T. C. SMITH

M. Sc.

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KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF ISOPRENOID COMPOUNDS OF IMPORTANCE IN ORGANIC GEOCHEMISTRY

Lt. T.C. SMITH
Department of Chemistry
Faculty of Military Studies
University of New South Wales
Royal Military College
DUNTROON.

Submitted as a requirement for the Degree of Master of Science.

1975.

DECLARATION

The work in this thesis has not been submitted for a higher degree to any other university or institution.

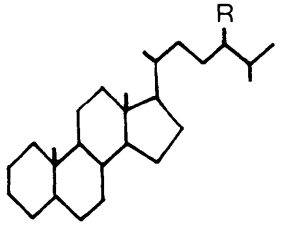
Acknowledgements

I wish to express my gratitude to Mr. J.W. Tardif for his advice and guidance throughout the research, Dr. D.J. McHugh for his helpful advice on the thesis, and other members of the staff for their co-operation and assistance. I also thank Ainslie for her encouragement.

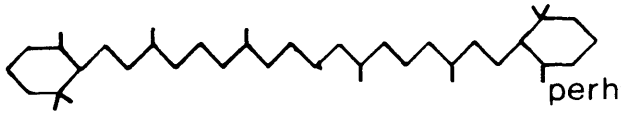
LIST OF COMPOUNDS

2,6,10,14-tetramethylpentadecane (pristane) I

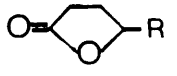
2,6,10,14-tetramethylhexadecane (phytane) II



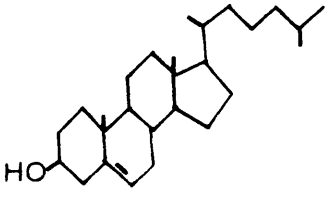
a. R = H cholestane
b. R = CH_3 ergostane
c. R = C_2H_5 sitostane III



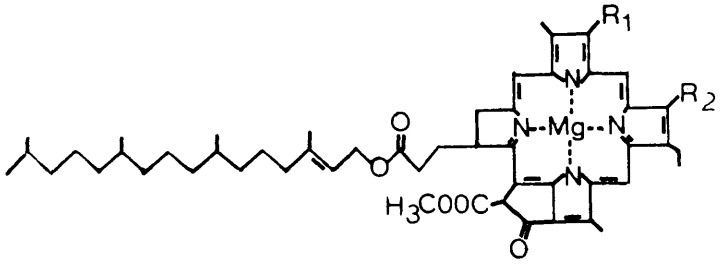
perhydro-β-carotene IV



R = C_3H_7 – $C_{15}H_{23}$ γ-lactones V



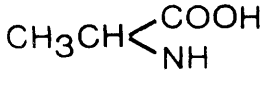
cholesterol VI



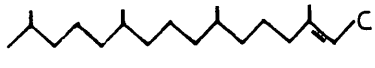
chlorophyll

	R_1	R_2
a.	$CH=CH_2$	CH_3
b.	"	CHO
d.	CHO	CH_3

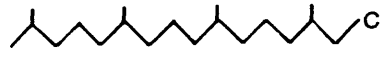
VII



alanine VIII

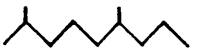


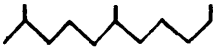
3,7,11,15-tetamethyl-2-hexadecen-1-ol (phytol) IX

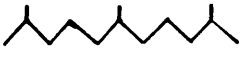


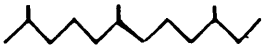
phytanic acid X

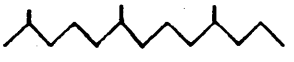
2,6-dimethyloctane XI

 2,6-dimethylnonane XII

 2,6-dimethylundecane XIII

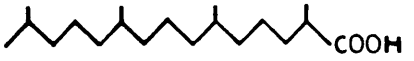
 2,6,10-trimethylundecane XIV

 2,6,10-trimethyldodecane XV

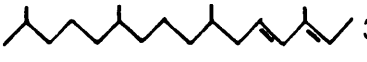
 2,6,10-trimethyltridecane XVI

 2,6,10-trimethylpentadecane XVII

 dihydrophytol XVIII

 pristanic acid XIX

 2-(4',8',12'-trimethyltridecyl)-buta-13-diene XX

 3,7,11,15-tetramethyl-2,4-hexadecadiene XXI

 3,7,11,15-tetramethyl-1,3-hexadecadiene XXII

SUMMARY

Experiments were carried out on the thermal decomposition of the isoprenoid compounds, pristane (2,6,10,14-tetramethylpentadecane) and phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol).

The rates of decomposition of pristane on a substrate were measured at temperatures in the range 150-400°C and the values extrapolated to low temperatures. The vapor pressure of pristane was found to be an important contributor to its stability. The experiments show that pristane is capable of existing in rocks for long periods of geological time provided the temperature of the sediment does not exceed approximately 80°C, since the decomposition rate is considerable above this temperature.

The thermal degradation products of phytol were obtained at 350°C and analysed by gas chromatography-mass spectrometry. Isoprenoid compounds in the homologous series from C-10 to C-20, including pristane but excluding C-12 and C-17, were identified. The pattern of the products obtained is similar to that found in sediments. A possible free radical mechanism was suggested for the thermal decomposition of phytol.

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INTRODUCTION

GENERAL

Organic geochemistry is defined as the study of the organic matter occurring in geological situations. It involves the extension of natural product chemistry to the whole path of carbon in nature (EGLINTON, 1969). Investigations of sedimentary rocks have found the existence of organic carbonaceous matter in rocks of all ages from Recent to Precambrian, though it is only in special geological situations that the organic molecules in rocks will be suitably preserved. A study of the inorganic matrix, in which the organic substances occur, can give some indication of the state of preservation of the organic matter and likelihood that it is an integral part of the rock (HOERING, 1967). For periods earlier than 600 million years ago, morphological remains are rare and molecular fossils are relied upon to give an indication of the origin of the fossil (fig.1; CALVIN, 1969).

Recent developments of the techniques of gas chromatography and mass spectrometry have enhanced the prospects for research into the complex reaction sequences which determine the geological fate of carbon compounds. This research into the processes of natural evolution is done using the aspect of comparative biochemistry. Fossils are examined in the hope that some of the information is still there in the form of protein structure, secondary metabolites, etc. Present day organisms are examined and phylogenetic comparisons are made in an attempt to infer evolutionary sequences in the development

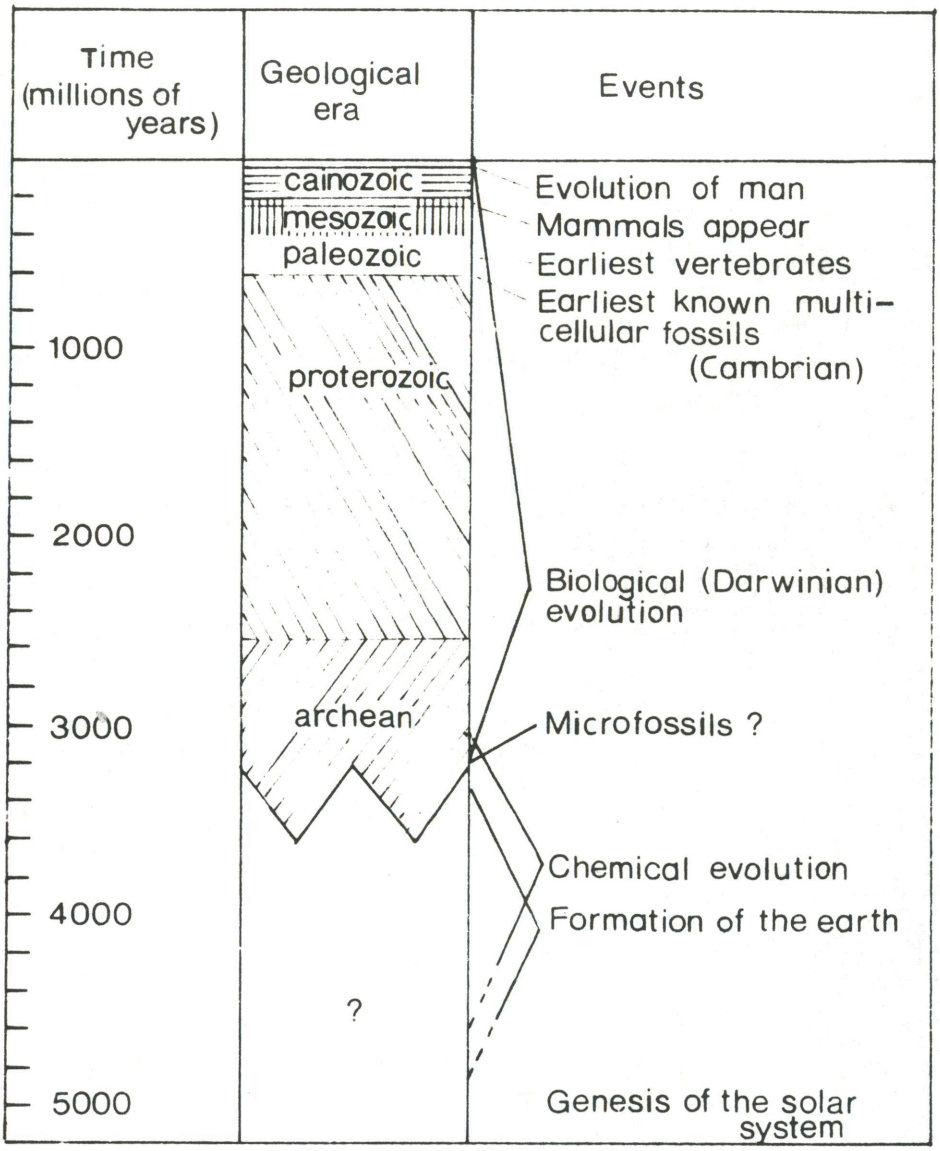


Fig. 1 .GEOLOGICAL TIME-SCALE (after CALVIN, 1969)

of biochemical processes (DAYHOFF and ECK, 1969).

Organic geochemistry also has immediate economic and social significance in that the understanding of the origin of fossil fuels, the search for them, and their proper chemical utilisation are major fields for the application of knowledge gained in this area of research.

DIAGENESIS

Biogeochemical alteration of organic matter takes place after burial where it undergoes the process of diagenesis. Diagenesis is the term used to comprise all those changes that take place after burial within a sediment, excluding crustal movement and the effects of weathering (ROLFE and BRETT, 1969). There are three main stages of diagenesis:

(1) Syndiagenesis;

(2) Anadiagenesis; and

(3) Epidiagenesis

Syndiagenesis involves the early burial during which the organic matter provides the nutrient for bacterial metabolism. Anadiagenesis is the deep burial phase of compaction and cementation, and may involve metamorphism. Inorganic chemical reactions predominate and minerals may form. Epidiagenesis is the meteoric phase which passes into weathering, and is initiated by the tectonic emergence of the basin.

