward. The descending flame front is monitored by 112 thermocouples placed throughout the retort. The heat generated at the flame front causes a chemical change (pyrolysis) in the kerogen of the oil shale and a subsequent oil release. The oil flows to the bottom of the retort into the recovery system, which consists of a tank mounted on load cells such that a continuous output of retort can be maintained. The gaseous products, which contain some oil and water, are passed through packed towers to remove most of the entrained material. Some of these gases are recycled back into the retort.

By adjusting the air flow and the oxygen content of the retorting gas, the flame can be made to move at dif-

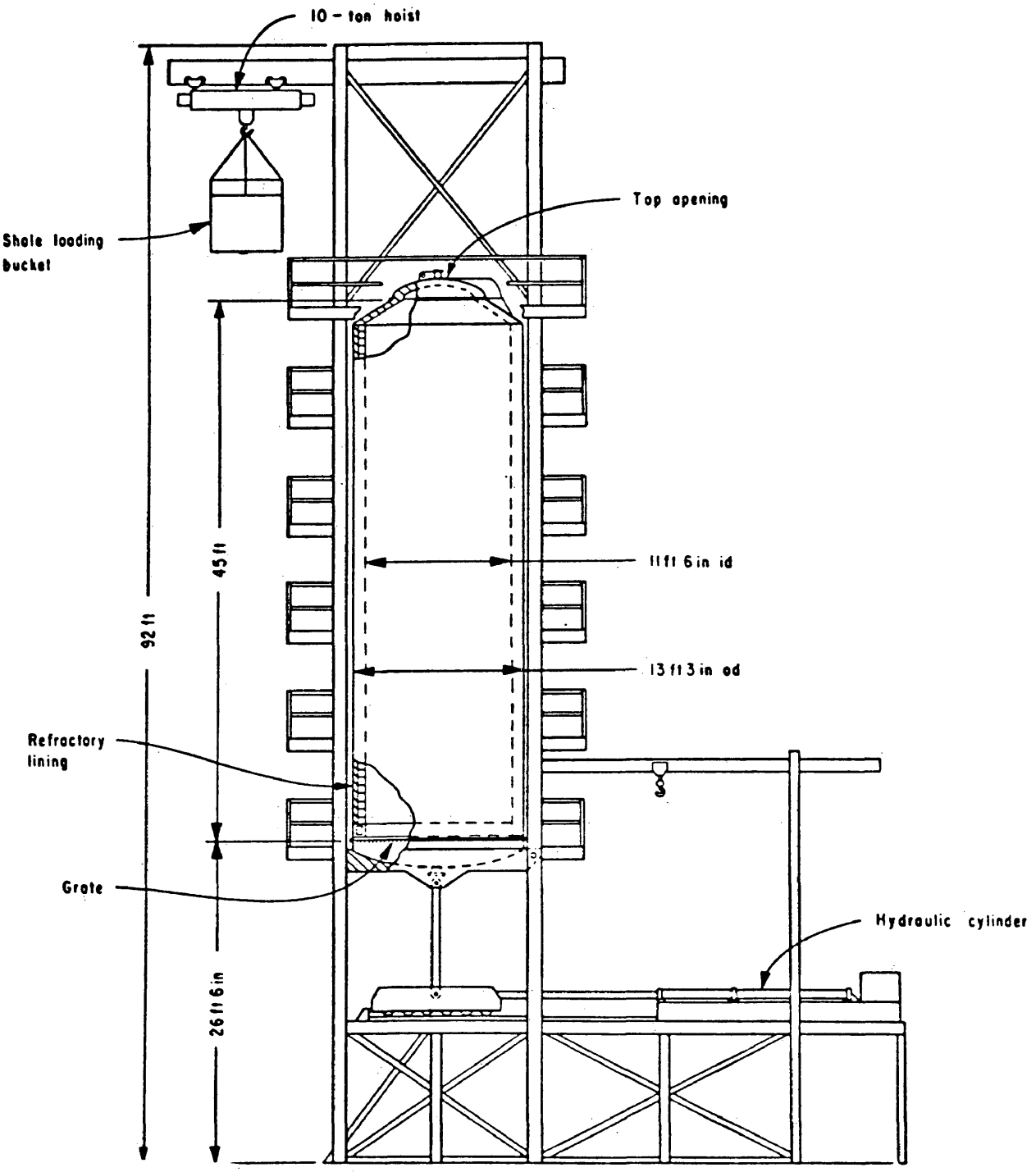


Figure 11. L.E.T.C. 150-ton Retort (From L.E.T.C. Technical Department)

ferent rates and burn at different temperatures. A maximum efficiency in oil recovery may be accomplished by a better understanding of controlling variables, such as burning rate and temperature.

Further information and illustrations on the L.E.T.C. 150-Ton retort are provided in references (39) and (40).

E. Kinetics of oil shale pyrolysis

The mechanism by which the oil shale pyrolysis takes place has been investigated for many years. However, with the very complex nature of the organic matter and the lack of data on relationships between temperature, heating time, pyrolytic bitumen formation and quality and quantity of products, the unraveling of the kinetics has not been a simple matter.

First order rate equations have been employed in most of the studies on thermal decomposition of oil shale (41), (42), (43), (44), (45). The equations describe an irreversible reaction of kerogen to yield products. Johnson (44) relates the first order kinetics of kerogen decomposition to the fact that the initial stage of the decomposition of organic polymers approximately conforms to first order law. This is true for synthetic and natural polymers, and kerogen is no exception.

The possible second order effect was first suggested by Allred in 1967 (42). He indicated that the rate of kerogen decomposition depends upon the amount of soluble organic matter present in the oil shale (bitumen). This would imply that the bitumen has a solvent or catalytic action on kerogen decomposition. In spite of the various mechanisms used by several workers in the study of the kinetics of the kerogen breakdown, the results in most of the studies consistently show that:

1) the temperature dependance on the rate of decomposition is in good agreement with the Arrhenius' equation
2) the quality and quantity of liquid products depends on the time-temperature history of the liberated oil and not on the thermal history of the kerogen.
3) oil yield decreases with increasing oxygen content in the heating gas
4) optimum retorting temperature is in the neighborhood of 550^{o}C.

The application of some of these kinetic models to the experimental data from L.E.T.C. 150-Ton retort (39),(44) showed good agreement with their prediction. The first theoretical version or "base model" made to simulate conditions and processes of the forward combustion in the 150-Ton retort appeared in 1978 (46). The results showed a good

qualitative agreement between the base model and experimental results. However, quantitative agreement was not established. This is probably due to the fact that the model has been considerably simplified by a variety of assumptions.

Further work is in progress at L.E.T.C. in order to improve agreement between the predicted and the observed yields and retorting rates. This could include the incorporation of more parameters in the model.

CHAPTER IV

EXPERIMENTAL METHODS AND INSTRUMENTATION

A. SAMPLE PREPARATION

The gas chromatographic-mass spectrometric analysis of shale oil as a whole is extremely complex, primarily because of its numerous unique compounds. In addition, the optical rotation in crudes is mainly associated with the saturated compounds (47). Therefore the present study was concerned only with the saturated compounds in the highest optically active distillate cut. The basic steps involved in the sample preparation and analysis are illustrated in Figure 12 and are discussed in the following sections.

1. Vacuum distillation

A sample (600 ml) of Green River shale oil from the Laramie Energy Technical Center 150-Ton retort run 17 (retorting conditions and shale oil properties of run 17 are reported in Appendix A) was subjected to vacuum distillation. The distillation apparatus comprises a heat resistant glass assembly, interfaced to a high vacuum mechanical pump.

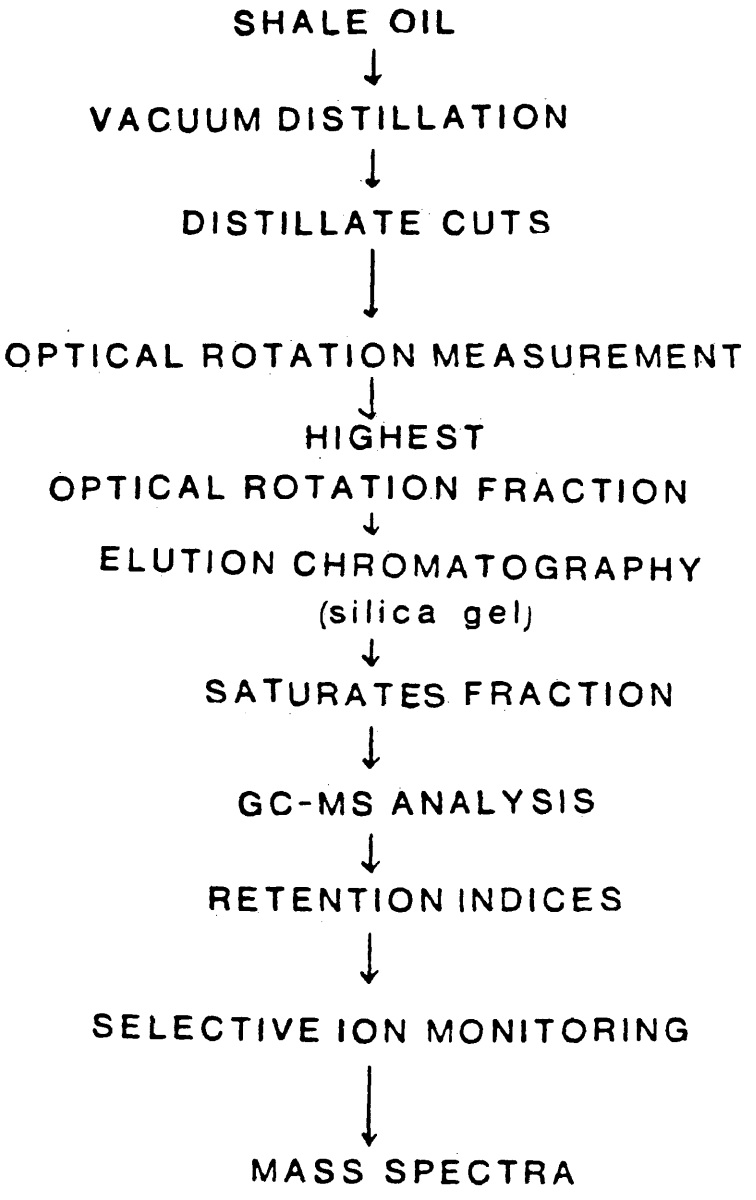


Figure 12. Sample Preparation and Analysis Scheme

A mercury manometer was connected to a vacuum adapter through a trap cooled by dry ice immersed in acetone. The pressure was maintained in the neiborhood of 0.8 mm (torr) throughout the distillation period. Narrow distillate cuts (15-20^{o}C intervals) were obtained. The distillation was stopped at about 500^{o}C , because of the occurrence of cracking, evident by the presence of light vapor and a significant increase in the pressure of the system. The conversion of the temperatures under vacuum to those at atmospheric pressure were made using a standard conversion chart.

2. Optical rotation measurement

The optical rotation measurements were made in the ORD mode with a JASCO, J-20 spectropolarimeter at The University of Wyoming (Laramie). The J-20 spectropolarimeter illumination was provided by a high intensity 450 watt xenon arc lamp with a fused quartz envelope. The instrument has very low stray light which permits the measurement of strongly absorbing samples. It also has a special device to reduce the noise level and to eliminate anomalous color effects. First, 500 mg of each distillate cut were diluted in 10 ml of cyclohexane (Philips Petroleum grade), then optical rotation was determined using a 0.1 decimeter cell at 500 nm.

3. Elution chromatography

The elution chromatographic separation technique used in this study is basically that described by Redfield (personal communication available from L.E.T.C. researchers). The procedure consists of 500 mg of sample being dissolved in cyclohexane, then placed on the head of (60-200) mesh silica gel column (2 X 105 cm) and finally eluted with purified hexane (all solvents used in this investigation were purified by distillation). Small fractions were collected. The solvent was then removed by aid of rotatory evaporator. The collection was terminated at the point when no sample could be detected in the eluant upon evaporation.

Nuclear magnetic resonance (NMR) was used to determine the presence of the aromatics in the collected sample. The results reported in Appendix B clearly indicate no evidence of the aromatics in the hexane eluted fraction.

B. COMPUTERIZED GC-MS SYSTEM

The gas chromatographic-mass spectrometric analysis were performed using a PERKIN-ELMER, SIGMA-3 gas chromatograph, a VACUUM GENERATOR (VG) Micromass 16F magnetic deflection mass spectrometer connected to a PDP-8 digital computer (Digital Equipment, Massachussetts) equipped with a 12 m X 0.20 mm Hewlett Packard fused silica capillary column coated with methyl silicone (SP 2100). Samples were introduced through an all glass injection port at constant temperature of 280°C and the column operated under temperature programming. The injection of the sample was made in the splitless mode with the injector containing quartz wool to minimize discrimination due to boiling point, polarity and functionality. The reduction of the solvent tailing caused by the diffusion of solvent molecules in the column, was achieved by backflushing the injection port for about 30 seconds.

The mass spectra from chemical ionization (methane) and electron impact (ionization potential = 70 ev) were obtained using a dual purpose ion source, which consists of a tight ion chamber that has two alternative ion exit slits. The wider slit was used when electron impact spectra was required, while the narrower slit, which allows a higher ion chamber pressure, was used for chemical ionization.

The variables subjected to changes during gas chromatographic-mass spectrometric (electron impact) runs were essentially the temperature program, sample size and flow rate. Table I lists the final conditions under which the best GC-MS data were obtained.

Carrier gas	Helium
Ionization potential	70 ev
Acceleration voltage	8000 V
Column length	12 meters
Column i.d.	0.2 mm
Column o.d.	~ 0.3 mm
No. of theoretical plates	> 36,000
Column pressure	~ 10 psi
Vacuum	5×10^{-6}
Injection port temperature	280°C
Temperature program	240 - 280°C (4.5°C/min)
Sample size	0.8 microliter
Mode of injection	Splitless

Table I : GC-MS conditions

C. DATA ACQUISITION

The signal from the mass spectrometer was converted by an A/D converter then stored on magnetic disk. The chromatograms were constructed from these data by the computer summing and plotting of the total ion current (TIC).

The selective ion monitoring was accomplished by directing the computer to trace the displayed specific ions from the spectra recorded during the chromatographic elution. The intensities of these ions were then divided by a normalization factor, which was also stored on magnetic disk.

The software also provides automatic background subtraction, multiple ions detection and highest mass plot monitoring. Thus, clever handling of the GC-MS raw data may result in extracting information about the compounds present, even when poorly separated by the gas chromatograph.

CHAPTER V

RESULTS AND DISCUSSION

A. OPTICAL ROTATION OF THE DISTILLATE FRACTIONS

The results from the measurements of optical rotation of each distillate cut (Figure 13) indicate that:

a) all optical rotation values were dextrorotatory.
b) sample 4 (280-300°C) did not show any detectable optical rotation.
c) the values of optical rotation are highest in the range of 450-485°C .