Alteration of the organic material takes place due to:

(a) enzymatic and microbial processes;

(b) physicochemical effects (acidic - basic and oxidising - reducing conditions); and

(c) changes effected by rising temperature, increased pressure and catalytic effects of the rock.
Most of the alteration takes place in the early stages of diagenesis (DEGENS et al, 1964), which is followed by slow non-biological maturation processes. Time as such has little effect, as instanced by the preservation of fungal, bacterial and algal remains in ancient rocks (MOORE, 1969). Severe changes ultimately convert the organic material into a carbonised or graphitic form, the principal factor involved being temperature (SAXBY, 1970).

A simplified outline of the changes that are incurred by the organic material is shown in figure 2 (ALBRECHT and OURISSON, 1971). The biochemical cycle may be measured in days, whilst the geochemical cycle takes millions of years. Oxygen is present in the biochemical cycle only. A small proportion of organic matter accumulates in the first cycle and is preserved in sediments while undergoing the second cycle. The organic matter occurs in sedimentary rocks in two characteristic forms, one of which can be extracted with common organic solvents, while the other, known as kerogen is insoluble in such solvents (ABELSON, 1967). It is suggested that the key to the study of early biochemical evolution lies in the analysis of the dominant insoluble kerogen fraction (SMITH et al, 1970).

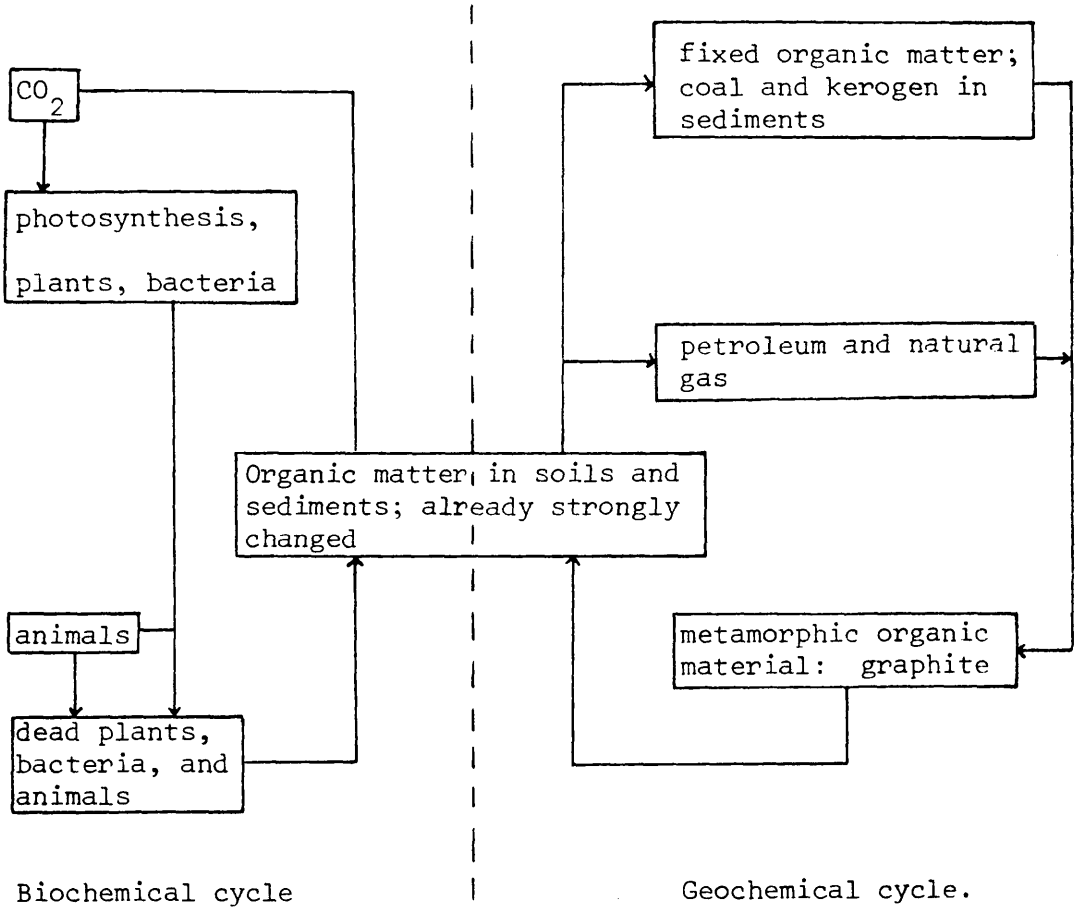


Fig. 2. CARBON CYCLE

HYDROCARBONS IN SEDIMENTS AND LIVING ORGANISMS

With the development of the techniques of gas chromatography-mass spectrometry (LEEMANS and McCLOSKEY, 1967), assisted by computers (CRAWFORD and MORRISON, 1968; HERTZ et al, 1971), many organic compounds have been identified in sediments of all ages, coals and petroleum. The compounds which are sought after are those from which information on biological processes can be drawn.

Normal alkanes have been isolated from most sediments containing organic matter ranging in age from Recent (MITTERER and HOERING, 1967) to Precambrian (ORO et al, 1965). The distributions observed are generally in the range C-10 to C-36, though higher members of the homologous series are often present in lesser amounts (MAXWELL et al, 1972).

The isoprenoid carbon skeleton has been isolated from sediments (JOHNS et al, 1966) of various geological formations ranging from early Precambrian (ORO and NOONER, 1967) to Recent samples (BLUMER and COOPER, 1967; BURLINGAME and SIMONEIT, 1968). The isoprenoids are of great geochemical interest because of their presence, especially pristane (I) and phytane (II), in sediments and crude oils of all ages. The presence of these compounds, together with other substances, is taken as chemical evidence for the existence of living organisms at the time of deposition of the sediment.

Isoprenoid acids (DOUGLAS et al, 1971), fatty acids (COOPER, 1962; HAN and CALVIN, 1969; SIMONEIT and BURLINGAME, 1973) and alcohols (SEVER and PARKER, 1969)

have been found in sediments. Several sesqui-, di-, tri-, and tetra-cyclic terpenoids (ANDERSON et al, 1969; ANDERS and ROBINSON, 1971) including cholestane (IIIa), ergostane (IIIb), and sitostane (IIIc), together with perhydro-beta-carotene (IV, MURPHY et al, 1967; GALLEGOS, 1971), have also been isolated. Aromatic hydrocarbons (ANDERS et al, 1973) and other compounds of interest such as gamma-lactones (V, HERTZ et al, 1973) have also been identified.

To some extent, the patterns of biological abundance of the carbon skeletons of organic compounds in living organisms are mirrored in the composition of the extracts from sediments (EGLINTON, 1969 a). There are few biosynthetic pathways by which carbon skeletons are assembled in living organisms, the main processes being (BU'LOCK, 1965):

(1) The acetate-malonate pathway for the biogenesis of straight chain carbon compounds; and

(2) The mevalonate pathway for the biogenesis of branched and cyclic compounds with repeating units of five carbon atoms (isoprenoids).

Straight and branched chain alkanes, alkenes, and fatty acids are widely distributed in plants and animals, though the total amounts of hydrocarbons are often small. Normal alkanes from C-1 to C-62 have been reported in organisms (MEINSCHEIN, 1969), but the most ubitiquous hydrocarbons are the isoprenoids. Steroids, such as cholesterol (VI), are important constituents of plants and animals.

Investigations of marine organisms such as zooplankton and algae have produced a number of straight and branched chain hydrocarbons and fatty acids. The normal C-17 alkane is the predominant hydrocarbon of various algae (JOHNS et al, 1966; HAN and CALVIN, 1969a), while the important acyclic isoprenoid alkane 2,6,10,14-tetramethylpentadecane (pristane, I) is found in many marine organisms (AVIGAN and BLUMER, 1968). The di- and tri-olefins of pristane have also been found in zooplanktons and fishes (BLUMER et al, 1969).

Another important isoprenoid, 2,6,10,14-tetramethylhexadecane (phytane, II) has been found in living organisms but not from marine sources (JOHNS et al, 1966). However, olefins of phytane have been isolated from zooplankton (BLUMER and THOMAS, 1965).

The study of the biosynthesis of organic geochemicals does provide partial explanations for the distribution patterns of hydrocarbons and fatty acids in sediments. Algal and bacterial remains contribute to the kerogen of many sediments (COOPER and MURCHISON, 1970) and oil shales (CANE and ALBION, 1970), and comparison of the hydrocarbon distributions of living organisms and sedimentary deposits may provide clues as to the origins of the sediments.

BIOLOGICAL MARKERS

In order to establish that period in time when the transition from chemical to biological evolutionary development was made, the search for intact organic molecules in ancient rocks has produced the concept of the

biological marker. Biological markers are organic compounds of characteristic structure which can be interpreted in terms of a previous biological origin (EGLINTON, 1969a). They must have sufficient stability to be able to survive long periods of geological time and their formation by non-biological means must be of negligible probability (JOHNS et al, 1966). The stereochemistry of these compounds is important in establishing their origins, as is the pattern of the number of carbons in their skeletons. For example, the production of a series of isoprenoids by biological means produces an uneven distribution of compounds differing by five carbon atoms, whereas a non-biogenic origin would produce an even distribution. Carbon isotopic studies also aid in establishing the origins of these compounds (WELTE, 1969; DEGENS, 1969).

Some of the main classes of compounds which have best survived from the earliest periods of geological time are (McKIRDY, 1974):

1. Alkanes.

(a) Normal, saturated and mono-unsaturated — these are major constituents of geolipid extracts.

(b) Isoprenoid — especially pristane (I) and phytane (II), possibly derived from chlorophylls (VII).

(c) Cyclic — for example, the steranes (III) which are derived from sterols such as cholesterol (VI).

2. Fatty acids.

(a) Normal, saturated and mono-unsaturated — an even carbon number distribution denotes a recent origin.

(b) Isoprenoid — evidence for photosynthesis.

3. Porphyrins (see main structure of chlorophyll, VII) — evidence of photosynthesis, respiration, protein and nucleotide synthesis.

4. Amino acids — for example, alanine (VIII), from algal or bacterial protein. These compounds lack geochemical stability.

The value of n-alkanes as biological markers lies in their characteristic overall distribution pattern with respect to carbon number — its range, concentration maximum, and the degree of preference for odd over even carbon-numbered chain lengths. Normal alkane fractions of Recent sediments show a marked odd over even carbon number preference (BRAY and EVANS, 1961; VITOROVIC and SABAN, 1972), though Precambrian sediments may never have had any preference. Primitive plants and marine bacteria and algae, which would comprise the bulk of Precambrian biomass, do not show any odd over even carbon number preference. Also, the predominance, where originally present, decreases during diagenesis so that the older the sample, the less predominance occurs (BROOKS and SMITH, 1967; LEYTHAEUSER and WELTE, 1969).

A problem in examining sediments for biological markers occurs in determining whether or not the extractable organic material is syngenetic with the sediment (SMITH et al, 1970). As well as contamination sources, the abiological synthesis of the markers has to be considered (McCARTHY and CALVIN, 1967). The production of compounds such as pristane and phytane by non-biogenic reactions could undermine the value of these hydrocarbons

as criteria for biological processes.

Fischer-Tropsch type reactions are common processes in the universe (STUDIER et al, 1968). These reactions occur when CO, H_2 and meteoric dust cool on a rapid time scale, and are common on the surface of the moon and in meteorites. These reactions could have occurred abundantly on primitive earth. Aromatic compounds (ORO and HAN, 1966) and porphyrins (HODGSON and PONNAMPERUMA, 1968) have been synthesised abiogenically from compounds such as methane, ammonia and water vapor. Isoprene units have been polymerised on clay catalysts producing a series of long chain isoprenoids, however, the distribution pattern is not similar to that found in sediments (EGLINTON, 1969a). GELPI et al (1970) could not find polyisoprenoids in their investigations of Fischer-Tropsch reaction processes.

Moreover, it seems unlikely that sediments containing the biological markers would foster such conditions that favour the release of abiotic carbon, hydrogen, and catalysts at temperatures and pressures that would permit their combination as complex hydrocarbons. Rocks with mild thermal histories and low permeability, which contain the majority of hydrocarbons, are better suited for the retention of altered and unaltered biological remnants than for the production of abiotic compounds (MEINSCHEIN, 1969).

KINETICS AND ORGANIC GEOCHEMISTRY

A study of the kinetics of organic geochemicals provides evidence of the stability of compounds such as the biological markers. JONES and VALLENTYNE (1960) proposed

two conditions for organic compounds to be stable geologically - thermal stability and insolubility in water. Most of the biological markers satisfy the latter condition, and since some geothermal temperatures are low and may not have exceeded 30°C, these compounds may have survived long periods of time. Kinetic studies may establish that some of these compounds may have been present at that period in pre-history when abiological material was present simultaneously with that produced by living things.

Determination of the stabilities of biological markers is done by laboratory simulation of diagenesis and maturation processes. The decomposition of amino acids has been simulated by simple heating of shell fragments in water (HARE and MITTERER, 1967). Further studies of the decomposition of various amino acids in natural waters (BADA, 1971) indicated that if the amino acids were not consumed by organisms, they would remain in the water for periods of thousands of years or longer. Half-lives of greater than 10^9 years at 300°K for the molecular decomposition of amino acids have been calculated (CALVIN, 1969), neglecting other effects such as catalysis or complex stabilisation. The decarboxylation rates of amino acids have also shown half-lives of about 10^9 years at room temperature (CONWAY and LIBBY, 1958).

JONES and VALLENTYNE (1960) studied the kinetics of some amino acids in an attempt to use them as indicators of life in the Precambrian, but concluded that the amino acids are not sufficiently stable to persist over such long periods of time. Small amounts of amino acids have

been found in Precambrian sediments but the amounts are not much larger than that which may be present as contaminants (ABELSON and HARE, 1967).

Recently, the kinetics of the racemisation of amino acids has become of interest as a possible age-dating technique (KVENVOLDEN et al, 1972). By measuring the ratio of D to L enantiomers of a particular amino acid, and knowing the rate of interconversion of the enantiomers, it is possible to estimate the age of the amino acid and hence the rate of sedimentation and age of the sediment.

A series of experiments on the pyrolysis of kerogens (ABELSON, 1967) showed the rate of evolution of methane at 400°C to be one million times that at 185°C. The gaseous products of these reactions were analysed and at 250°C, 90 percent of the gases evolved were saturated. Since straight-chain hydrocarbon cracking gives equal amounts of saturated and unsaturated products, these experiments provide evidence that the processes at low temperatures are different from those of ordinary pyrolysis. However, though the pyrolysis models are questionable, they can be useful in demonstrating possible reactions.

Experiments on the decomposition of porphyrins have shown them to be 1000 times less stable than hydrocarbons. The hydrocarbons are the most stable group of compounds and may be expected to retain a significant part of their original molecular structure. The half-life for the cracking of a C-C bond has been calculated to be greater than 10^{27} years at 300°K and $10^{14.5}$ years at 400°K, whilst that for C-H bond breaking is 10^{25} years at 300°K and

$10^{13.5}$ years at 400°K (CALVIN, 1969). These figures of course neglect such other factors as oxidation, reduction, catalysis and so on.

Pristane (I) is used widely as a biological marker because it is found in sediments of all ages and has a structure understandable in terms of known biosynthetic pathways. In terms of C-C bond breaking, pristane appears to be thermally stable. McKENNA and KALLIO (1971) suggest that the stability of pristane may be due to the inability of micro-organisms to carry out its anaerobic destruction. Thermal cracking experiments have been done with pristane (BRICTEUX, 1966) and seventy products identified, however, the decomposition rates have not been reported.

It is postulated that phytol (IX) is derived from the side chain of chlorophyll (VII) by hydrolysis. The decomposition of phytol may lead to the formation of the series of isoprenoid skeletons from C-10 to C-20 in carbon number found in sediments. Phytol is also the precursor of pristane, however, the mechanism for this reaction has not been elucidated. The process may involve a purely thermal mechanism or a series of reactions including hydrogenation, oxidation, and dehydration to form phytanic acid (X) during early diagenesis, followed by decarboxylation at a later stage to form pristane.

The aim of this research is to investigate the kinetics of the decomposition of the isoprenoid alkane, pristane, and its precursor, phytol. To date there has been little study of the kinetics of the hydrocarbon biological markers. Kinetic data provides such information as

the expected life of the particular compound and the maximum temperature that the sediment containing the compound may have been subjected to continuously (VALLENTYNE, 1964). The effect of this maximal continuous temperature on the rate of decomposition of pristane may be calculated. The determination of the original amount of pristane present in a sediment may also be done, thus providing a possible clue as to the environment of deposition of the sediment. The elucidation of the reaction pathway for the decomposition of phytol may provide the mechanism for the formation of pristane and other isoprenoids found in sediments.

PART A. THE THERMAL DECOMPOSITION OF PRISTANE

EXPERIMENTAL

PREPARATION OF PRISTANE ON THE SUBSTRATE

Chromosorb P (100 g) was placed in an indented pear-shaped flask (250 ml) and covered with hexane. Pristane (Koch-Light, 100 mg) was then added and the flask rotated for about one hour to aid in the mixing process. The solvent was then slowly removed with the aid of a Buchi rotary evaporator. The flask was then placed in an oven at 100°C for about an hour.

Several pristane-on-Chromosorb P samples (1 g) were washed with benzene in a column (10 cm) fitted with a tap. The amount of pristane in each sample was measured by concentrating the washings and subjecting them to gas chromatography as described later. The method was found to produce a uniform distribution of the pristane on Chromosorb P.

PREPARATION OF THE SOLVENTS

All the solvents used were distilled using a fractionating column (30 cm) containing glass helices. Some of the solvent (10 ml) was evaporated down by passing a stream of nitrogen over the surface and then subjected to gas chromatography analysis. The appearance of one peak in the gas chromatogram corresponding to the solvent showed that particular solvent was pure.

PREPARATION OF THE SAMPLES

Several lengths of Pyrex glass tube (15 cm; 10 mm outside diameter, 5 mm inside diameter) were sealed at one end in a flame. A narrow neck was placed about 2 cm from the other end by drawing the tube in a hot flame.

Pristane-on-Chromosorb P (1 g) was added to each tube. This was then evacuated using a Dynavac high vacuum pumping system and the tube sealed at the neck under vacuum.

KINETIC EXPERIMENTS

The prepared samples of pristane-on-Chromosorb P were placed in an oven at temperatures ranging from 150 to 380°C for periods up to 180 hours. Samples were removed at time intervals of between 2 and 24 hours. These experiments were repeated using new sets of samples and different temperatures.

The heated samples of pristane-on-Chromosorb P were then washed with benzene several times until no more pristane was detected in the washings by gas chromatography. The washings were then concentrated in a small vial (1 ml) by slowly evaporating the solvent with the aid of a steady stream of nitrogen passing over the surface. Analysis of the products was carried out using gas chromatography.

CONSTANT-TEMPERATURE APPARATUS

A constant-temperature apparatus was set up to supplement the use of the oven so that more samples could be heated simultaneously. Several cylindrical holes were bored in an aluminium cylinder (18 cm; 10 cm diameter) and the cylinder placed on a hot-plate (fig.3). A contact thermometer was installed in the centre of the aluminium block and a voltage (200 V) applied to the hot plate. The voltage was controlled by the contact thermometer which was preset at the required temperature. The temperature variation was measured by a thermocouple placed in one of the bore holes connected to a recorder. The temperature was