B. GC-MS ANALYSIS.

A preliminary GC-MS examination and comparison of fraction 15 (460-470°C) and 16 (470-485°C) using both mass spectra and total ion currents (Appendix C) indicate a very definite similarity between the two samples. In fact, both fractions contain practically the same compounds in different proportions. This is similar to the results published by Whitehead (48) in his study of two distillate fractions from a Nigerian petroleum. The conclusion reached from this

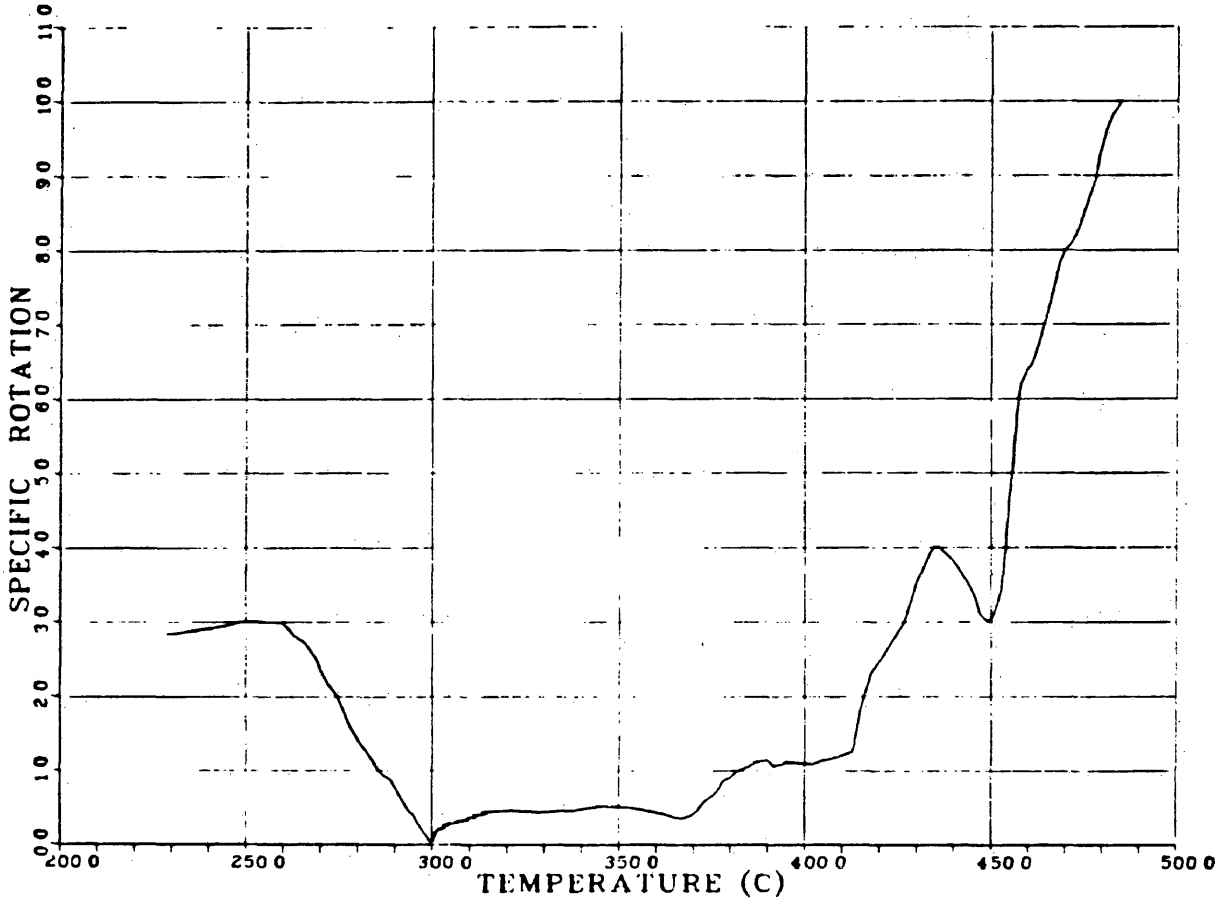


Figure 13. Optical Rotation of the Distillate Fractions Versus the Temperature of distillation

observation is that the separation of high boiling point fractions by vacuum distillation is basically not realized.

In this chapter, results from the gas chromatographic-mass spectrometric analysis of sample 16 will be discussed. The procedure basically involves:

1) the generation of chromatographic retention data
2) the selective ion monitoring for compound type recognition
3) the generation of mass spectra for individual compound identification

According to initial selective ion monitoring and mass spectra processing, most peaks were found to pertain to the major classes of alkanes (acyclic), pentacyclic triterpanes and steranes. The detailed investigation of these compounds was the major emphasis of this study.

1) Generation of retention data (Kovats indices)

The Kovats indices (49) were obtained by co-injection with a reference mixture of (n-C_{24}-C_{30}). The co-injected reference mixture permits the recognition of the normal alkanes present in the sample. The Kovats indices were then calculated from the retention times of the sample normal alkanes. This allowed for more accurate Kovats indices values. Table II summarizes the Kovats indices for the major

PEAK	KOVATS INDICES
2B	2806.02
3	2824.1
4	2875.9
6	2943.53
7	2965.88
9	3023.08
10	3055.77
12	3126.61
13	3159.68

Table II : The Kovats indices

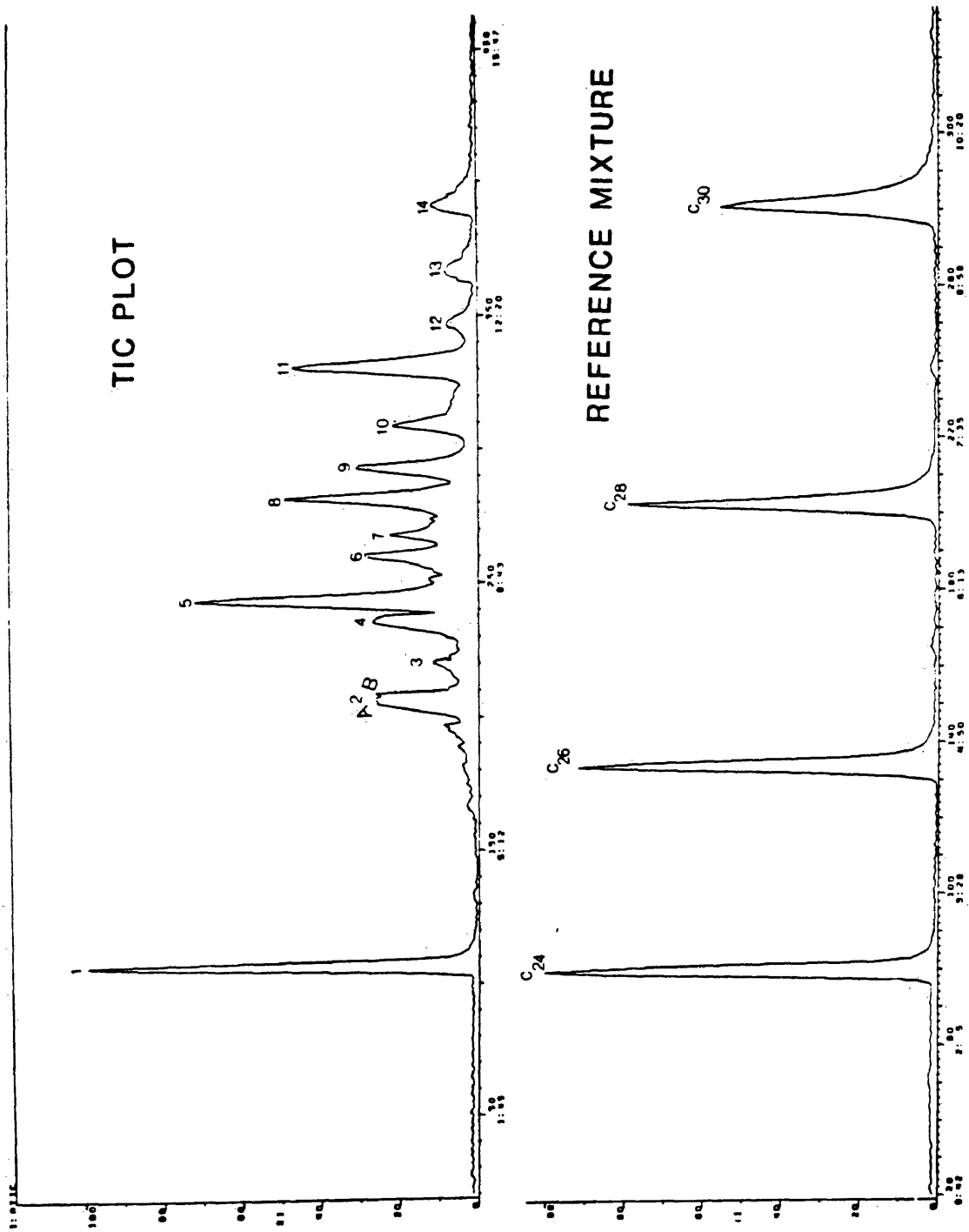


Figure 14. Total Ion Current Plot of Sample 16 and the Reference Mixture

peaks in the reconstructed chromatogram. Intercomparison and correlation of the retention data form the sample and the reference mixture reconstructed chromatograms (Figure 14) indicates that the hydrocarbon components in the sample fall basically in the carbon range of (C_{27}-C_{32}). Peak 1 is due to impurities which are usually found in routine laboratory experiments, especially when solvent removal is involved. Therefore, it was excluded from the analysis.

2) Selective ion monitoring (SIM)

Selective ion monitoring consists of simultaneous detection of one (single ion detection) or more (multiple ion detection) ions as opposed to the scan of the entire spectrum in the conventional mass spectra. In the selective ion monitoring, the mass spectrometer is used as a selective gas chromatograph detector which focuses on the ion of interest. A response is seen only when a peak containing a compound which gives rise to the monitored ion is eluted from the gas chromatograph.

Since each plot delineates the history of a single mass throughout the chromatogram, these graphs are called mass chromatograms. The mass chromatograms preserve the relative ion distribution with the peak areas representative of the intensities of the ions in the mass spectrum. Thus, the

approach of selective ion monitoring gives rapid informations about the types of compounds present in the sample. It is particularly valuable in the analysis of partially resolved components.

The success of the selective ion monitoring technique relies totally on the careful selection of the diagnostic ions. These ions must represent intense and characteristic ions in the compound-class of interest.

a) Alkanes (acyclic))

Normal, branched, and isoprenoid alkanes can be characterized by groups of peaks spaced 14 mass unit apart, corresponding to a difference of CH_2 units and each having as the most abundant species the $(C_nH_{2n+1})^+$ ions. The relative abundance of these groups of peaks decreases as their mass to charge ratio increases, due to the fact that the loss of larger radicals is more favorable in such a fragmentation. This results in a gradual decrease in intensities of peaks toward higher mass to charge ratios.

The decline of the relative abundance of fragment ions is often used to distinguish between normal and branched alkanes. Whereas normal alkanes show a gradual decline in the abundance of fragments with increasing fragment mass to charge ratio, branching causes a sharp break in the spectrum

which results from better stabilization of secondary and tertiary cation over a primary cation.

The diagnostic fragment ion selected for the characterization of alkanes in this sample are those previously reported by Hood & O'Neal (50) : $(C_5H_{11})^+$, 71; $(C_6H_{13})^+$, 85; $(C_7H_5)^+$, 99; $(C_8H_{17})^+$, 113. The points of fragmentation giving such ions in both normal alkanes and regular isoprenoid alkanes are shown in Figure 15.

The mass chromatograms of these ions along with the total ion current plot are presented in Figure 16. The occurrence of these ions in high abundance indicates that there are compounds present in the sample which yield this specific ion upon fragmentation. The coincidence of these selected ions with the same peaks in the total ion current plot reinforces their diagnostic power, and indicates that the corresponding peaks have a strong alkane characteristic. It can be concluded, at this stage, that there is no evidence of the regular isoprenoid alkane structure (isoprene units linked together head to tail) in the major peaks which normally give unusually intense ions at m/q 113 (51).

b) Steranes

A typical sterane structure is shown in Figure 17 and comprises three fused six-membered rings linked to a five-

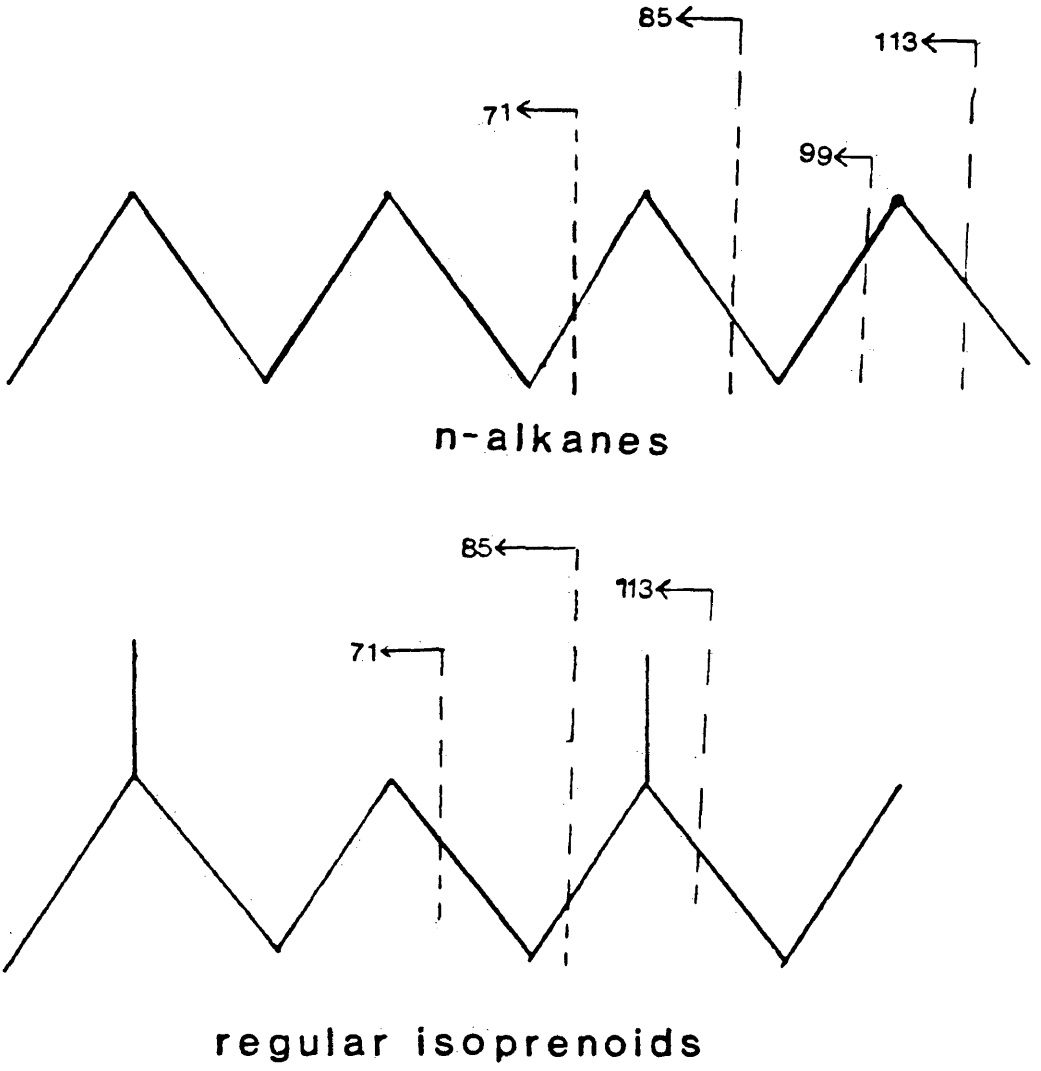


Figure 15. Fragmentation Points in Normal Alkanes and Regular Isoprenoids

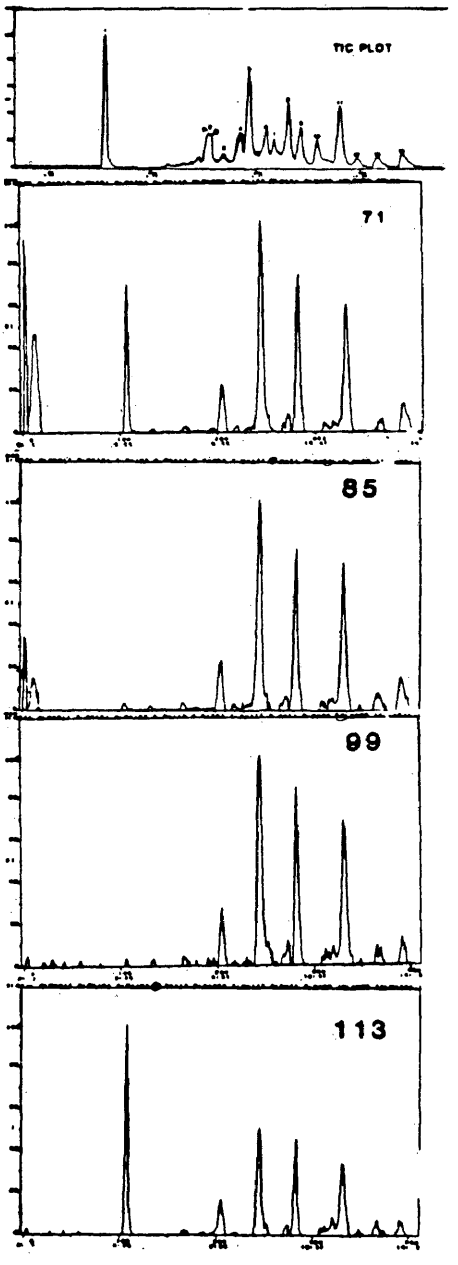


Figure 16. Total Ion Current and Selected Diagnostic Ions of Alkanes Plots

member ring. Joined to this nucleus are two angular methyl groups at C-10 and C-13, and a side chain at C-17. This polycyclic structure, upon fragmentation, can give rise to primary, secondary and tertiary cationic species, of which the latter is clearly most favored.