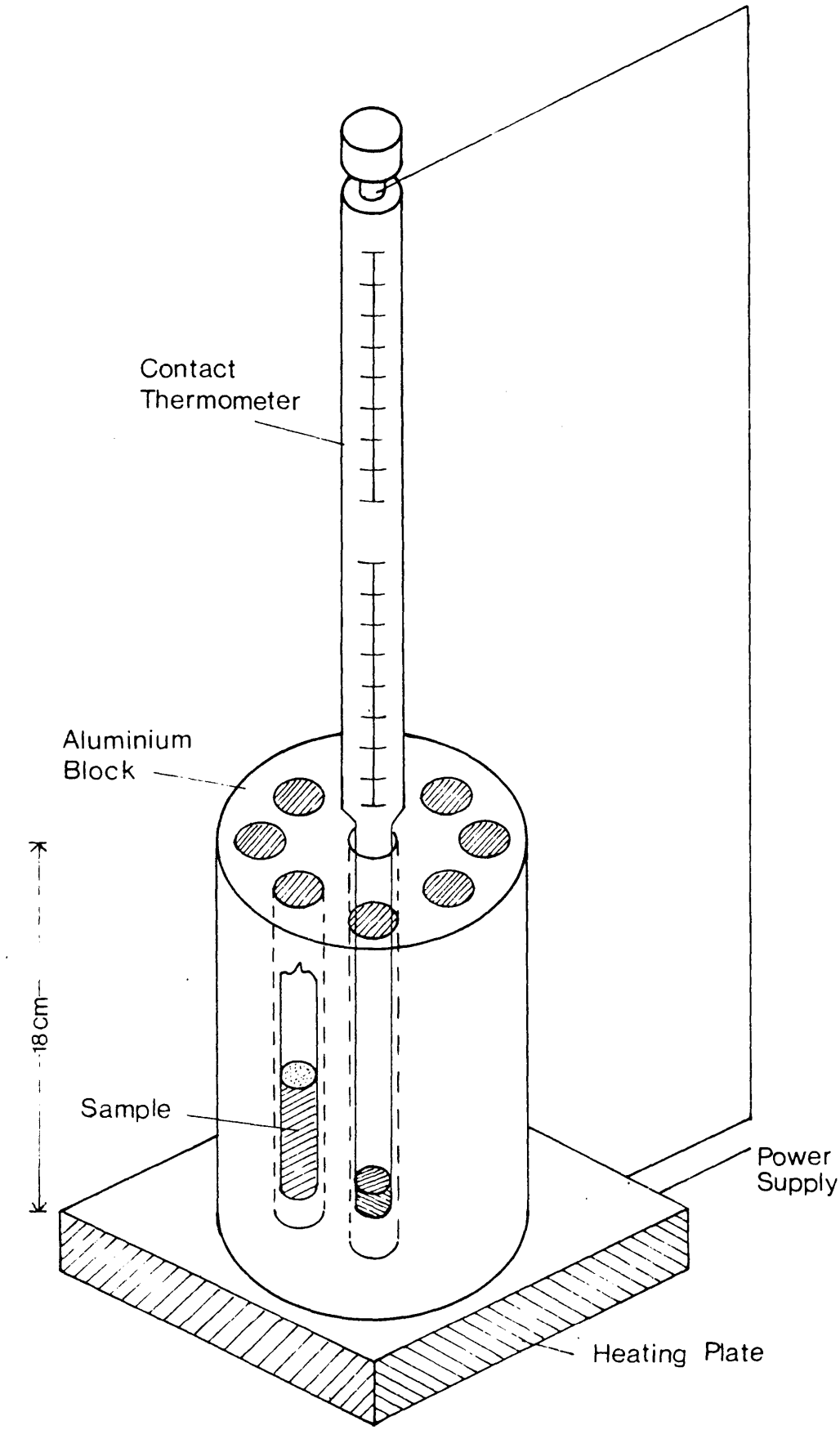


Fig. 3. CONSTANT-TEMPERATURE APPARATUS

found to vary over a range of 1°C.

ANALYSIS OF THE SAMPLES

Gas chromatography was used to measure the amount of pristane in each sample of previously-heated pristane-on-Chromosorb P. The settings used on the Perkin-Elmer model F-30 gas chromatograph were:

Injection temperature	=	300°C;
Detection temperature	=	250°C;
Column temperature	=	190°C;
Carrier gas (He) flow rate	=	25 ml/min;
Hydrogen pressure	=	20 psi;
Air pressure	=	20 psi.

The column used was a SE-30 support-coated open tubular column of length 50 ft and diameter 0.02 ins. The size of the injection sample was 0.3 microlitres with a split ratio of 6 : 1.

A standard reference solution was prepared by adding nonadecane (analytical standard, 15 microlitres) to a small vial containing benzene (1 ml). Equal quantities (50 microlitres) of this standard solution were then added to each pristane sample using an Agla micrometer syringe.

In early GC runs of the pristane samples, excessive tailing of the nonadecane peaks was found to prevent accurate measurement of the peak areas. The use of hexadecane as the standard reference compound proved to be more successful. Peak area measurements were done using a Shimadzu recorder with an inbuilt integrator.

INVESTIGATION FOR PHYSICAL ADSORPTION

The possibility that the pristane was being retained by physical adsorption on the Chromosorb P was investigated by extraction of a sample of the heated pristane-on-Chromosorb P. The free pristane was removed by washing the Chromosorb P with benzene until no more pristane was detected in the washings. The Chromosorb P was then placed in a flask (100 ml) and refluxed in benzene (25 ml) for one hour. The benzene was then decanted from the Chromosorb P into a flask (100 ml). The Chromosorb P was washed several times with benzene and the washings added to the flask. The benzene was then concentrated to about 0.2 ml and subjected to gas chromatography using the same conditions as in the previous section. No pristane was detected in the gas chromatograms.

Another sample of Chromosorb P, washed of the free pristane, was placed in a polythene beaker (100 ml). This was covered with water (20 ml) and hydrofluoric acid (20 ml, concentrated) added. This was stirred with the aid of a magnetic stirrer for about 24 hours and the Chromosorb P was seen to dissolve. This solution was diluted with water, and placed in a separating funnel. Several extractions with benzene were then carried out. The benzene extractions were concentrated to about 0.2 ml and subjected to gas chromatography under the same conditions as before. No pristane was detected in the gas chromatograms. These results showed no evidence that the pristane was being retained on the Chromosorb P by physical adsorption.

INVESTIGATION FOR THE INTERMEDIATE

The possibility that an intermediate existed between the pristane and its lower molecular weight products was investigated. An unsaturated form of pristane, pristene, was considered the most likely candidate for reasons discussed later. A previously heated pristane-on-Chromosorb P sample was washed free of the pristane and its products and the washings concentrated as before. This was then subjected to gas chromatography and the amount of pristane in the sample measured by comparing the area of the pristane peak to that of the reference standard.

A hydrogenation apparatus was constructed (fig.4) along similar lines to that of BEROZA and SARMIENTO, 1965. The hydrogenator tube was packed with 1% palladium chloride on-Chromosorb W with the aid of an electric vibrator. The tube was then connected, via Swagelok fittings, to a splitter consisting of a T-junction with a length of column (10 ft, 0.02 ins diameter) attached to one outlet. This T-junction was connected to the column contained in the oven and the hydrogenation apparatus heated to 300°C with the aid of heating tape. The pristane decomposition products were injected into the hydrogenator and passed through the tube with the aid of hydrogen gas as the carrier. The hydrogenated products were subjected to gas chromatography under the same conditions as before.

If pristene was present it would have been detected as pristane when the products were hydrogenated. However, no increase in the amount of pristane was detected over that found before the sample was hydrogenated. This evid-

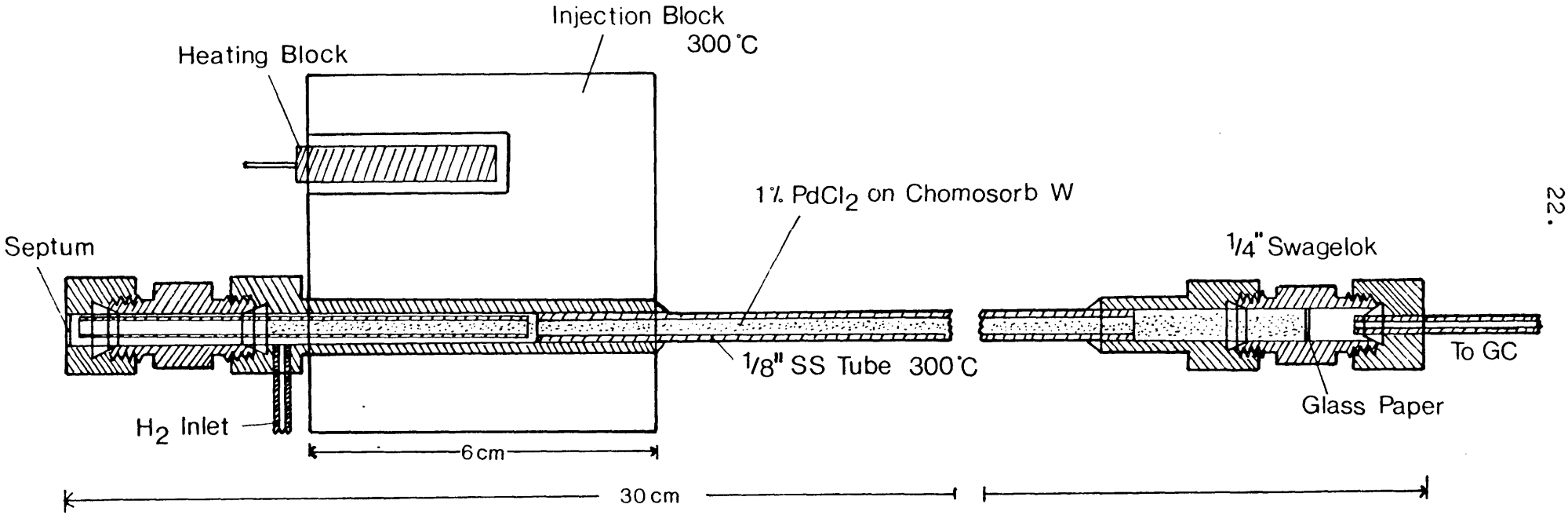


Fig. 4. HYDROGENATOR

dence showed that pristene was not present as the intermediate.

EXPERIMENTS WITH DIFFERENT SUBSTRATES

The effect of using different substrates on the decomposition of pristane was studied by preparing samples of pristane (10 mg) on Chromosorb W, aluminium oxide and sand (10 g). The samples were prepared in the same manner as that done with the Chromosorb P. They were then placed in the oven at 380°C and removed at different times.

The tubes containing the aluminium oxide were found to explode at this temperature due to the difficulty of removing all the adsorbed gases from the fine powder, which made the attainment of low pressures in the evacuation procedure difficult. The results for the decomposition of the pristane on Chromosorb W and sand were obtained.

EXPERIMENT WITH NO SUBSTRATE

Pyrex glass tubes (5 cm; 5 mm outside diameter, 3 mm inside diameter) were prepared as before and weighed. Pristane (2 microlitres) was injected into each tube and the whole weighed. They were then evacuated and sealed under vacuum and placed in an oven at 420°C after marking. The samples were then removed at different times.

The products were washed from the tubes with benzene, concentrated, and subjected to gas chromatography for analysis as before. The results for the decomposition of pristane without a substrate were thus obtained.

MEASUREMENT OF THE VAPOR PRESSURE OF PRISTANE

An isoteniscope apparatus was set up as in figure 5. The temperature of the oil bath was set at 150°C with the aid of a contact thermometer. The circulation of the oil around the isoteniscope was ensured by using a magnetic stirrer. The cold finger condenser was removed and the lower bulb half filled with pristane by using a length of thin polythene tubing with a syringe attached to one end. The condenser was then replaced.

The water through the condenser was turned on and the apparatus evacuated until the pristane boiled. When the pristane was observed to be condensing on the cold finger, the air inlet was opened until the levels of pristane in the two limbs of the U-tube were equal. This equilibrium condition was maintained until the pressure in the apparatus was constant, the pressure being measured with the manometer. A cathetometer, reading to 0.01 mm, was used to measure the height of liquid in the manometer. The vacuum was then released, the apparatus re-evacuated, and the pressure at equilibrium again obtained. This was repeated until the pressure readings obtained were constant.