The most diagnostically important fragment ion of steranes occurs at m/q 217. Several mechanisms leading to this fragment ion involving different bond fissions and various hydrogen transfers have been suggested (52), (53). However, extensive deuterium labeling experiments (54) have revealed the precise course of this fragmentation, and indicates that the process giving m/q 217 in steranes occurs predominantly from the cleavage of the D ring with single hydrogen transfer. The most important source of the migrating hydrogen atom is at C-14 as illustrated in Figure 18. The mass chromatogram of the sterane characteristic fragment ion m/q 217 and the total ion chromatogram are presented in Figure 19. This figure clearly indicates the presence of structures that yield m/q 217 in considerable concentration.

c) Pentacyclic triterpanes

Triterpanes are a very important group of cyclic isoprenoid containing six isoprene units. They are mainly pentacyclic systems made of five fused six-membered rings or

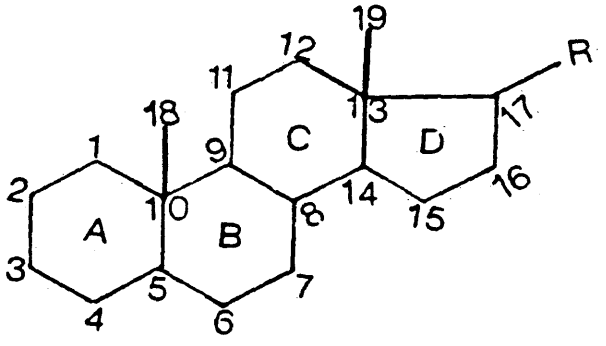


Figure 17. Numbering and Lettering in a Typical Sterane Structure

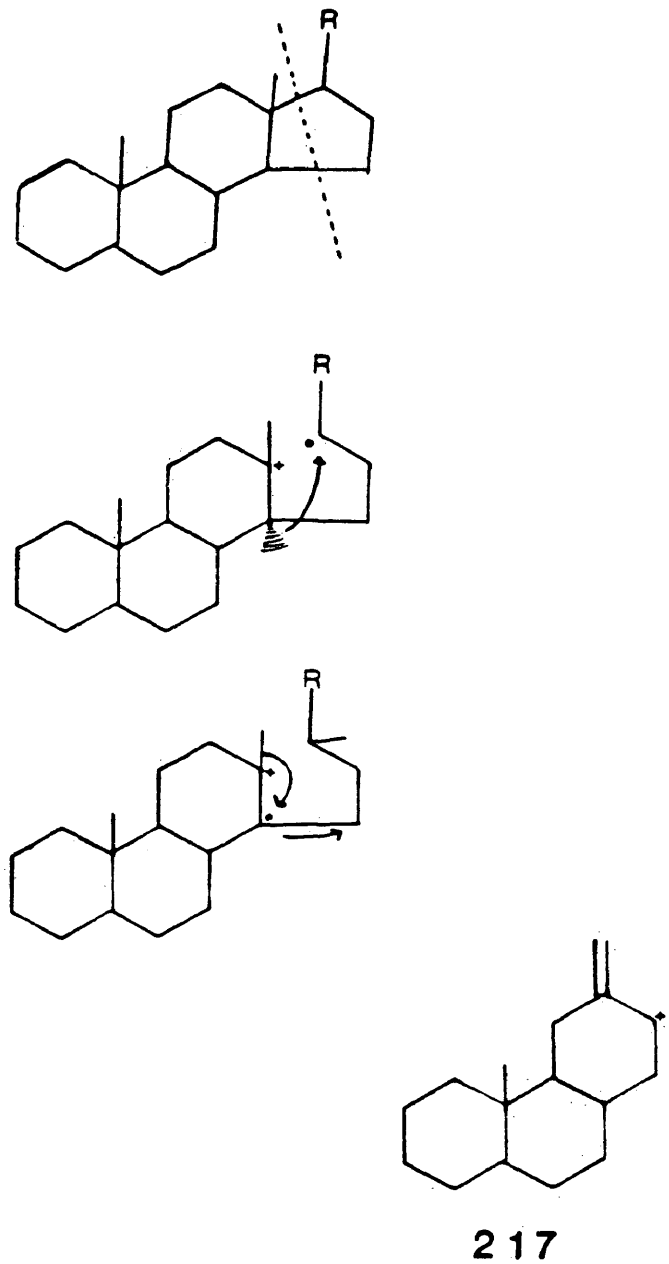


Figure 18. Possible Mechanism for the Formation of the Fragment Ion m/q 217 in Steranes (54)

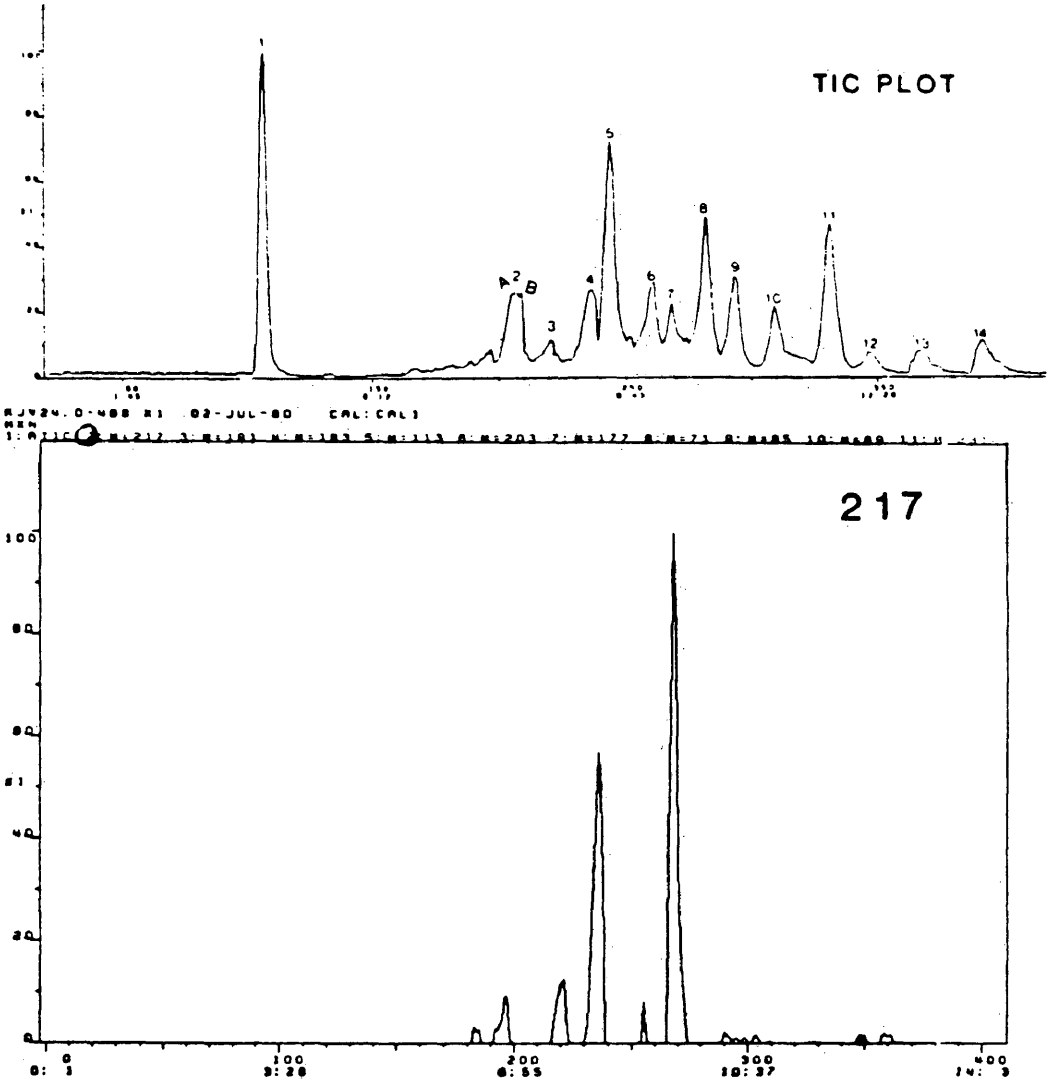


Figure 19. The Total Ion Current and the Diagnostic Ion of Steranes Plots

of four six-membered rings and one five-membered ring, and normally contain thirty carbon atoms (Figure 20). Pentacyclic triterpanes series are known to give a prominent peak at m/q 191 (55). The occurrence of ion 191 in high abundance in triterpanes is due to a contribution from several fragmentations routes, depending on the triterpane present. The fragmentation sequence usually involves a rupture at two positions in the C ring as shown by the dotted lines in Figure 21, followed by a subsequent hydrogen transfer leading to a series of m/q 191 fragment species of A-B and D-E ring systems.

The total ion current, the diagnostic fragment m/q 191 and the mass ion m/q 370 mass chromatograms are shown in Figure 22. The occurrence of m/q 191 ion in high abundance indicates strong evidence of the presence of pentacyclic triterpanes in the sample. The display of the specific molecular ion m/q 370 provides further information on the triterpane found in the partially resolved peak 2.

d) Summary of the selective ion monitoring technique

The selective ion monitoring technique instantly provides information on specific classes or homologous series and their relative distribution in the sample. The scaling involved can also be a useful tracer in estimating the rela-

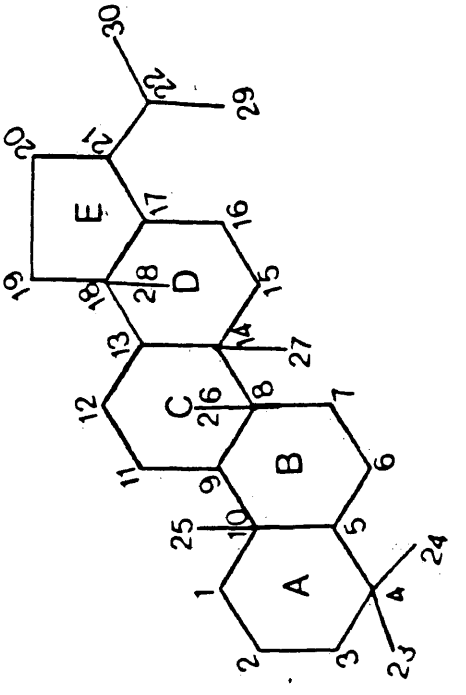


Figure 20. Lettering and Numbering in a Typical Triterpane Structure

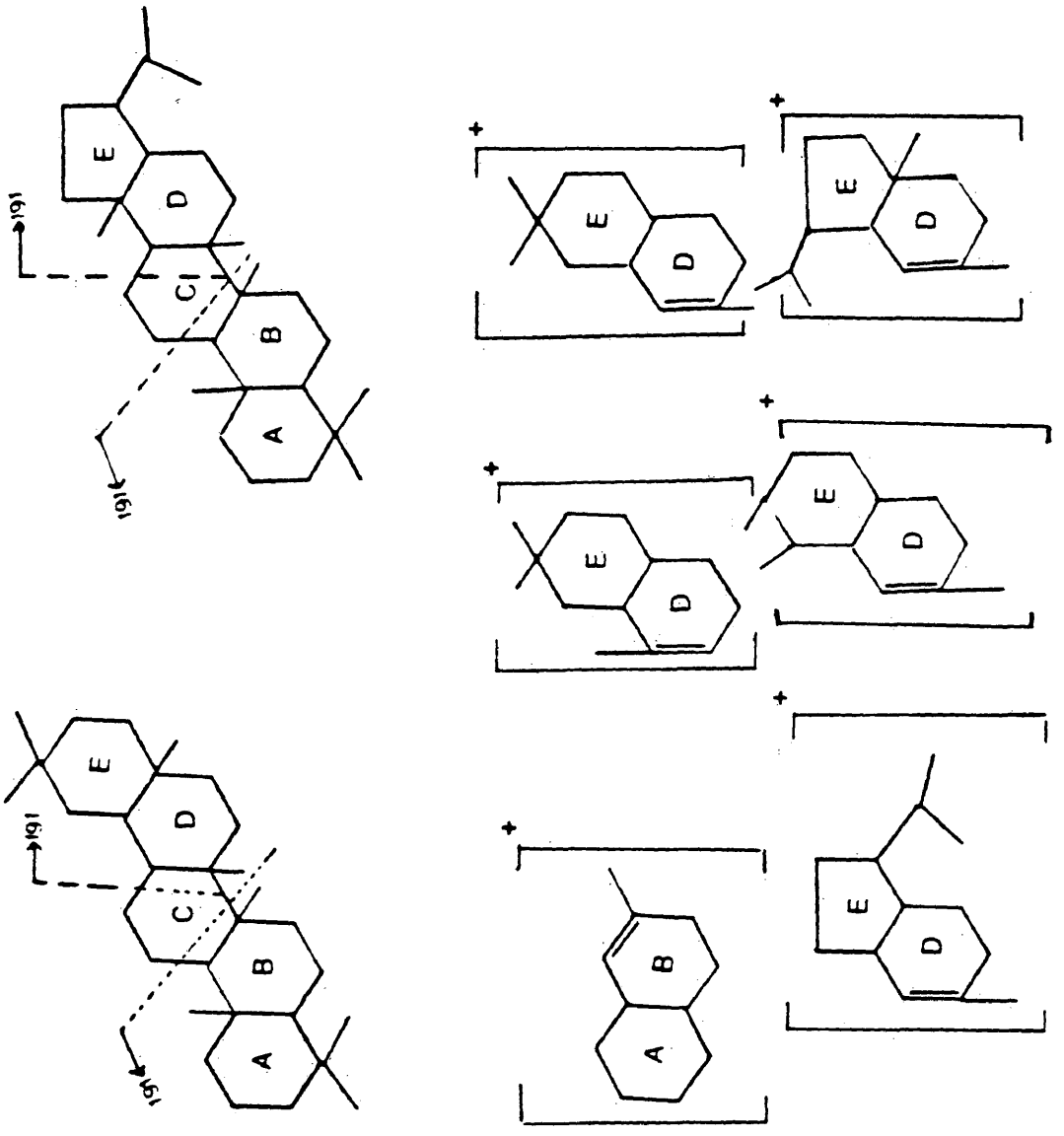


Figure 21. Fragment Ion m/q 191 from Common Pentacyclic Triterpanes (32)

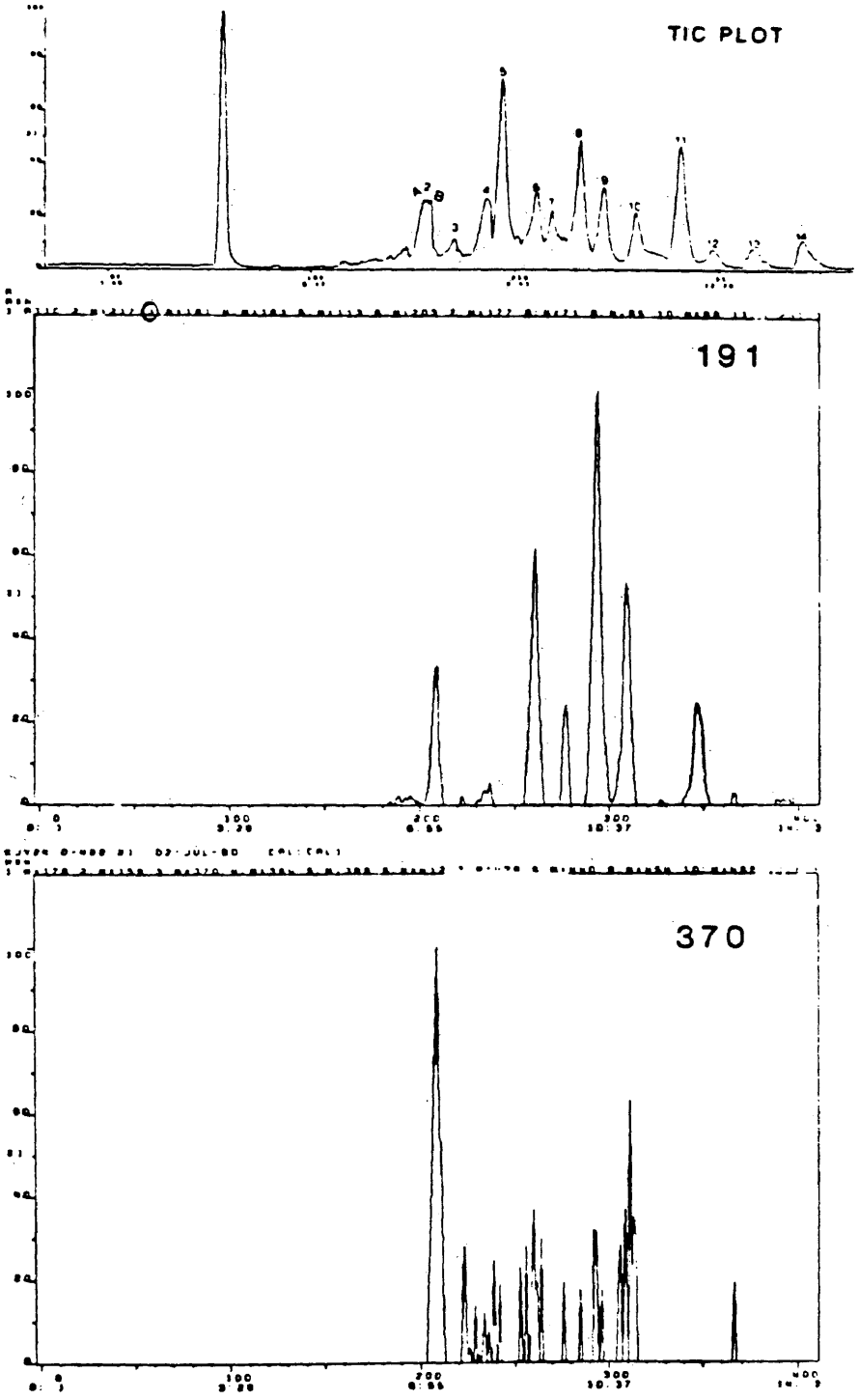


Figure 22. Total Ion Current and the Diagnostic Fragment Ion of Pentacyclic Triterpanes Plots

tive abundance of components of a common diagnostic fragment ion. The SIM plot also offers more accurate retention data than the total ion current plot and may reveal the presence of undetected components.

Considering the fact that the displayed ions are diagnostic of the compound type discussed, the SIM technique suggests that peaks 5, 8, 11, 13 and 14 are alkanes, peaks 3, 4 and 7 are steranes, peaks 6, 9, 10 and 12 are triterpanes and peak 2 consists of unresolved triterpane and alkane. The preliminary display of the mass spectra of the scans in the unresolved peak 2 indicates that the triterpane character increases in the peak as the retention time increases, thus suggesting that portion A of peak 2 is an alkane and portion B a triterpane. The separation of these two compounds was later realized using a Hewlett Packard gas chromatograph, with flame ionization detector and with the same capillary column used in the GC-MS runs (Appendix D). The relatively poor resolution obtained in the GC-MS system arises probably from the fact that the VG 16F Micromass spectrometer is not totally set up for capillary columns.

3) Mass spectra

The mass spectra presented in this investigation are standard histograms using mass to charge ratio versus intensity. For clarity, structurally insignificant ions of very low intensity (less than 5 percent of the base peak) are not reported in the spectrum, and the very low intensity significant ions are enhanced by multiplication by a factor of 5. In this section, the mass spectrum of each gas chromatographic peak will be individually discussed.

a) Alkanes

The poor chromatographic separation of compounds in peak 2 did not permit a deconvoluted spectrum of component 2A to be recorded, as shown in Figure 23. The spectrum clearly shows fragment ions fitting both triterpanes and alkanes structures. As mentioned in the previous section, portion A of peak 2 is assumed to be an alkane. The retention time of this alkane corresponds very closely to that of the $n\text{-}C_{28}H_{58}$ of the co-injected standard reference mixture. Thus, component A is tentatively identified as n-octacosane ($n\text{-}C_{28}H_{58}$).

Components labeled 5, 8, 11 and 14 produce nearly identical mass spectral fragmentation patterns and are undoubtedly homologs having the same basic alkane skeleton,

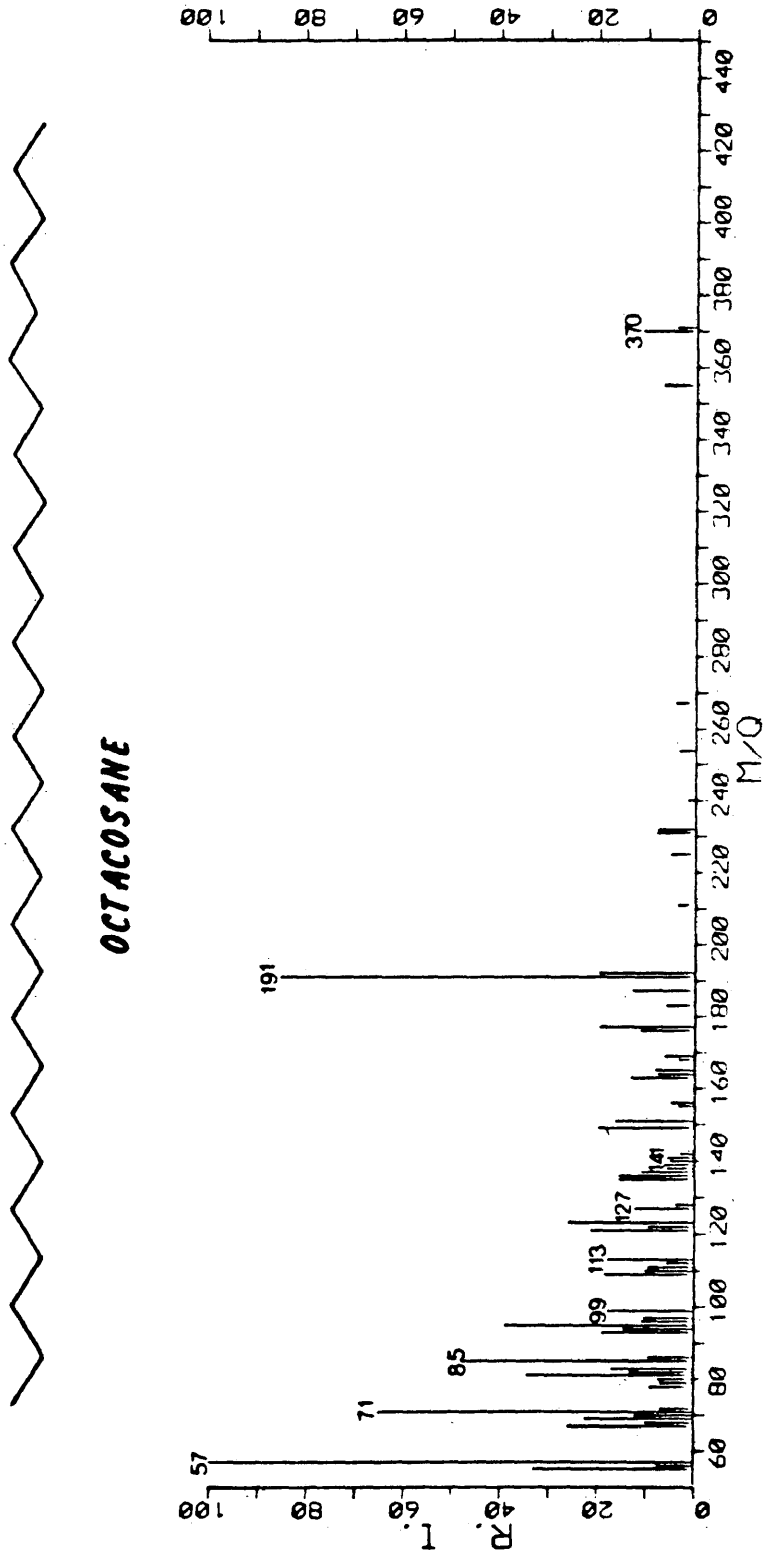


Figure 23. Mass Spectrum of Peak 2A.

differing from one another only by the length of their carbon chain (Figures 24, 25, 26, 27). The smooth decrease in fragment ion intensities toward higher mass indicates the absence of branching and suggests that these alkanes have a normal structure.

Component 5 showed a weak molecular ion at m/q 408, and was identified as n-nonacosane (n-$C_{29}H_{60}$). It was not possible to record the parent ion of components 8, 11 and 14, and therefore their identification was made possible only from the comparison of their retention indices with that of the co-injected reference mixture. They are identified as n-triacontane (n-$C_{30}H_{62}$), n-hentriacontane (n-$C_{31}H_{64}$) and n-dotriacontane (n-$C_{32}H_{66}$) respectively.

The mass spectrum of component 13 (Figure 28) shows a similarity with the mass spectra of component 5, 8, 11 and 14, with the notable differences that the base peak occurs at m/q 71 instead of m/q 57, and the gradual intensity decrease with fragment ion mass increase is not observed. The compound is probably a highly branched alkane with an empirical formula of $C_{31}H_{64}$.

b) Steranes

Compounds labeled 3, 4 and 7 show fragmentation patterns analogous to those of known steranes (Figure 29) with