The above sequence of operations was repeated at different temperatures in the range 150 to 200°C. Because of the low vapor pressures involved, silicone oil (density 1.1) was used in the manometer.

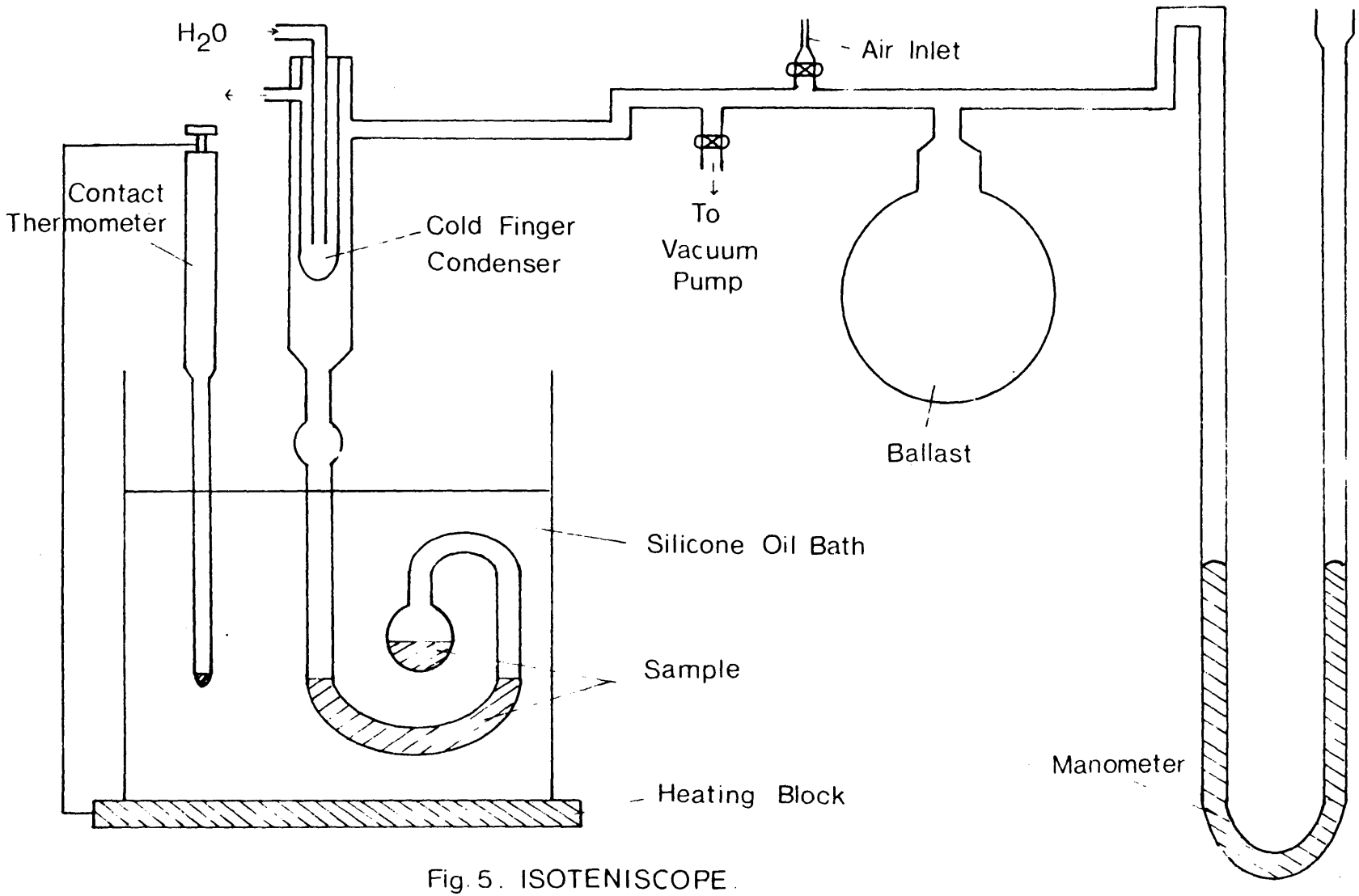


Fig. 5. ISOTENISCOPE.

RESULTS

KINETIC EXPERIMENTS

The plot of concentration versus time, for the decomposition of pristane on Chromosorb P (fig.6), showed the following:

(a) An initial, rapid decomposition which develops into;

(b) A slow first order decomposition.

The experiments were carried out at 380, 320, 250, 225, 200 and 150°C respectively. The experiment at 150°C was carried out over a period of 57 days with no detectable decomposition of the pristane. The curves drawn in figure 6 are derived from the mathematical expressions, determined in the discussion section, for the lines of best fit through the experimental points.

The results obtained for the decomposition of pristane at each temperature are summarised in tables I to VII. The concentration of pristane is expressed as a ratio of the quantity of pristane to that of the reference compound. The log concentration-versus-time plots were obtained using the method of least squares (fig.7), which showed the slow decomposition to be first order, and the average deviation in the value of the rate constant for the first order part of the curve was calculated (table VIII). The cracking reactions of paraffins generally approximate first-order kinetics (FABUSS et al, 1962), and the results did show a first-order decay for the slow decomposition part of the curve.