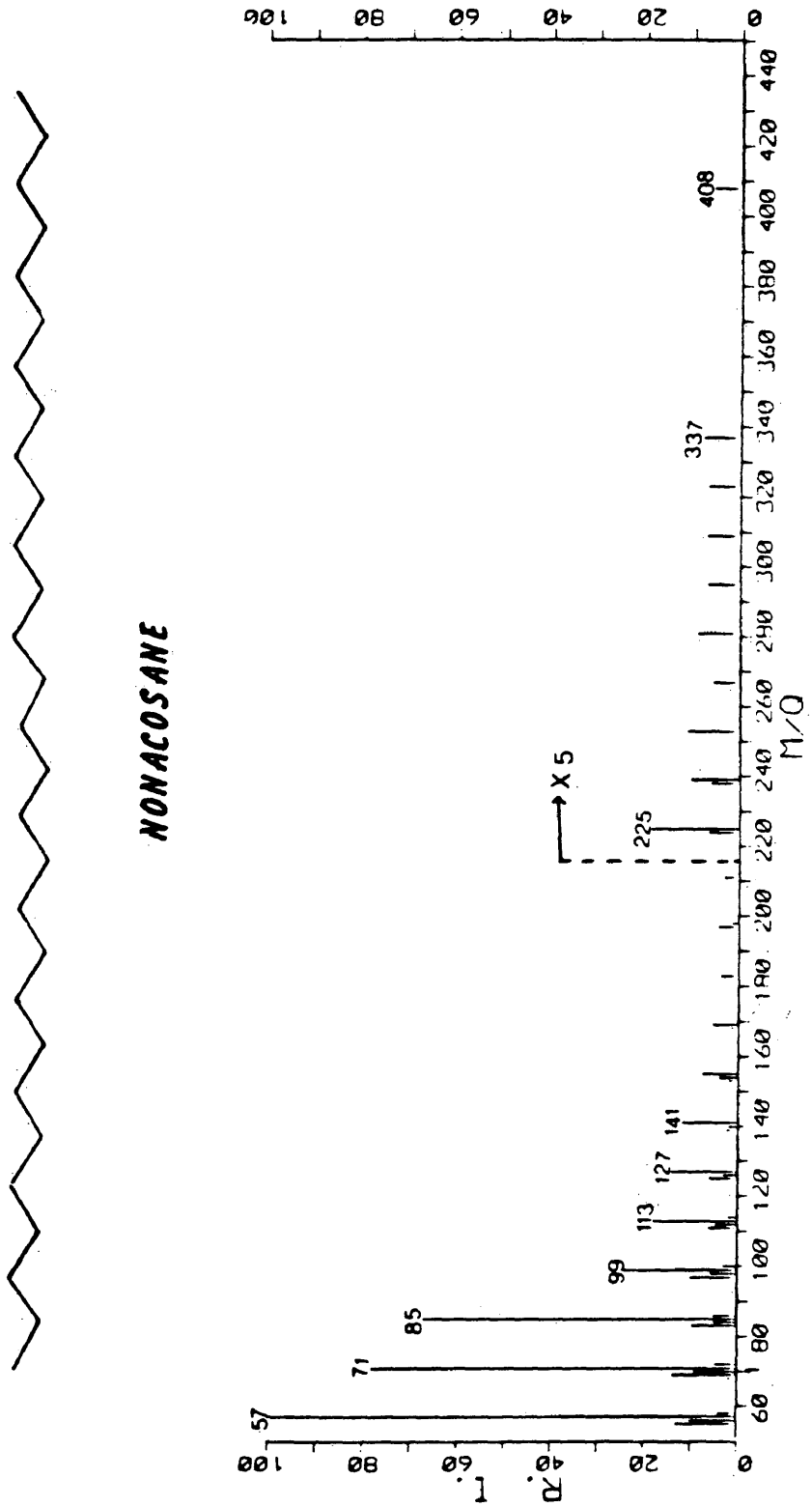


Figure 24. Mass Spectrum of Peak 5

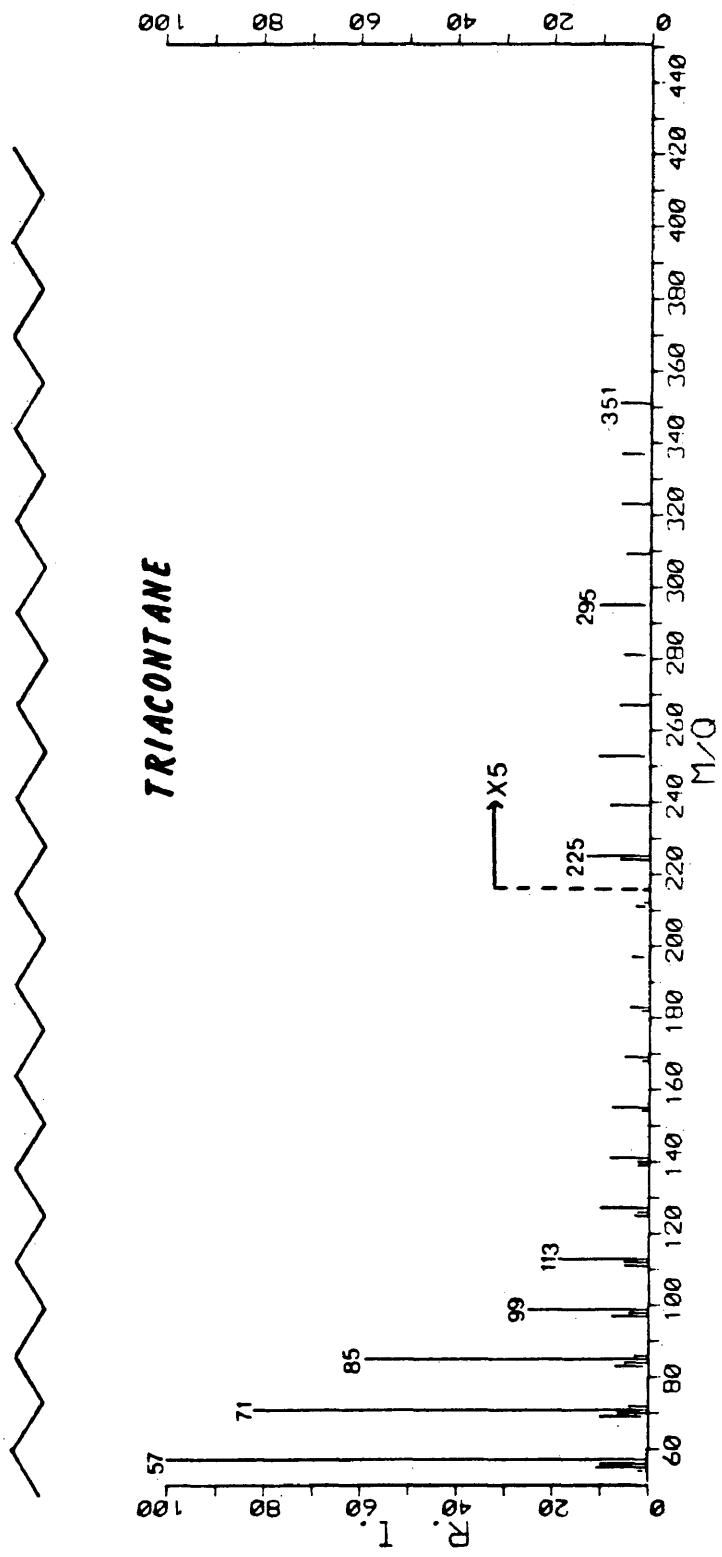


Figure 25. Mass Spectrum of Peak 8

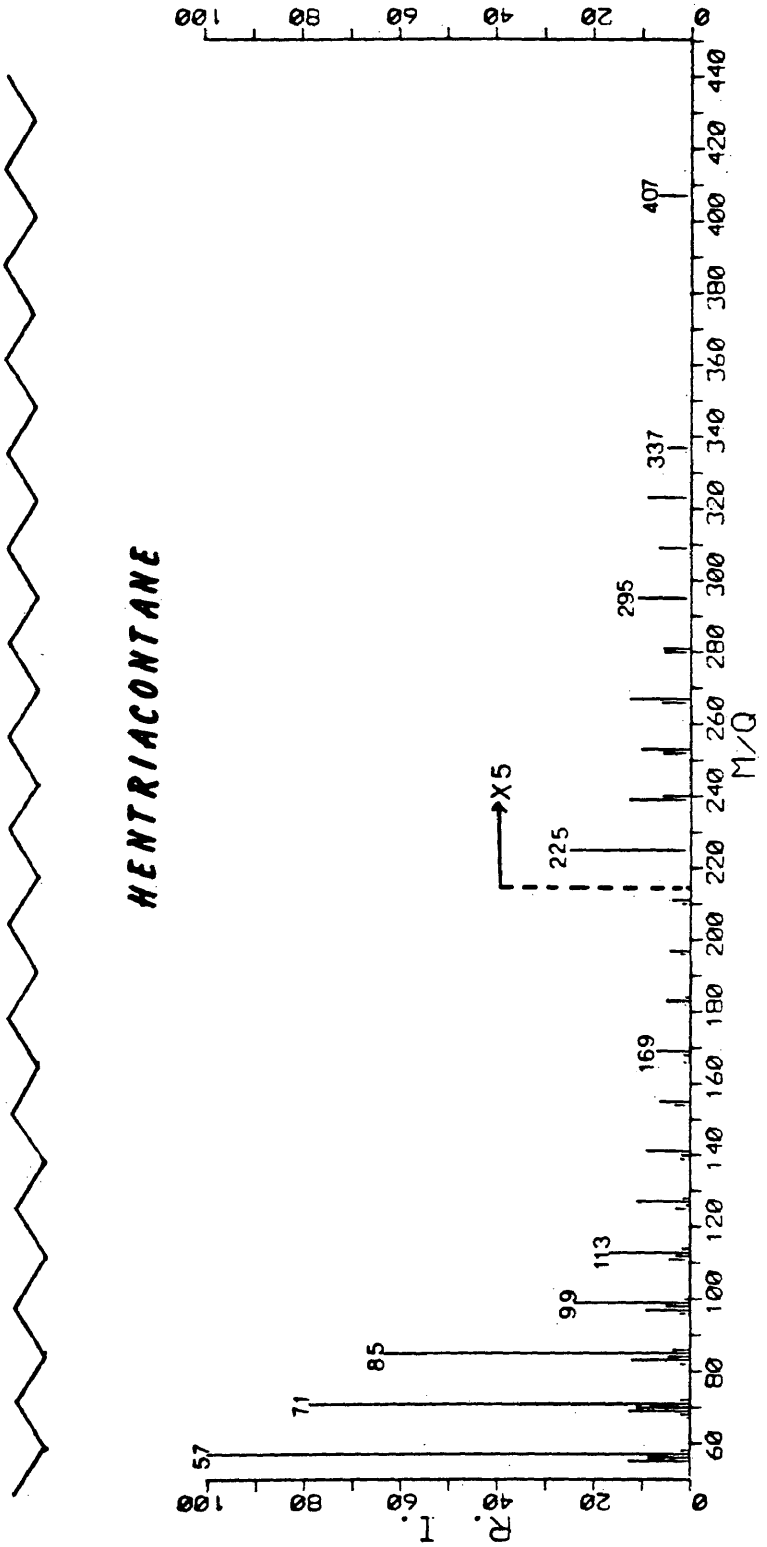


Figure 26. Mass Spectrum of Peak 11

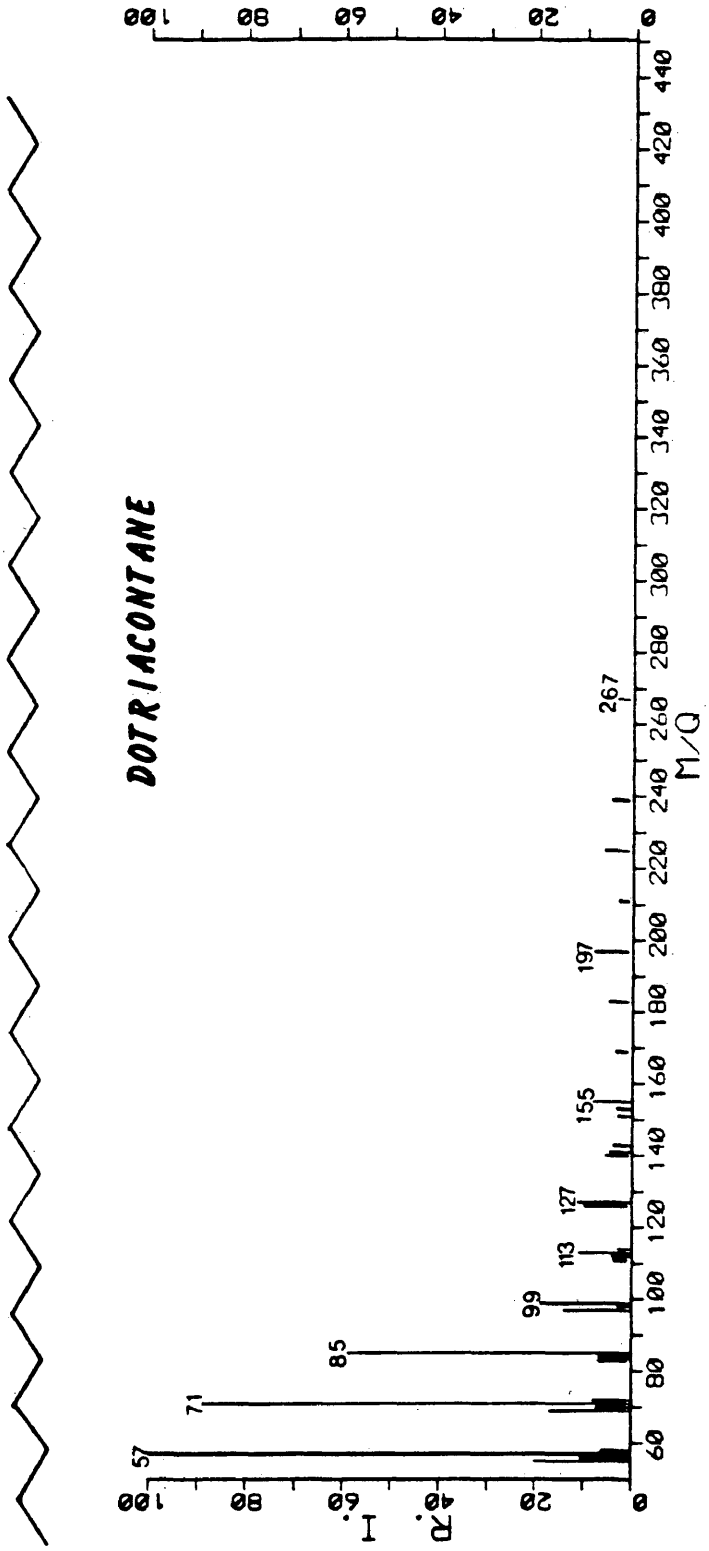


Figure 27. Mass Spectrum of Peak 14

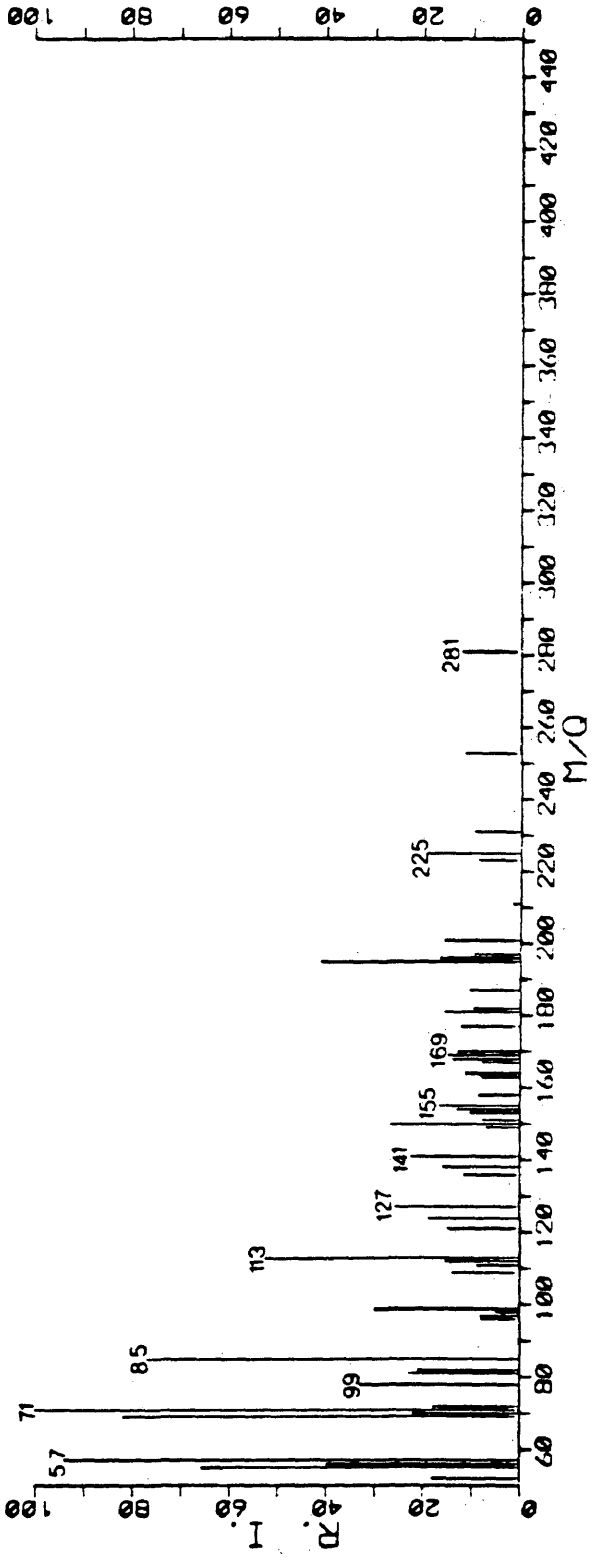


Figure 28. Mass Spectrum of Peak 13

a prominent fragment at m/q 149 + n (n=number of carbons in the side chain) with a base peak at m/q 217.

Components 3 and 4 show a similarity in their mass spectra with a molecular ion at m/q 386, suggesting two sterane isomers with an empirical formula of $C_{28}H_{50}$. The occurrence of the base peak at m/q 217 instead of 231 excludes the possibility of ring-substituted methylcholestane (56) and suggests an ergostane structure. These ergostane isomers are identified as 5β,14α-ergostane and 5α,14α-ergostane (all stereochemical specifications in this investigation refer to the configuration of the hydrogen atom) and are shown in Figures 30 and 31. The stereochemistry at C-5 and C-14 is determined from the structurally significant ions, m/q 149, m/q 151, m/q 217 and m/q 218. While the occurrence of the fragment ion m/q 217 with higher intensity than m/q 218 suggests the 14α-stereochemistry (57). The difference in the relative intensities of the m/q 149 and m/q 151 ions provides more general and reliable differentiation between the two C-5 epimers (58), (59).

It is noteworthy to add that the difference in intensities of m/q 259 formed as a consequence of the cleavage of the large side chain in both spectra, is in a good agreement with what has been recently reported by Ciccioli (60). He indicated that sterane isomers with more intense m/q 259

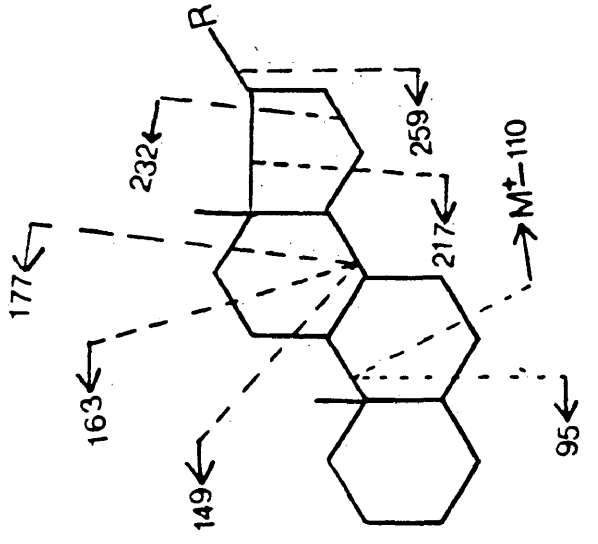


Figure 29. Typical Fragmentation in Steranes

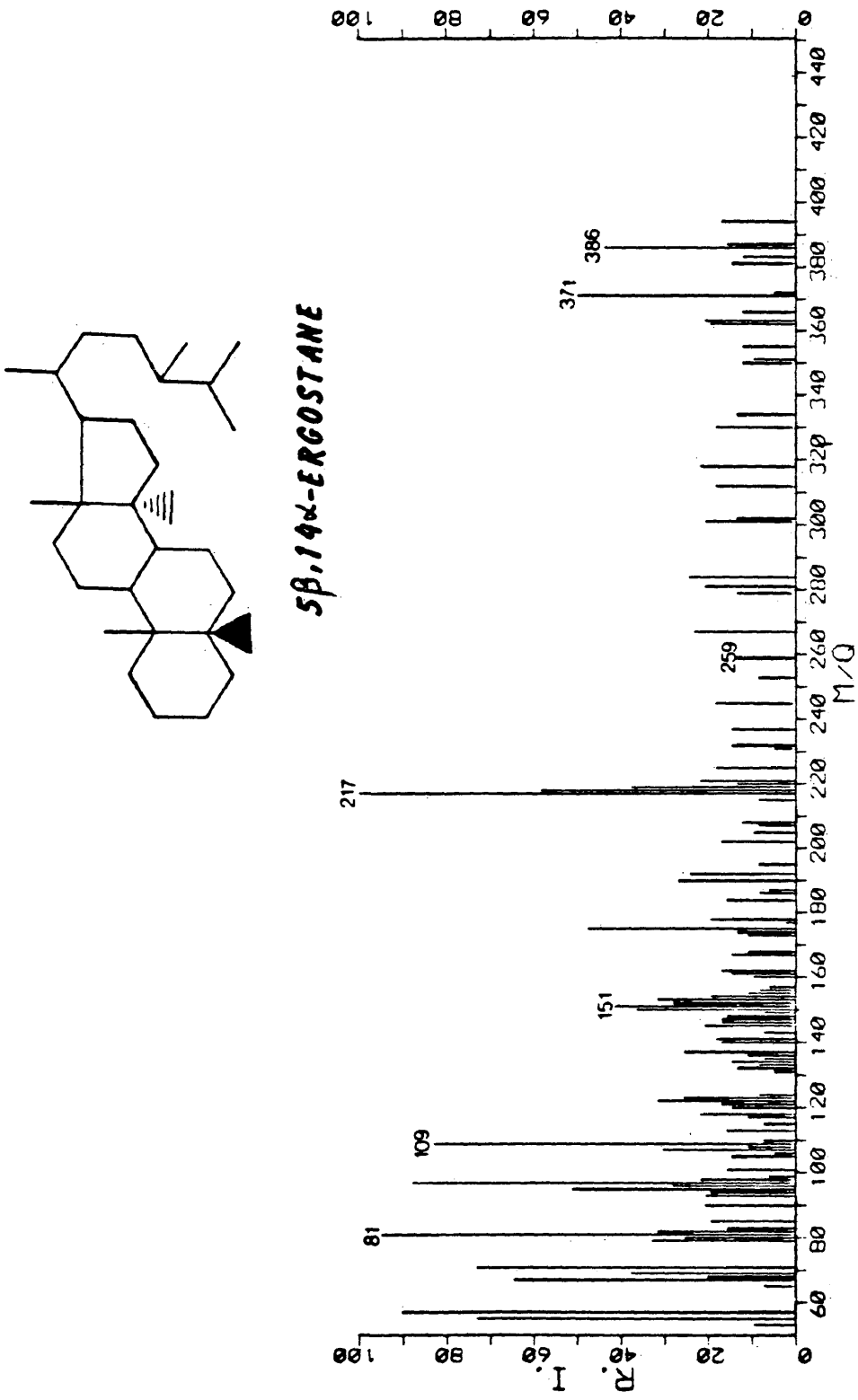


Figure 30. Mass Spectrum of Peak 3

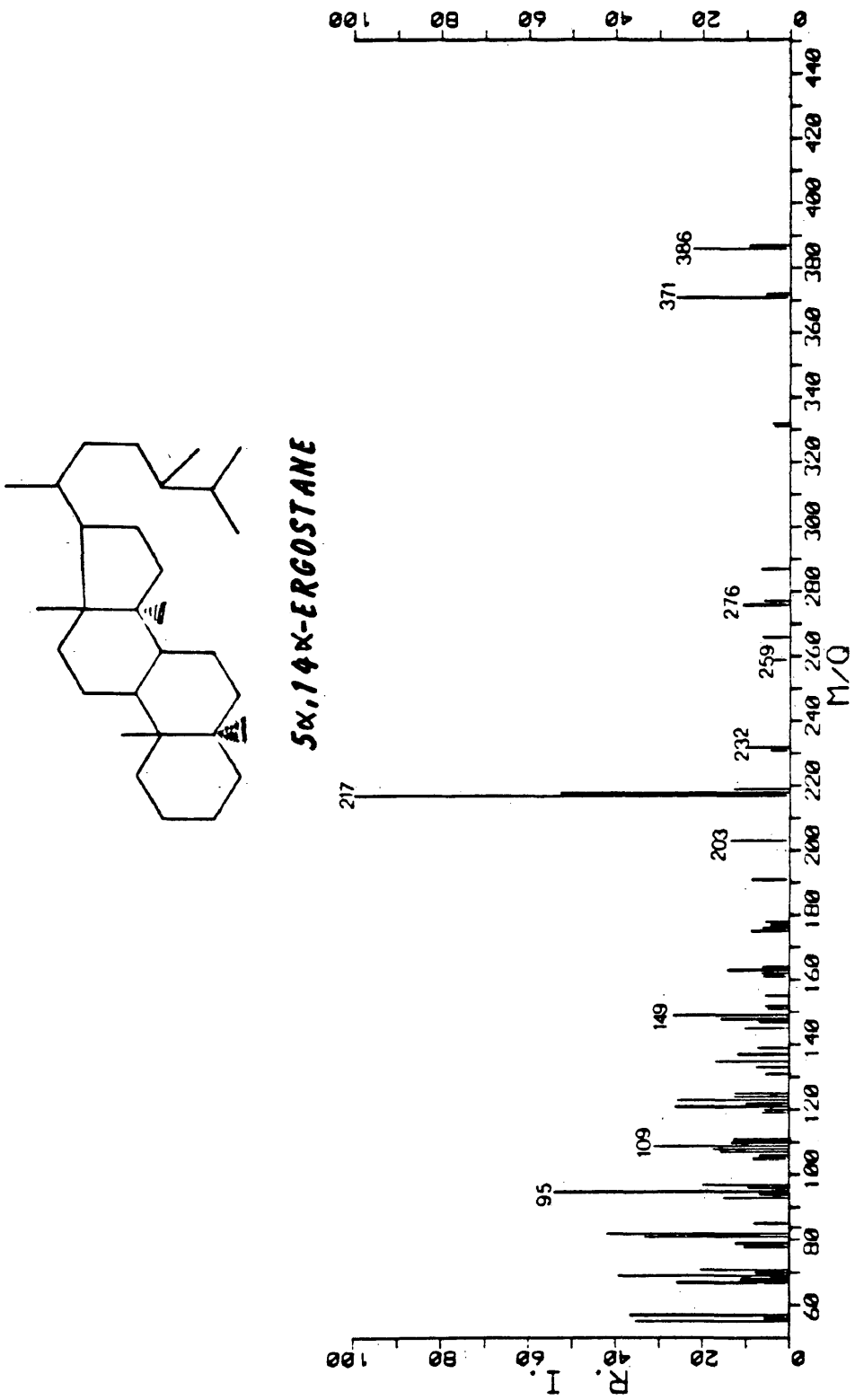


Figure 31. Mass Spectrum of Peak 4

have a shorter chromatographic retention time. Although accurate peaks area measurement were not accomplished, the ratio of the two ergostane stereoisomers appears to be in good agreement with the results published by Gallegos (59). Similarly, component labeled 7, shown in Figure 32, is identified as 5α,14α-stigmastane (sitostane). This was further confirmed by comparison with literature spectra of ergostane and stigmastane (56), (59), (61).

The spectrum of component 3 is obscured by fragment ions pertaining to contaminants of close retention time. However, there are enough similarities between the two mass spectra to assume that the minor differences are due to stereochemical changes and contamination.

c) Pentacyclic triterpanes

Components labeled 2B, 6, 9, 10 and 12 exhibit fragmentation patterns that account remarkably well for those normally observed in triterpanes (Figure 33). The mass spectrum of component 2B revealed a molecular ion at m/q 370 suggesting a saturated pentacyclic structure of $C_{27}H_{46}$ empirical formula (32). The prominent fragment ion at m/q 355 (M^{+}-15) indicates the loss of a labile methyl group. Furthermore, the abundance of the m/q 191 and other fragments involving A, B and C rings are characteristic of those

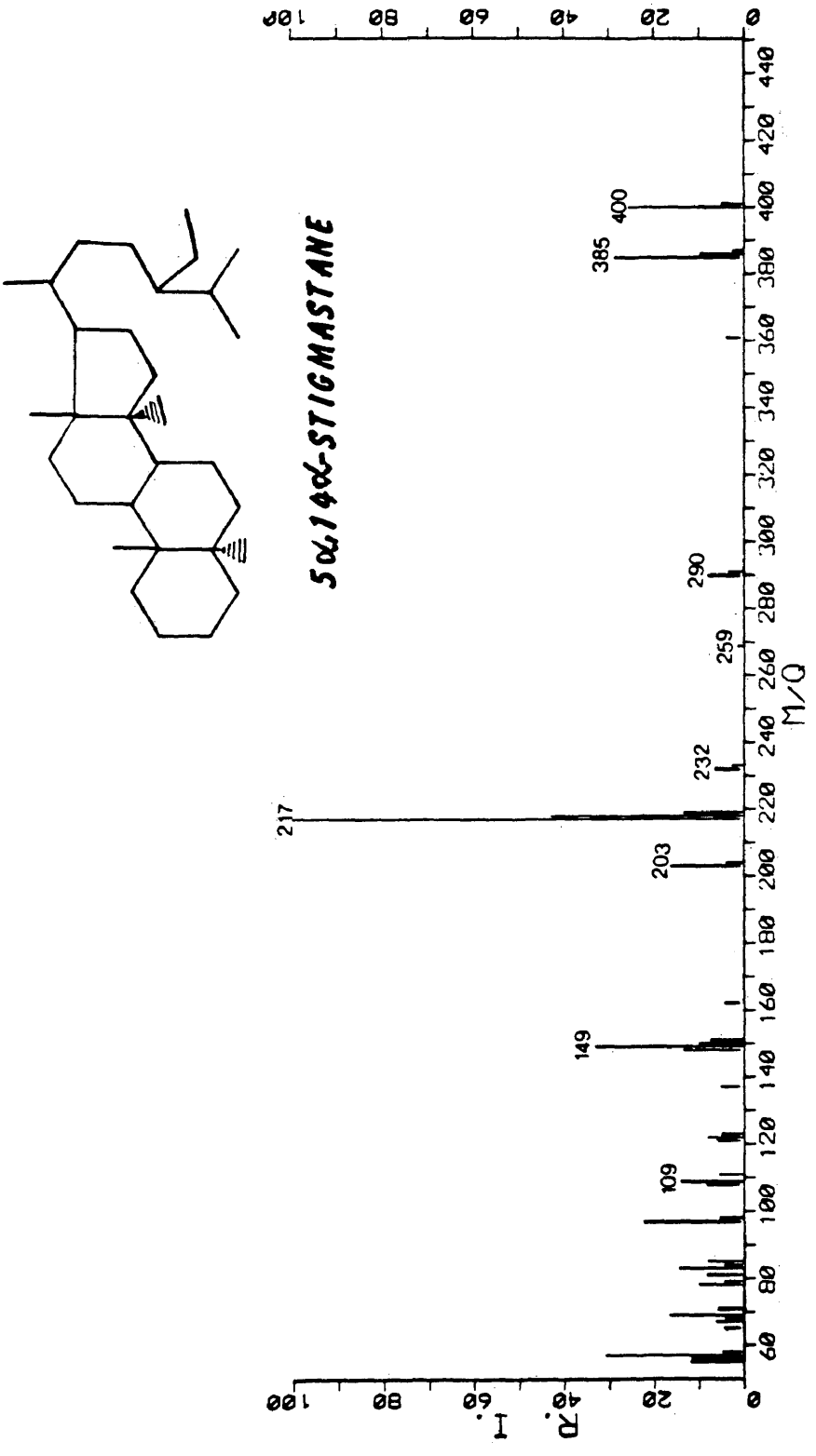


Figure 32. Mass Spectrum of Peak 7

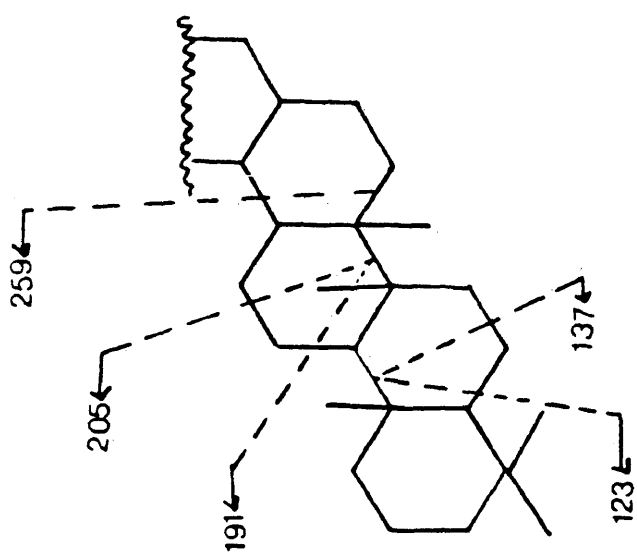


Figure 33. Typical Fragmentation in Pentacyclic Triterpanes

normally observed in triterpanes with side chain at ring E. This strongly suggests that the A, B and C portions of the molecule ring system remain intact upon methyl loss. Therefore, the methyl group is more likely to be lost from the C-18 ring juncture.

Component 2B, shown in figure 34, is identified as trisnor-17α,21β-hopane. The stereochemical specification at C-17 and C-21 epimeric centers was deduced from the diagnostic ion intensity ratio, m/q 191 to m/q (149 + 14n), where n is the number of carbons in the side chain (57), (62).

The component labeled 6 (Figure 35) is identified as nor-17α,21β-hopane on the basis of the following spectral evidence. The molecular ion at m/q 398, along with the fragment ion at m/q 369 (M^{+}-29), indicates an intact ethyl side chain and a terminal five-membered ring system. The configuration at C-17 and C-21 was deduced similarly to compound 2B.

Mass spectra of component 9 and 10 (Figures 36 and 37) show a marked resemblance and appear to be isomers that produce a molecular ion at m/q 412 which is consistent with a pentacyclic structure with an empirical formula of $C_{30}H_{52}$. The fragment at m/q 369 (M^{+}-43) indicates the presence of an isopropyl side chain and consequently a pentacyclic triterpane nucleus with a terminal five-membered ring. In addi-

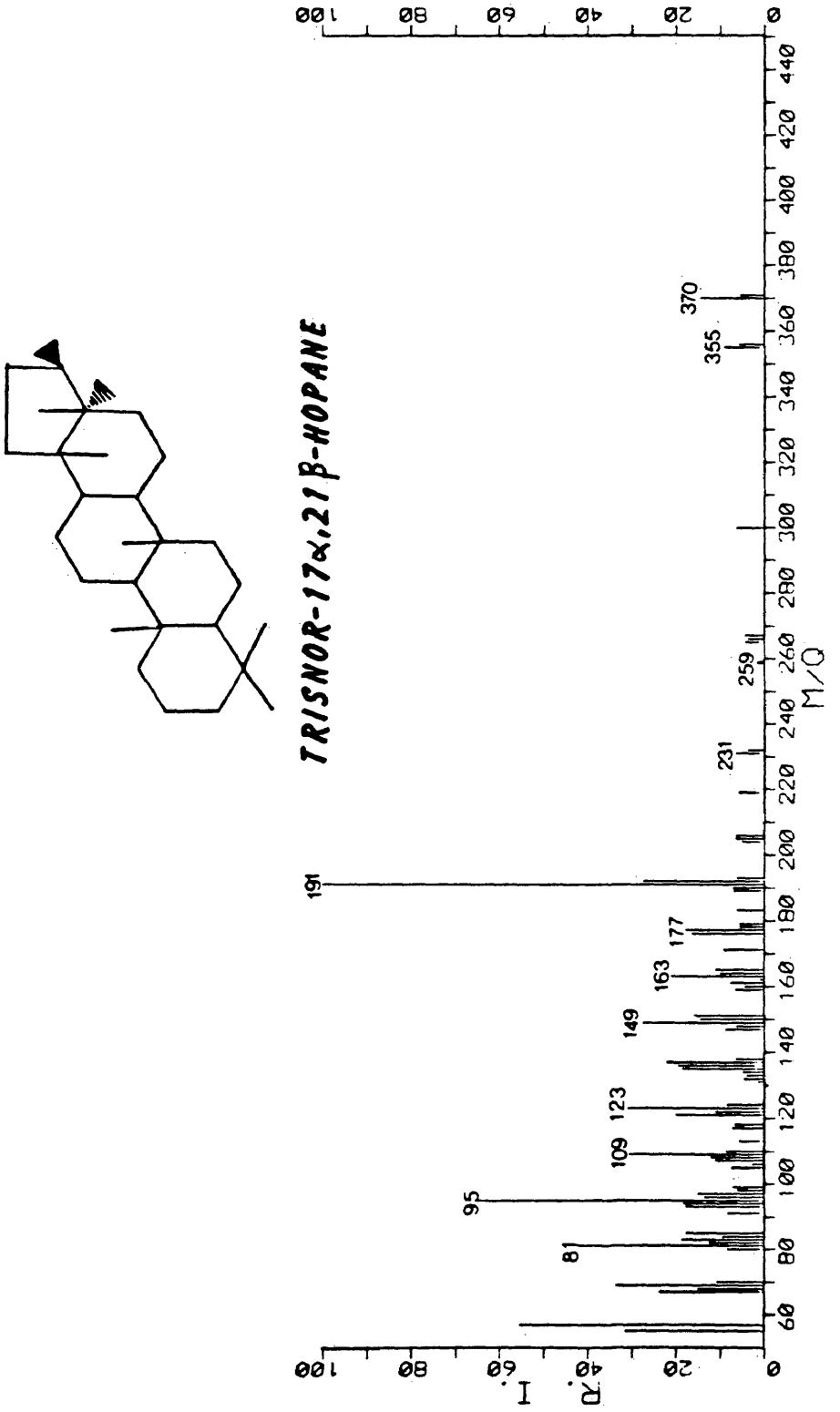


Figure 34. Mass Spectrum of Peak 2B

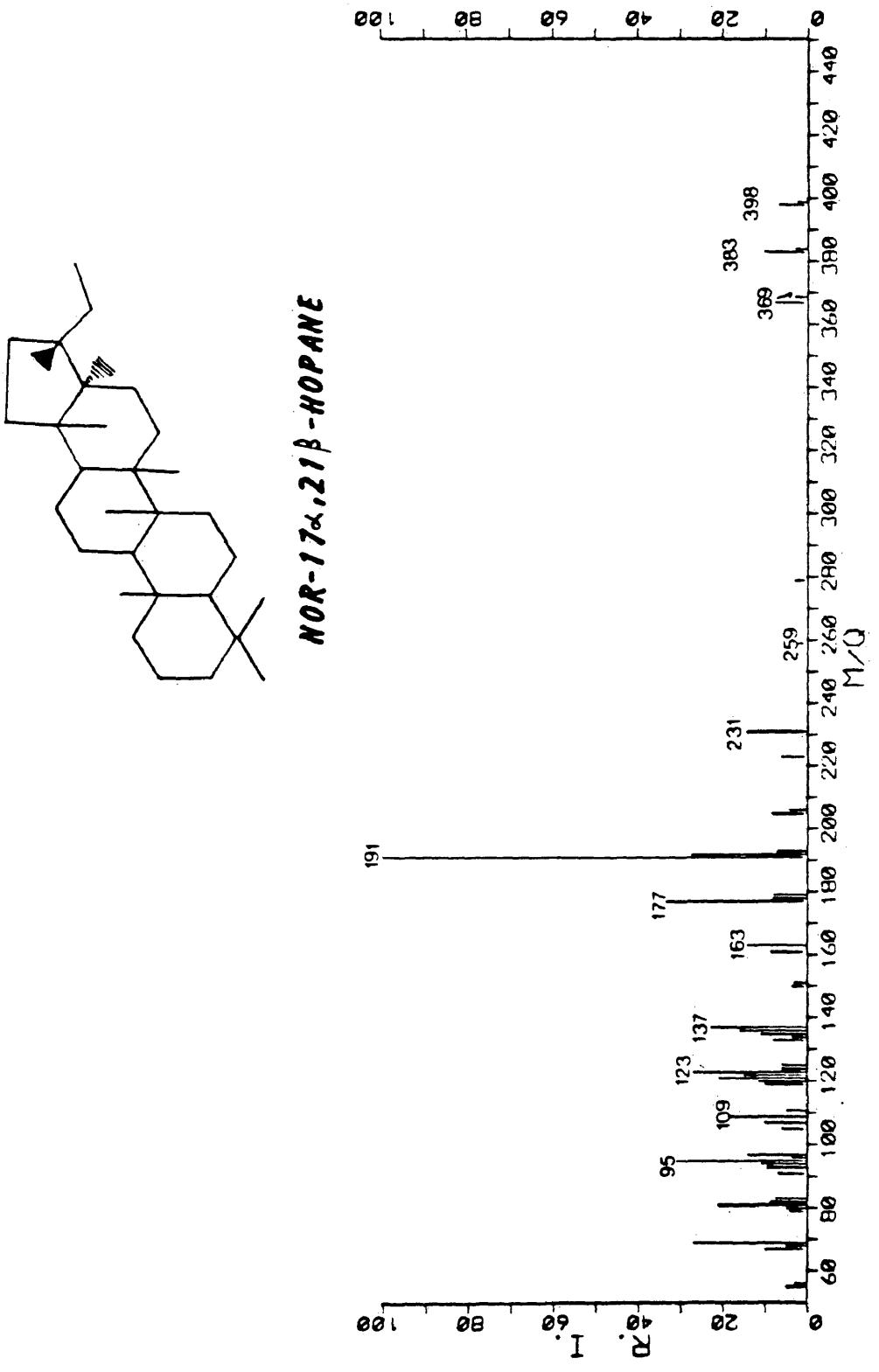


Figure 35. Mass Spectrum of Peak 6

tion, the occurrence of the base peak at m/q 191 suggests a hopane-lupane variety (63).