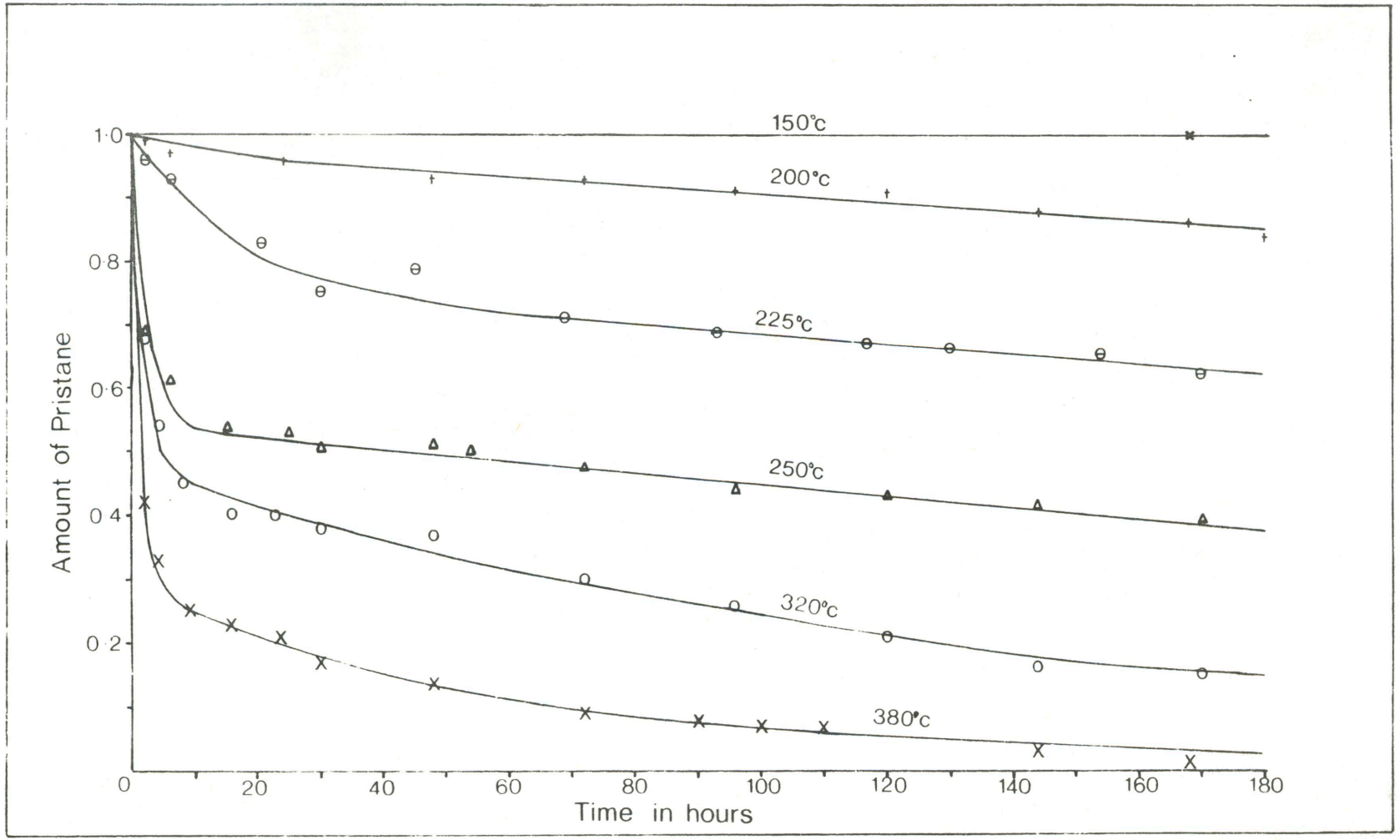


Fig. 6. PRISTANE DECOMPOSITION ON CHROMOSORB P AT DIFFERENT TEMPERATURES

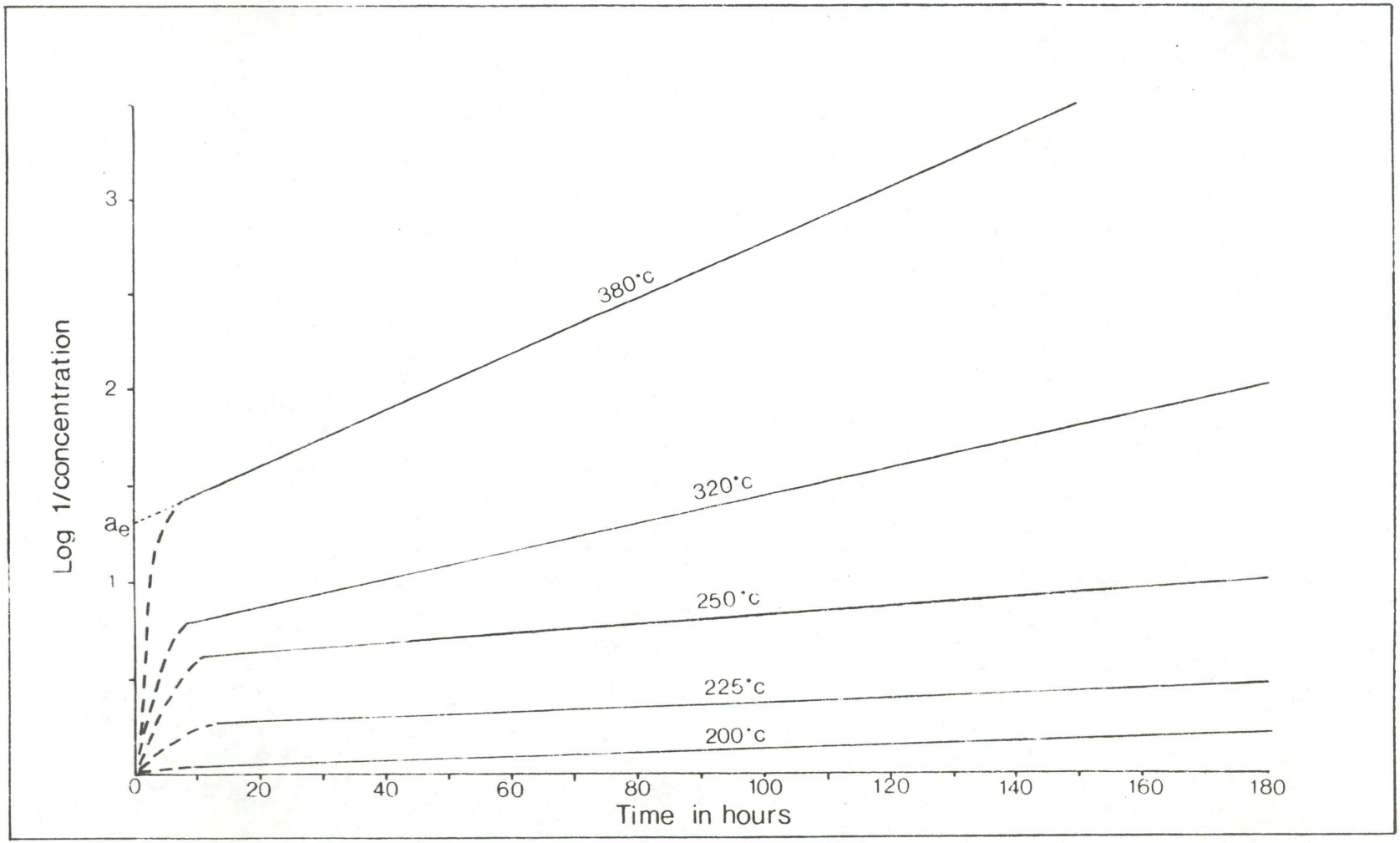


Fig. 7. LEAST SQUARES PLOT OF LOG 1/C Vs. TIME AT DIFFERENT TEMPERATURES

TABLES OF RESULTS

The concentration of pristane, a, is represented as a ratio of the amount of pristane to that of the coinjected reference compound and thus is dimensionless. The equation for a first order reaction is given by

$$\ln(a_o/a) = kt$$

where a_o is the initial concentration of pristane, which in this case is unity, and k is the rate constant. The initial concentration for the first order decomposition, a_e, is obtained by extrapolating the log 1/a versus time plot (fig.7) to time zero.

t hrs.	a	ln1/a
0	1.0	0
2	0.42	0.87
4	0.33	1.11
8	0.25	1.39
16	0.23	1.47
24	0.21	1.56
30	0.17	1.77
48	0.14	1.97
72	0.09	2.41
85	0.08	2.53
100	0.07	2.66
110	0.07	2.66
144	0.03	3.51
168	0.01	4.61

Table I. Pristane decomposition on Chromosorb P at 380°C.

t hrs.	a	ln1/a
0	1.0	0
2	0.68	0.39
4	0.54	0.62
8	0.45	0.80
16	0.40	0.92
23	0.40	0.92
24	0.41	0.89
31	0.38	0.97
48	0.37	0.99
72	0.30	1.20
96	0.26	1.35
120	0.21	1.56
144	0.16	1.83
170	0.15	1.90

Table II. Pristane decomposition on Chromosorb P at 320°C.

t hrs.	a	ln1/a
0	1.0	0
2	0.69	0.37
6	0.61	0.49
15	0.54	0.62
25	0.53	0.63
30	0.51	0.67
48	0.51	0.67
54	0.50	0.70
72	0.48	0.74
96	0.44	0.81
120	0.43	0.85
144	0.41	0.88
170	0.39	0.93

Table III. Pristane decomposition on Chromosorb P at 250°C.

t hrs.	a	ln1/a
0	1.0	0
2	0.97	0.03
6	0.93	0.07
21	0.83	0.19
30	0.75	0.29
45	0.79	0.24
69	0.71	0.34
93	0.69	0.37
117	0.67	0.40
130	0.66	0.42
154	0.65	0.43
170	0.62	0.48

Table IV. Pristane decomposition on Chromosorb P at 225°C.

t hrs.	a	ln1/a
0	1.0	0
2	0.99	0.01
6	0.97	0.03
24	0.96	0.05
48	0.93	0.07
72	0.92	0.08
96	0.91	0.09
120	0.91	0.09
144	0.88	0.13
168	0.86	0.15
180	0.84	0.19

Table V. Pristane decomposition on Chromosorb P at 200°C.

t hrs.	a	ln1/a
0	1.0	0
168	1.0	0
336	0.99	0.01
480	1.0	-0.02
552	1.02	-0.02
696	1.01	-0.01
840	1.0	0
984	0.98	0.02
1080	1.01	-0.01
1224	1.0	0
1368	0.99	0.01

Table VI. Pristane decomposition on Chromosorb P at 150°C.

t hrs	a	ℓn 1/a	k hr
0	1.0	0	0.007
4	0.97	0.03	
16	0.98	0.12	
24	0.85	0.16	
48	0.72	0.33	
96	0.51	0.67	
120	0.43	0.84	

Table VII. Pristane decomposition on Chromosorb P at 320°C with solvent present on the substrate.

T°C	10^3/K	Ae	% deviation in K
380	14.47	0.28	9.7
320	7.0	0.48	6.6
250	2.13	0.55	10.8
225	1.10	0.76	10.0
200	0.78	0.98	14.1
150	0	1.0	-

Table VIII. The rate constants end the initial concentrations for the first order decompositions.

	a	
t hrs.	Chromosorb W	sand
0	1.0	1.0
2	0.5	0.75
4	0.4	0.55
8	0.35	0.42
16	0.3	0.25
24	0.25	0.12

Table IX. Pristane decomposition on different substrates at 380°C.

t hrs.	a	ln1/a
0	1	0
1	0.85	0.16
2	0.71	0.34
4	0.64	0.65
6	0.56	0.58
8	0.47	0.76

Table X. Pristane decomposition without a substrate at 420°C.

T°C	VP torr
151.9	4.4
161.9	6.8
175.2	17.4
185.1	25.1
194.6	36.3

Table XI. The vapor pressures of pristane at various temperatures.

EXPERIMENT WITH SOLVENT PRESENT ON THE SUBSTRATE

One experiment carried out at 320°C, with solvent present on the substrate due to incomplete removal, did not show an initial, rapid decomposition but decomposed at a regular first order rate (table VII). The rate constant was the same as that of another experiment carried out at 320°C with no solvent on the substrate (table VIII).

EXPERIMENTS USING DIFFERENT SUBSTRATES

The plot of concentration versus time for the decomposition of pristane on Chromosorb W, showed a similar pattern to that of the decomposition on Chromosorb P (fig.8). The results using sand as the substrate did not show an initial rapid decline in the curve but decomposed at a constant rate. Experiments to determine the order of the reaction were not carried out. The results were summarised in table IX.

EXPERIMENT USING NO SUBSTRATE

The results obtained for the decomposition of pristane in the vapor phase showed that the pristane decomposed at a constant first order rate (fig.9). The results were summarised in table X.

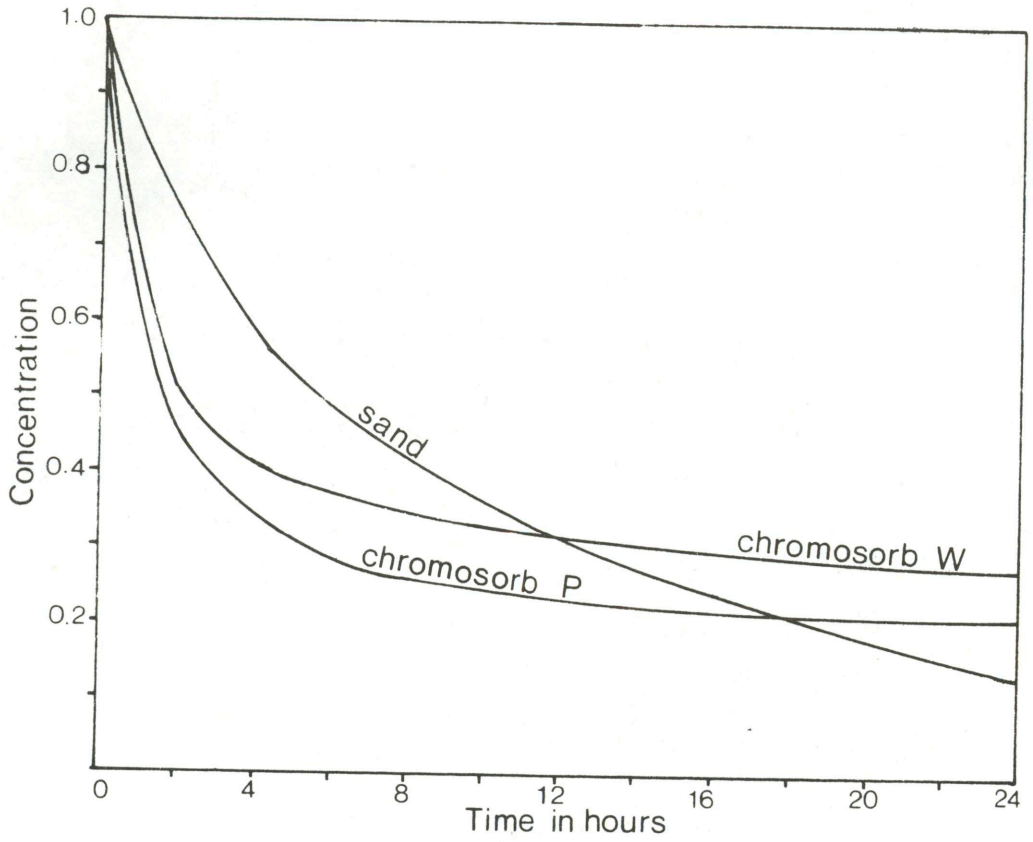


Fig.8. GRAPHS OF PRISTANE CONCENTRATION Vs.TIME FOR DIFFERENT SUBSTRATES AT 380°C

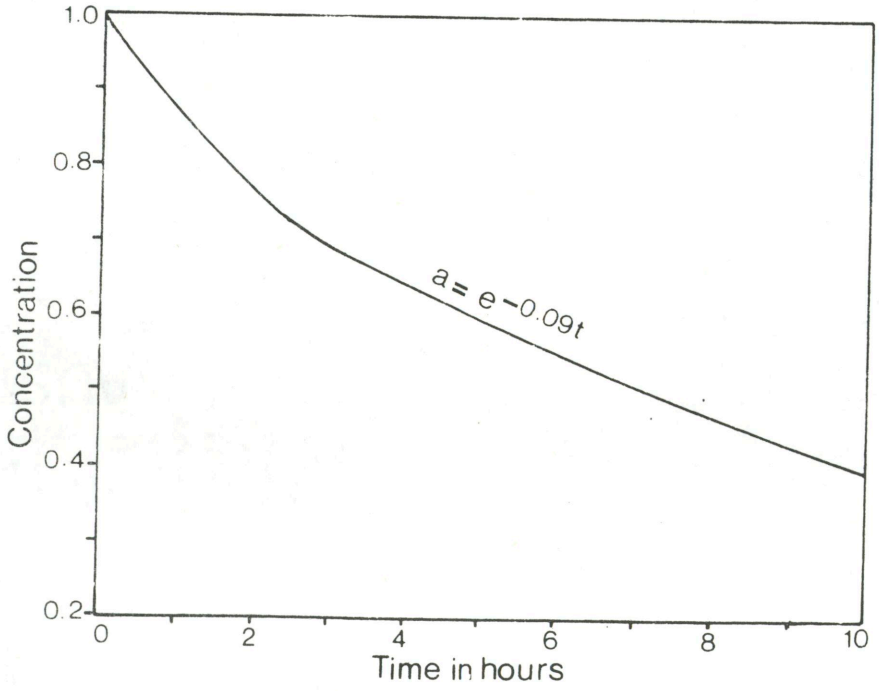


Fig. 9. PRISTANE DECAY IN THE GAS PHASE AT 420°C

DISCUSSION

GENERAL

Work on the kinetic data of organic compounds of geochemical interest must assume that some degree of relationship exists between pyrolysis and diagenesis (ABELSON, 1954). Kinetic data can provide information such as the expected life of a particular compound and the maximal continuous temperature to which a particular sedimentary deposit may have been subjected (VALLENTYNE, 1964). The search for forms of life in earliest periods of geological time must assume that certain characteristic molecules, the biological markers, show a reasonable stability to degradation over long periods of geological time (McCARTHY and CALVIN, 1967). Pristane is studied thus because of its supposed stability to diagenesis, its specificity of structure understandable in terms of known biosynthetic sequences, and its improbability of being formed by abiological synthesis.

In obtaining kinetic data of compounds in organic geochemical situations, a laboratory model must be set up which proposes to simulate the conditions that may exist in nature. It must be assumed that the decomposition rates obtained are equivalent to those under geological conditions in the actual sedimentary deposit. The predicted decomposition rates obtained from the simple laboratory model really only pertain to pristane singly present in the sedimentary deposit. In fact, pristane is usually found in parts per million quantities along with a large variety of hydrocarbons.

The comparison of the kinetic data obtained from the laboratory model with that of the more complex geochemical situation is complicated by many factors. The influence of microbial oxidation (McKENNA and KALLIO, 1971) and the presence of water would bring about rapid decreases in the concentration of pristane in a sediment during diagenesis. The effect of natural radiations and the presence of inorganic catalysts would exert kinetic influence in certain cases. Some decrease in concentration may be accounted for by diffusion of the pristane from one source bed to another. Furthermore, the kinetic experiments must be carried out at high temperatures if decomposition rates are to be determined in a convenient time span. This data must then be extrapolated to temperatures far below those used in the experimental work. The justification for setting up such a laboratory model is found in the parallel obtained between the predictions from the model and the facts of geological preservation.

The choice of a substrate, on which to base a laboratory model for the decomposition of pristane, must be comparable to that which would exist in a sedimentary deposit. It must have a catalytic activity comparable to that of sedimentary rock, and be sufficiently free-flowing to distribute the pristane liquid evenly throughout the solid granules. Chromosorb P, a diatomaceous earth of surface area 10 sq. metres per gram, was considered to be a suitable material.

DECOMPOSITION CURVES OF PRISTANE

The decomposition curves of pristane (figs.6,8) suggested that two independent, simultaneous reactions were involved in the pristane decomposition:

(a) A rapid decomposition which ceases before the pristane has completely decomposed, and

(b) A slow, first order decomposition.

The rapid decomposition may correspond to a system of two compounds in a reversible reaction which ceases on reaching equilibrium, so that the overall reaction is represented by the models:

1. $C \longleftarrow A \rightleftharpoons B$; or

2. $A \rightleftharpoons B \longrightarrow C$ where A is pristane, C the first order decomposition products, and B the unknown intermediate compound.

In the following sections, the kinetics of the above reactions are developed and it is shown that they adequately represent the kinetics of decomposition. However, these models are not likely to be correct because no evidence of the existence of compound B could be found. This compound should have the same carbon skeleton as pristane because it would be unlikely that pristane would reversibly form a compound of lower carbon number. To overcome this difficulty a third model, involving chemisorption was examined. This model is based on the following observations.

The decomposition of pristane on Chromosorb W (fig.8) did not differ substantially from that on Chromosorb P. However, in the following experiments, pristane underwent

a regular first order decay without an initial rapid decomposition:

i. Using sand as a substrate (fig.8, table IX);

ii. Using no substrate (fig.9, table X); and

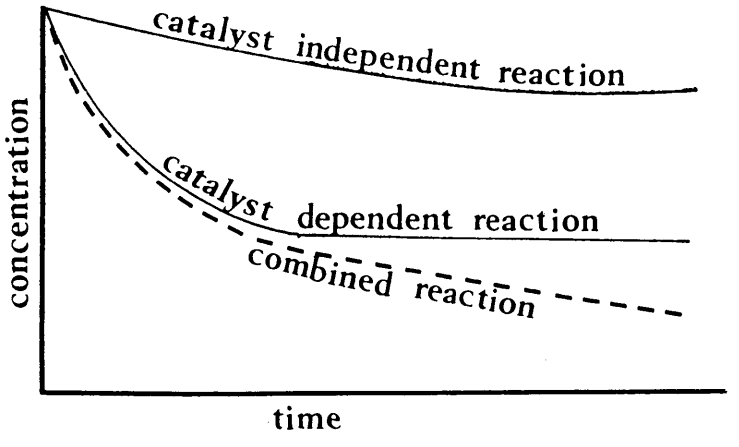
iii. Using Chromosorb P from which the solvent (benzene) had not been completely removed (table VII).

These experiments suggest that the pristane decomposition is catalysed by the substrate, in that the initial rapid decomposition does not occur if the substrate has insufficient surface area or the active sites are saturated by another compound. Hence the decomposition of pristane on Chromosorb P may consist of:

(1) A catalyst dependent decomposition which occurs rapidly; and

(2) A concurrent, catalyst independent decomposition which occurs at a first order rate.

The catalyst dependent reaction may be a process such as chemisorption, in which the products act as a catalytic poison causing the reaction to stop after a period of time. The catalyst independent reaction may be a gas phase decomposition of the pristane. The following diagram is a representation of this process:



Hence, the chemisorption model constitutes:

(3) A chemisorption system in which gaseous pristane gives decomposition products (A $\longrightarrow$ C) concurrently with a catalytic reaction between the pristane and the substrate. This chemisorption model cannot be analysed mathematically in such a facile manner as for models 1 and 2, but qualitatively can be shown to be kinetically equivalent.

However, assuming the chemisorption model to be correct, in geochemical situations the catalyst dependent reaction is not likely to be of any importance because it is probable that the pristane would be a minor competitor for any active sites on the substrate where chemisorption could occur. Consequently, in the subsequent discussion of the kinetic data of the pristane decomposition, only the reaction A $\longrightarrow$ C is considered. This reaction is involved in each of the models considered and its rate constant is derived independently of the catalyst dependent reaction from figure 7.

KINETIC TREATMENT USING THE MODEL $C \longleftarrow A \rightleftharpoons B$

The proposed reaction for the overall process is

$$C \xleftarrow{k_3} A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where A represents pristane, B and C the products.

k_1, k_2 and k_3 are the rate constants.

$A \rightleftharpoons B$

Assume the reactions $A \rightleftharpoons B$ and $A \longrightarrow C$ are independent. Provided the equilibrium is reached rapidly compared with the secondary decomposition (k_1 and $k_2 \gg k_3$) then for the reaction $A \rightleftharpoons B$

$$-da/dt = -k_2 b + k_1 a$$

where a and b are the concentrations of A and B respectively. Taking the initial concentration of A as $a_o = 1$ and $b = 1-a$.

Therefore, $-da/dt = -k_2 + (k_1 + k_2)a$

Integrating from $t = 0$, $a = 1$ to $t = t$, $a = a_t$

$$a_t = k_1/(k_1 + k_2) \exp\left[-(k_1 + k_2)t\right] + k_2/(k_1 + k_2) \qquad \text{—— (1)}$$

This agrees with the expression obtained by CAPELLOS and BIELSKI (1972).

Now, at equilibrium $k_1 a_e = k_2(1 - a_e)$ —— (2)

where a_e and $(1 - a_e)$ are the concentrations of A and B respectively at equilibrium. From eqn.(2)

$$a_e = k_2/(k_1 + k_2) \qquad \text{—— (3)}$$

Substituting for a_e in eqn.(1) yields

$$a_t = (1 - a_e) \exp\left[-(k_1 = k_2)t\right] + a_e \qquad \text{—— (4)}$$

Substituting k_2 from eqn.(2) into eqn.(4) yields

$$-k_1 t = (1 - a_e) \ln\left[(a_t - a_e)/(1 - a_e)\right] \qquad \text{—— (5)}$$

Hence, knowing the value for a_e obtained from figure 7, the rate constants k_1 and k_2 may be calculated from eqns.(5) and (2) respectively (table XII).

<u>A ⟶ C</u>

Assume that the initial concentration of A for the reaction A ⟶ C is a_e where a_e is the equilibrium concentration of A. Provided k_1 and $k_2 \gg k_3$, this causes little error. Therefore

$$-da/dt = k_3 a$$

integrating

$$a_t = a_e \exp(-k_3 t).$$

<u>Overall process</u>

For the process A ⟶ C, at time t, the concentration of A is decreased by a quantity

$$a_e - a_e \exp(-k_3 t)$$

Subtracting this from eqn.(4) yields, for the overall process,

$$a_t = (1 - a_e) \exp\left[-(k_1 + k_2)t\right] + a_e \exp(-k_3 t) \qquad \text{—— (6)}$$

Substitution of the variables calculated (a_e is obtained from fig.7) into the above exponential expression (table XIII) leads to a series of values for the concentration at different times. A plot of these values for a particular temperature does fit the experimental data obtained in figure 6, where the curves drawn are the actual plots of the calculated values of concentration.