Components 9 and 10 are identified as two stereoisomers of hopane. The assignment of the hopane rather than lupane structure is based on comparison with literature spectra and notably that published by Henderson (64).

Marked differences may be observed between the two spectra, like the occurrence of m/q 205 and m/q 259 in relatively high intensity in the spectrum of component 10. This may be attributed to the fact that the ease of hydrogen transfer at the point of the cleavage depends on the stereochemistry at the carbon centers involved.

The configuration at C-17 epimeric center can be assigned to both isomers based on the published literature, in which it has been clearly stated that the 17β-hopanes, lying in sediments (17α-hopanes have never been found in living organisms), are thermally unstable and do not survive thermal maturation (62). Therefore, they are usually not found or are found in very low concentration in crudes, with the 17α-hopane predominant species. However, the unavailability of reliable spectra of authentic hopane isomers in the literature makes it difficult to discern with confidence a distinguishable stereochemistry to component 9 and 10. They are identified as 17α-hopane I and 17α-hopane II.

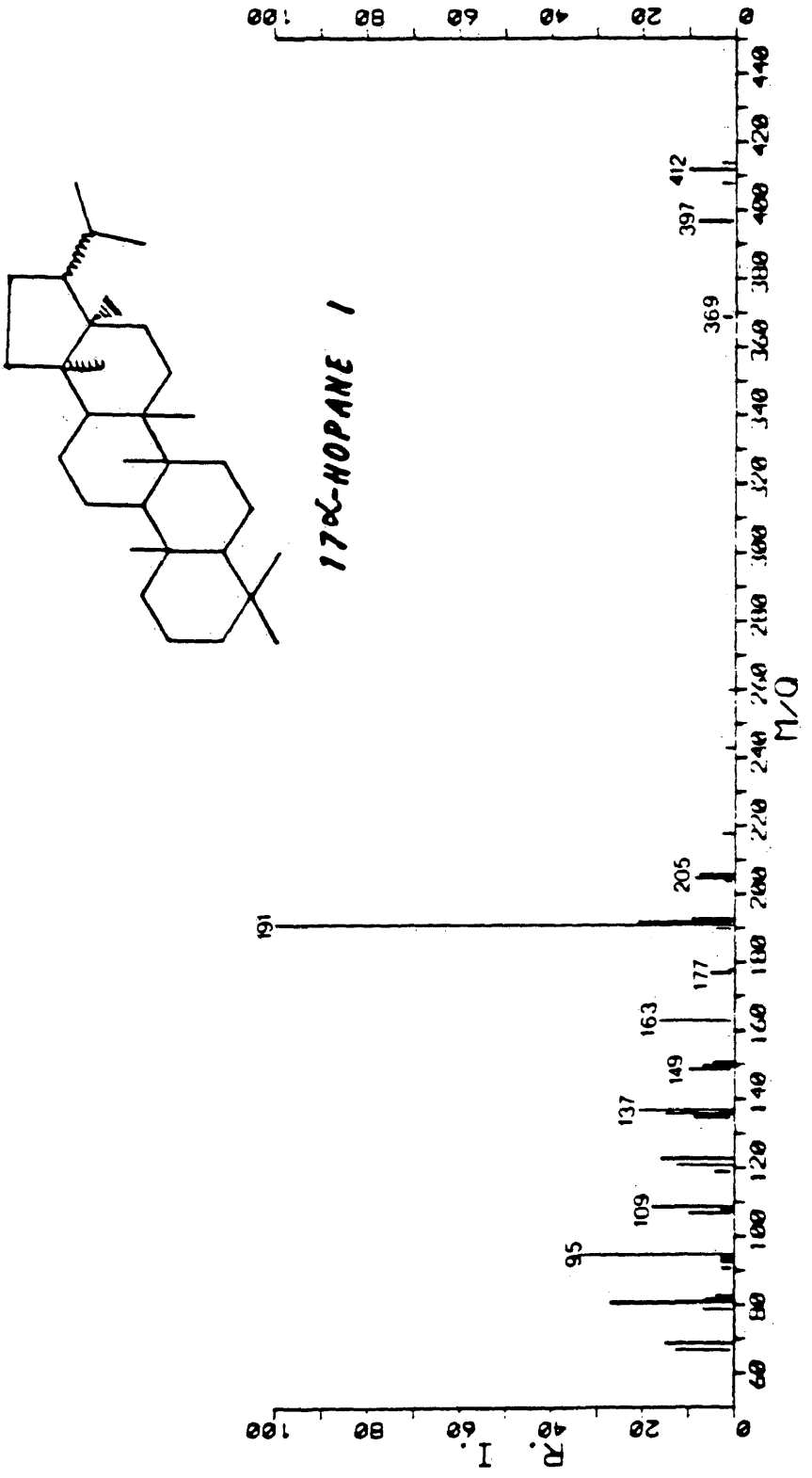


Figure 36. Mass Spectrum of Peak 9

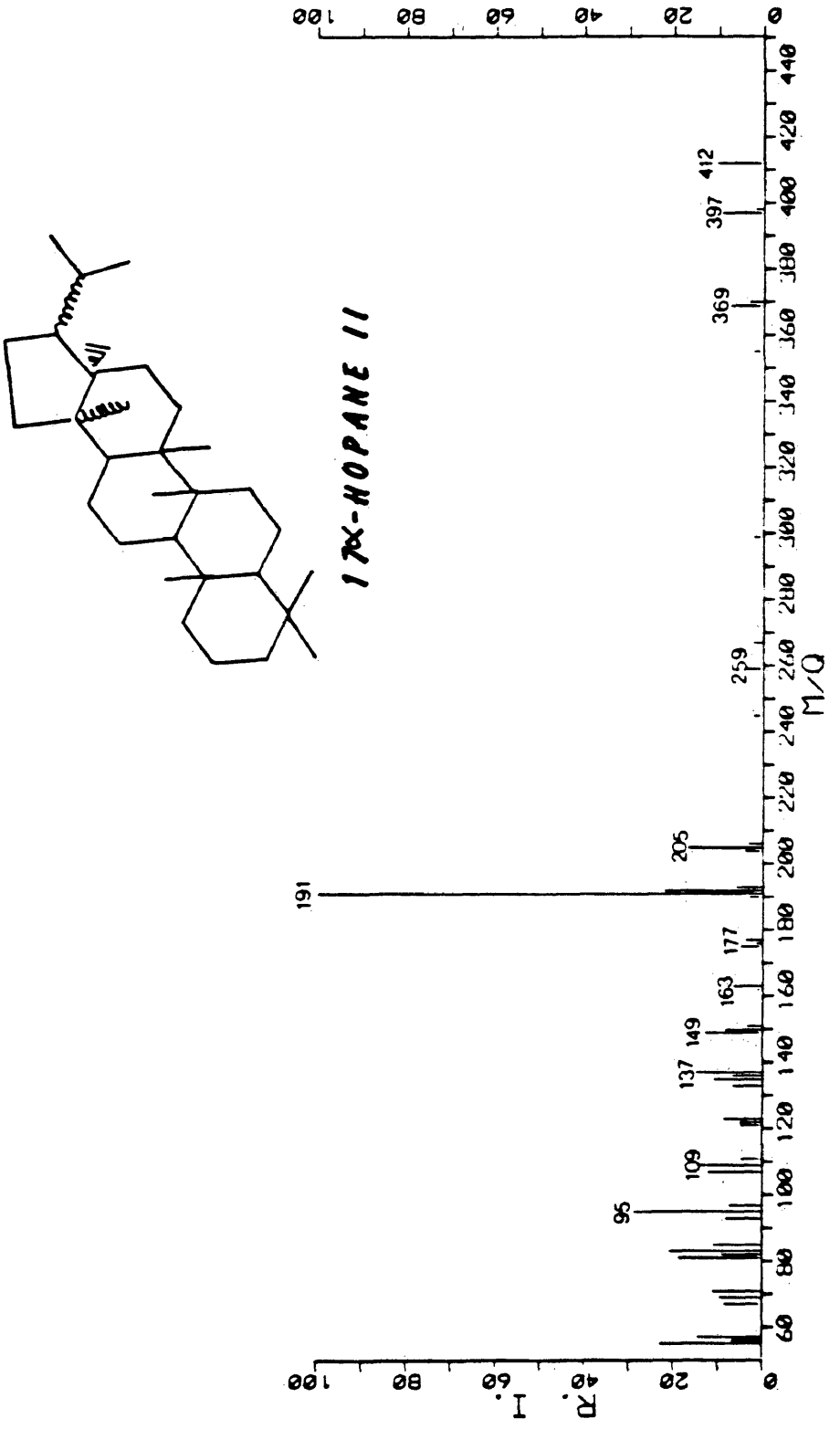


Figure 37. Mass Spectrum of Peak 10

Structural information from the mass spectrum of component 12 (Figure 38) is limited, primarily due to the absence of fragmentation in the high mass portion of the spectrum. Therefore, identification of this compound can be only tentative. From the general features of the triterpanes discussed, along with retention data, it is possible to predict that the component 12 nucleus is composed only of a six-membered ring system. This would explain the absence of the relatively small fragment ions at high mass, because of the introduction of facile competing fragmentation from both A-B and B-C moieties of the triterpane nucleus. In addition, its relatively longer retention time is compatible with such a structure (64).

Further structural specifications of component 12 arise from the presence of a prominent fragment ion at m/q 259, which indicates a methyl group at C-13 instead of the usual C-14 (57).

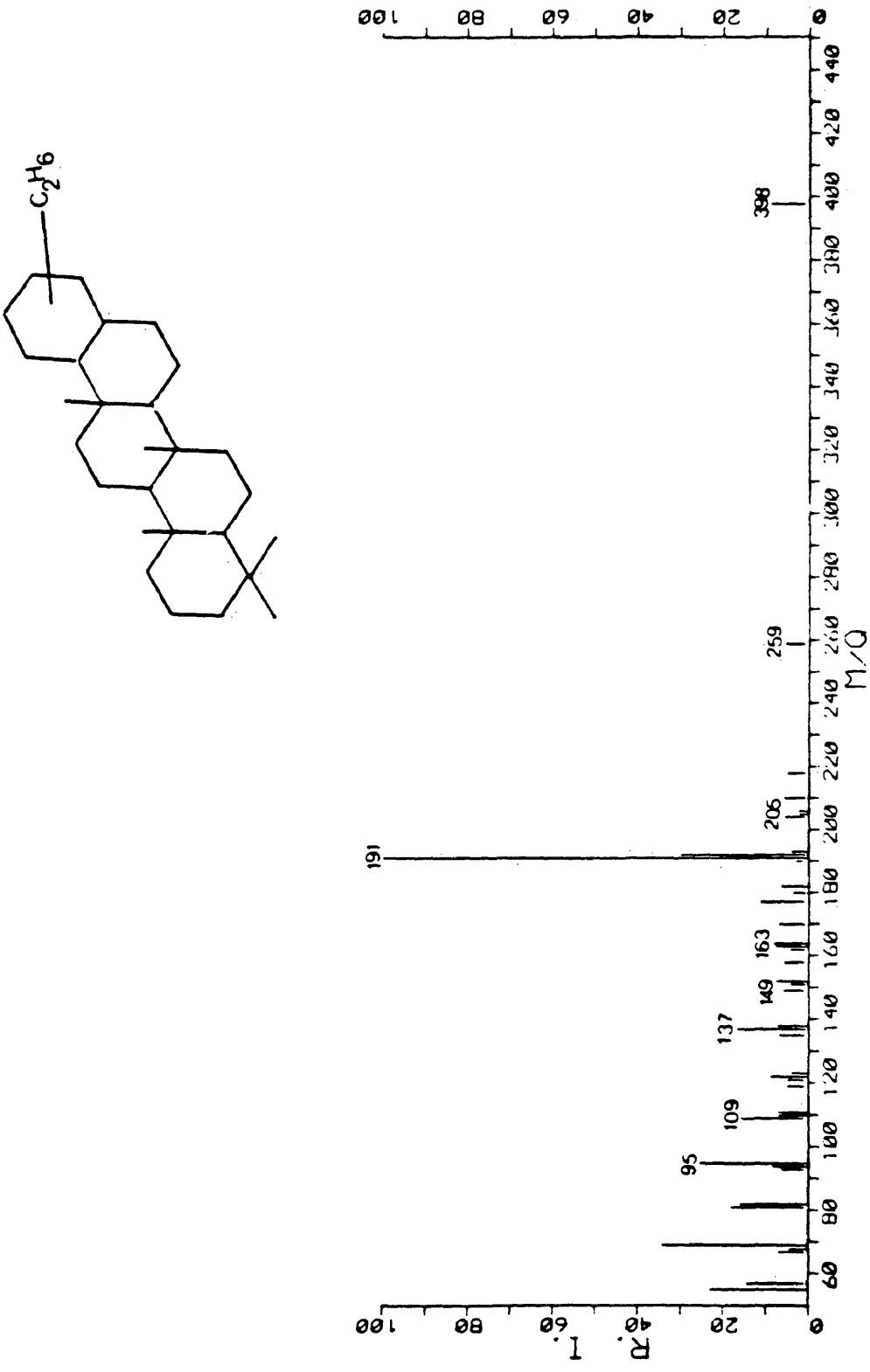


Figure 38. Mass Spectrum of Peak 12

4) Summary of identification

The collective use of chromatographic retention data, selective ion monitoring and mass spectra provide a complementary, versatile method of analyzing organic mixtures. In this investigation, twelve compounds (five normal alkanes, three steranes and four pentacyclic triterpanes) were identified (Table III) and partial structure for the two remaining major chromatographic peaks is postulated. In addition, the technique permits the recognition and the detection of compounds present in very low concentrations.

Although it is difficult to compare spectra from several investigators who have used different instruments and different conditions, the comparison of the mass spectra of the compounds identified in this investigation with literature spectra appear to be valid in most cases. For instance, the spectrum in Figure 34 is identical in almost every respect to that published by Hills & Whitehead, thirteen years ago (65).

The major disadvantage of the GC-MS technique is the fact that the absolute configuration and stereochemical specifications cannot be elucidated from the mass spectra and retention behavior alone and require the synthesis of authentic standards for confirmatory identification evidence.

It is worthwhile to add that similar GC-MS runs were performed on the benzene eluted (aromatics) and methanol eluted (polars) compounds. The resulting total ion current plots showed a broad envelope of poorly resolved peaks, analogous to that recently reported by Crowley (66).

GC PEAK	COMPOUND IDENTIFIED
2A	n - OCTACOSANE
2B	TRISNOR-17α,21β-HOPANE
3	5β,14α-ERGOSTANE
4	5α,14α-ERGOSTANE
5	n-NONACOSANE
6	NOR-17α,21β-HOPANE
7	5α,14α-STIGMASTANE
8	n-TRIACONTANE
9	17α-HOPANE I
10	17α-HOPANE II
11	n-HENTRIACONTANE
14	n-DOTRIACONTANE

Table III : Summary of identified compounds

CONCLUSION

The results of this investigation indicate that the saturated fraction of the highest optically active distillate fraction contains predominantly n-alkanes, pentacyclic triterpanes and steranes. The results agree remarkably well with what has been published on optical rotation of distillate cuts from petroleum, notably that these distillate cuts are usually dextrorotatory, the observed maximum optical rotation is in the 425-500^{o}C range, and the optical rotation is caused mainly by steranes and triterpanes in the C_{27}-C_{30} carbon range (18), (47).

Although n-alkanes do not contribute to the observed optical rotation, they were nonetheless considered in this investigation because of their diagnostic power in generating the Kovats indices. However, their presence in relatively high concentration introduced the inconvenience of column overloading, when trying to enhance the steranes and triterpanes present in very low concentration. Therefore, a suggestion for future studies is to remove n-alkanes from the saturated fraction (using, for instance, urea and thiouria adduction or molecular sieve (51), (65)) and to investigate the optically active compounds separately.

The identification of the major compounds responsible for the occurrence of optical activity in shale oil is probably not sufficient for a development of a routine-type analysis based on the optical rotation of the produced shale oil. Further work should also be accomplished in the characterization of the optically active compounds in the shale kerogen matrix. It is also helpful to know the individual contribution of each major optically active compound to the overall optical rotation. Then data correlation may be possible by comparing the relative abundance of the pyrolysis surviving optically active compounds (and consequently the temperature and optical rotation), with respect to the optically active compounds originally present in the kerogen matrix. However this technique is still subject to complications arising from the possible degradation of the shale oil and exposure of the released oil to different retorting temperatures. Such problems are not easy to overcome in a large field in-situ process.

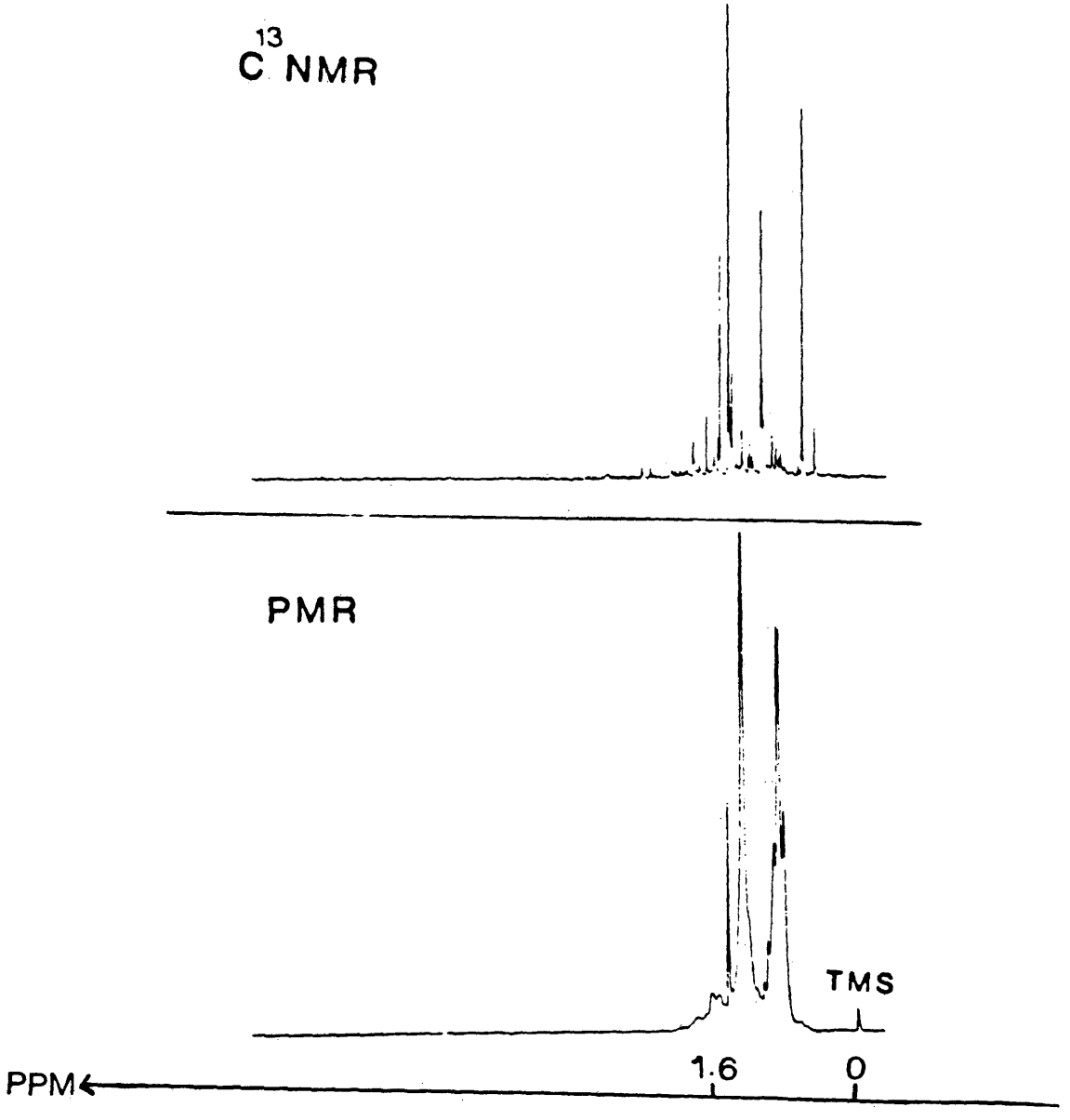
APPENDIX A : Operating conditions for retort run 17

Length of run	
including ignition	396.3 hr
excluding ignition	371.4
Air rate	5311 scfh
Steam rate	96.3 lb/hr
Average maximum bed temperature	1212 F
Retorting rate	1.287 in/hr
Shale charge	185.82 ton
Fischer Assay	26.7 gal/ton
Oil recovery	64.7 % of FA

OIL PROPERTIES

Naphta, vol pct	2.7
Light distillate, vol pct	27.3
Heavy distillate, vol pct	45.3
Residuum, vol pct	23.8
Specific gravity, 60 /60 F	0.92
Pour point, F	50
Viscosity, SUS @ 100 F	98
Hydrogen, wt pct	12.9
Nitrogen, wt pct	1.9
Sulfur, wt pct	1.2
Carbon, wt pct	84.8
Ash, wt pct	0.1

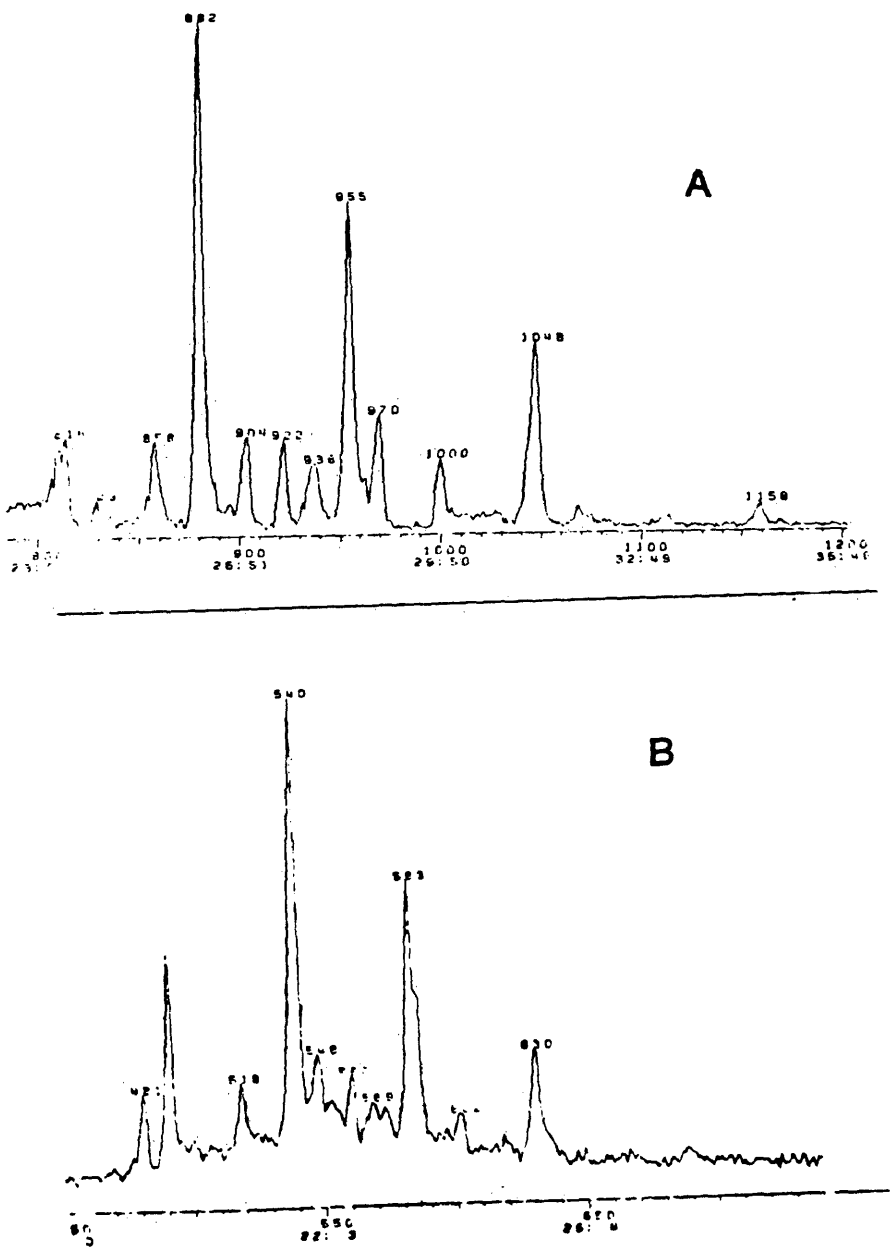
Appendix B: Nuclear Magnetic Resonance Spectra



Appendix C: 1-Total Ion Current Plot

A. Sample 16

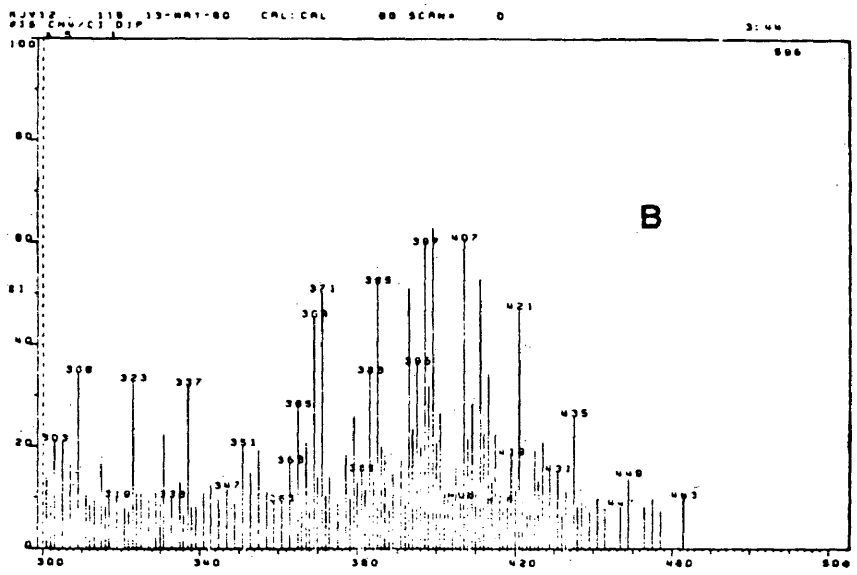
B. Sample 15

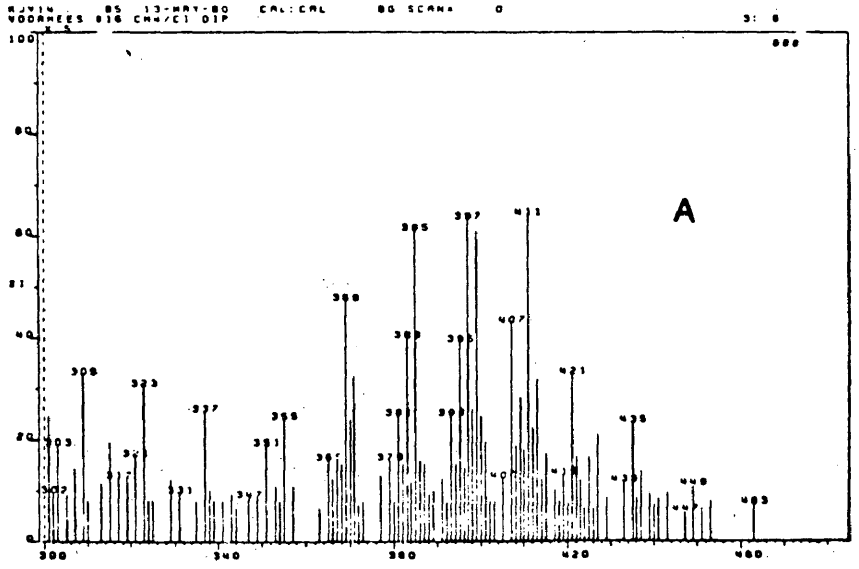


2. Mass Spectra (C.I.)

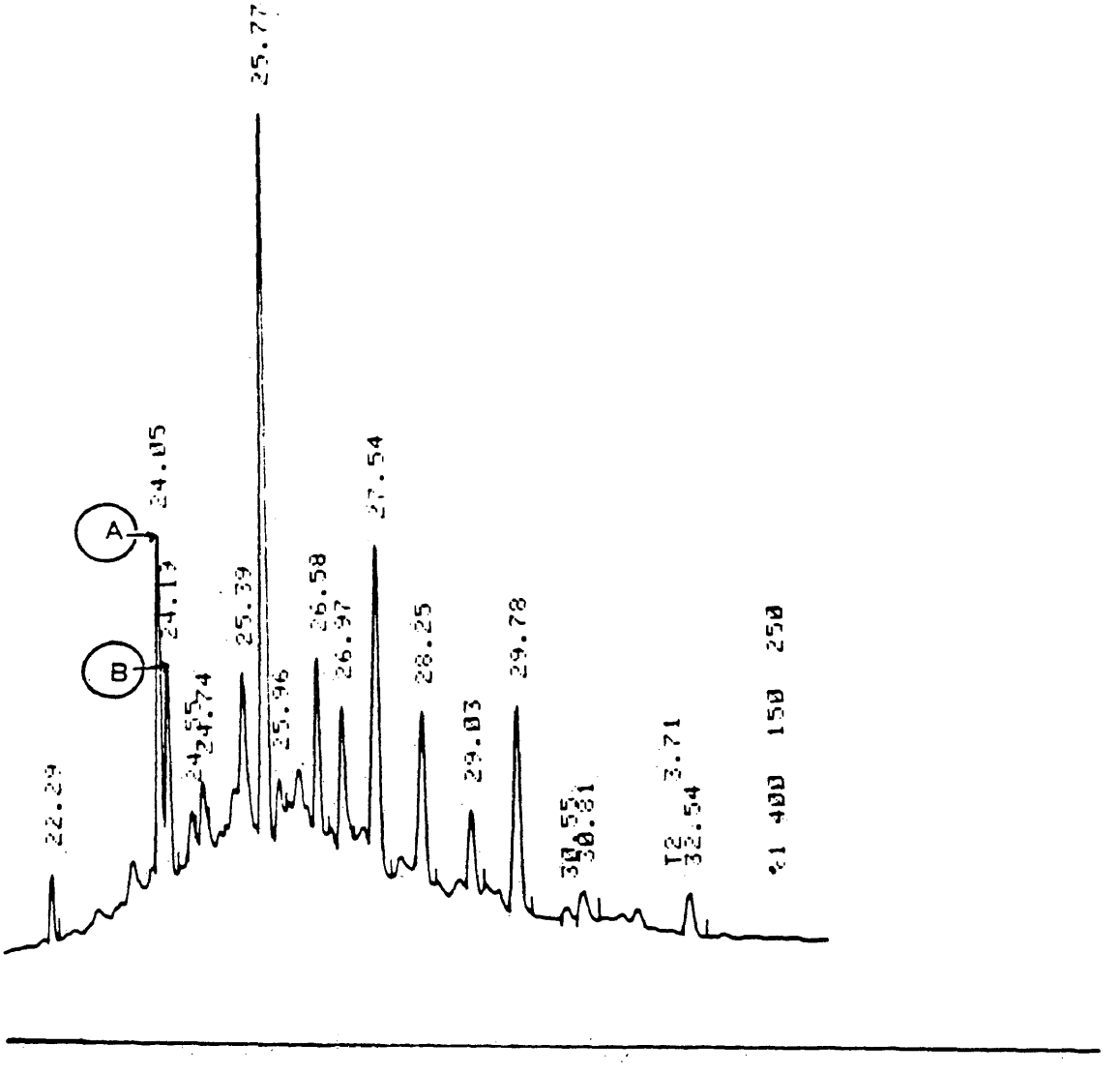
   A. Sample 16

   B. Sample 15





Appendix D: Chromatogram Using HP-GC and an F.I.D. Detector



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