T°C	k_1	k_2	k_3
200	0.01	0.34	0.00078
225	0.02	0.05	0.0011
250	0.20	0.24	0.00213
320	0.25	0.23	0.007
380	0.50	0.19	0.01447

Table XII. Values for the rate constants at different temperatures.

T°C	Expression for a_t
200	0.02 exp(-0.35t) + 0.98 exp(-0.00078t)
225	0.24 exp(-0.07t) + 0.76 exp(-0.0011t)
250	0.45 exp(-0.44t) + 0.55 exp(-0.00213t)
320	0.52 exp (-0.48t) + 0.48 exp(-0.007t)
380	0.72 exp(-0.69t) + 0.28 exp(-0.01447t)

Table XIII. Expressions for a_t at different temperatures.

KINETIC TREATMENT USING THE MODEL $A \rightleftharpoons B \longrightarrow C$

A kinetic treatment was also carried out using the model

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_3} C$$

$A \rightleftharpoons B$

Assume the reactions $A \rightleftharpoons B$ and $B \longrightarrow C$ are independent. Provided that the equilibrium is reached rapidly compared with the secondary decomposition (k_1 and $k_2 \gg k_3$) then for the reaction $A \rightleftharpoons B$

$$a_t = (1 - a_e) \exp \left[-(k_1 + k_2)t\right] + a_e \qquad \text{---(4)}$$

where a_e is obtained from figure 7.

$B \longrightarrow C$

Assume that the initial concentration of B for the reaction $B \longrightarrow C$ is $(1 - a_e)$ where a_e is the equilibrium concentration of A. Provided that k_1 and $k_2 \gg k_3$, this causes little error. Therefore

$$b_t = (1 - a_e) \exp (- k_3 t)$$

Overall process

In order to maintain equilibrium, A decreases to:

$$a_t = k_2/k_1 \ (1 - a_e) \exp (- k_3 t)$$
$$= a_e \exp (- k_3 t),$$

so that a is decreased by $a_e - a_e \exp (- k_3 t)$.

Thus, combining eqn.(4) with this yields

$$a_t = (1 - a_e) \exp \left[-(k_1 + k_2)t\right] + a_e$$
$$-\left[a_e - a_e \exp (- k_3 t)\right],$$
$$a_t = (1 - a_e) \exp \left[-(k_1 + k_2)t\right] + a_e \exp (- k_3 t).$$

This expression is the same as that derived in equation 6. Hence, the decomposition curves do not indicate whether the reaction was

$$A \rightleftharpoons B \longrightarrow C \text{ or}$$

$$C \longleftarrow A \rightleftharpoons B$$

The fact that the reaction curves fit the above reactions led to a search for the intermediate B. This compound would have existed in substantial concentration; for example, at 250°C, A (pristane) and B would have approximately equal concentrations after the initial equilibrium was reached (fig.6). The search, conducted by hydrogenation of the products, further extraction of the substrate, and dissolving the substrate in HF, indicated that this intermediate did not, in fact, exist. Any alternative mechanism should predict a decomposition corresponding closely to equation 6.

The following section describes a model involving chemisorption reactions, which qualitatively gives a similar decomposition to that described above.

KINETIC TREATMENT USING CHEMISORPTION REACTIONS

The kinetics of surface reactions are less accessible than those of homogeneous reactions. A homogeneous reaction may occur throughout the entire volume of the reaction vessel, whereas a heterogeneous reaction is confined to a thin layer at the surface of the catalyst. The majority of surface reactions cannot be assigned a simple order and hence are classified according to the number of reactant molecules involved (THOMSON and WEBB, 1968). Surface reactions of molecularity greater than two are unknown. The bonds formed in chemisorption reactions are chemical bonds rather than simple Van der Waals type forces of the kind which hold molecules together in a liquid.

Investigation of the relation between the quantity of gas adsorbed and the pressure of the gas over the solid is done in terms of adsorption isotherms. Gas adsorption isotherms show that the quantity of gas adsorbed at first rises rapidly with the pressure, but ultimately, when the available surface is covered, the quantity adsorbed can rise no further and is then independent of the equilibrium pressure (BOND, 1972). The best known isotherm is that derived by Langmuir (a full derivation is given in FLOOD, 1967).

Consider a reaction involving the chemisorption of a gas, an equilibrium is reached where the rate of adsorption equals the rate of desorption.

$$A + S \underset{k_B}{\overset{k_A}{\rightleftharpoons}} AS$$

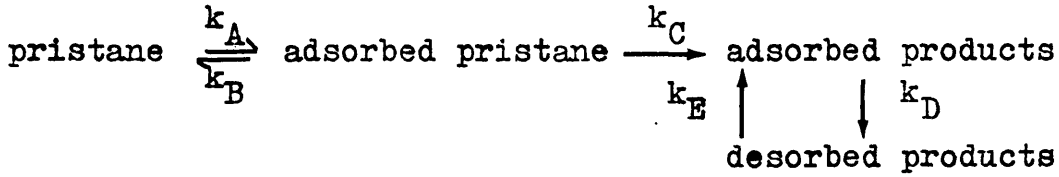
where A represents the gas, S the adsorption sites, and

k_A and k_B are the rates of adsorption and desorption respectively. If n is the number of sites per unit area, an expression for the fraction of sites occupied, θ , may be derived.

$$\theta = k_A Pn/(k_B n + k_A Pn)$$
$$= bP/(1 + bP)$$

where P is the pressure and b is the ratio of k_A to k_B and is termed the adsorption coefficient. This expression is known as the Langmuir isotherm.

The proposed chemisorption reaction of the pristane is as follows:



This heterogeneous process may be regarded as a homogeneous reaction taking place on the two-dimensional surface (STEVENS, 1965, p.72). The pristane is adsorbed and activated, the activated pristane then decomposes to form adsorbed products which are, in turn, desorbed. The adsorption and desorption reactions are reversible.

Initially, the reaction involving the rate constant k_C is fast. As the reaction proceeds, the number of molecules of products being formed increases substantially, increasing the rate of desorption of the products. Re-adsorption of this large number of molecules, compared with the number of pristane molecules available, causes the number of active sites available for adsorption of pristane to occur to become progressively less. This has the effect of strongly inhibiting or poisoning the overall reaction.

Consider the reaction involving the adsorbed pristane forming products,

$$A \longrightarrow X.$$

If the product X is strongly adsorbed, it will occupy a progressively larger fraction of the surface as the reaction proceeds. The rate of decomposition is determined by the pressure of A through the Langmuir isotherm. The rate equation becomes

$$-dP_A/dt = k\theta_A$$
$$= kb_AP_A/(1 + b_AP_A + b_XP_X)$$

and if b_X is very large,

$$-dP_A/dt = k\theta_A = kb_AP_A/b_XP_X$$
$$= KP_A/P_X$$

The rate is inversely proportional to the pressure of the products, and X is acting as the inhibitor.

If $P_X = (1 - P_A)$,

$$-dP_A/dt = KP_A/(1 - P_A)$$

Integrating from $t = 0$, $P_A = 1$ to $t = t$, $P_A = P_A$,

$$P_A \exp(-P_A) = \exp -(kt + 1)$$

which represents an exponential decay of A. Also, if S_A is the fraction of surface area utilised by reactant A, and S_X by the product X, the fraction of the total surface area at which reaction takes place is $(1 - S_X)S_A$ and the rate expression becomes (STEVENS, 1965, p.82)

$$-dP_A/dt = k(1 - S_X)S_A$$

where k is the rate constant, then the rate of reaction $\longrightarrow 0$ as $S_X \longrightarrow 1$, i.e. when all the sites available for reaction are occupied by X.

Hence, the decomposition curve of A would show an exponential decay to a value of P_A at a time depending on when $S_X \simeq 1$. The shape of this curve is, in fact, similar to that obtained experimentally for the initial part of the decomposition curve. If the chemisorption reaction is considered to be occurring concurrently with a gas phase decomposition of the pristane, then the overall plot does represent the decomposition of pristane obtained experimentally (fig.6).

The shape of the pristane decomposition curves suggest that the higher the temperature, the more pristane is decomposed in the chemisorption process, which is consistent with the chemisorption scheme proposed above. Increased temperature would favour the reaction involving the activated pristane forming products, and hence more pristane would be adsorbed and thus decomposed in the chemisorption process.

EXTRAPOLATION OF THE KINETIC DATA TO LOW TEMPERATURES

It has been established that in the model, the pristane decomposes initially due to a chemisorption process, at the same time undergoing a decomposition in the vapor phase. Also, it has been shown that, if other compounds are present in much larger quantity than the pristane, the competition to undergo any chemisorption reaction rules out the possibility of the pristane being dependent on the nature of the substrate and may be insignificant on some surfaces.

Thus, in order to gain useful information, the kinetic data of the gas phase decomposition reaction (represented

by the secondary part of the experimental curve) must be studied (fig.7). The dependence of reaction rate on temperature is shown by the Arrhenius equation (SWINBOURNE, 1971).

$$k = A \exp (- E/RT)$$

where k is the rate constant, A is the frequency factor, E is the activation energy, R is the gas constant, and T is the temperature.

Hence, from the least squares plot of log k_3 versus 1/T (fig.10; table XIV)

$$\text{the slope} = - 2.27 \times 10^3$$

Thus the Arrhenius equation is obtained in the form,

$$k = 44.7 \exp (-10388/RT).$$

From this expression the values for the rate constants at lower temperatures may be calculated (table XV).

From this data, the rate constant at 20°C,

$$k = 7.99 \times 10^{-7} \text{ hrs.}^{-1}.$$

Thus the half-life of the pristane is given by,

$$t\ 0.5 = \ln 2/k = 99 \text{ years at } 20^{\circ}C.$$

The low value obtained for the activation energy (10,388 cal) may be due to catalysis, though this is difficult to verify. The energy involved in breaking a carbon-carbon bond is of the order of 30 kcal per mole (BAMFORD and TIPPER, 1972). The substrate, Chromosorb P, consists of a silicon dioxide matrix. Catalysts involving alumina-silica compounds are used in the petroleum industry for cracking processes (WISEMAN, 1972), but the mechanisms of these catalytic reactions are not fully understood though they appear to be due to the formation of carbonium ion intermediates at the surface.

$T^{o}C.$	$T^{o}K$	$10^{3}/T$	$10^{3}k$	log k
380	653	1.53	14.47	-1.84
320	593	1.69	7.0	-2.15
250	523	1.91	2.13	-2.67
225	498	2.01	1.10	-2.96
200	473	2.11	0.78	-3.11
150	423	2.36	0	-

Table XIV. The rate constants for the Arrhenius plot.

$T^{o}C$	$10^{-7}k(hrs.^{-1})$
20	7.99
50	41.9
80	166.0
100	367.0
120	748.0
150	1920.0
200	7150.0

Table XV. The values of the rate constants at low temperatures.

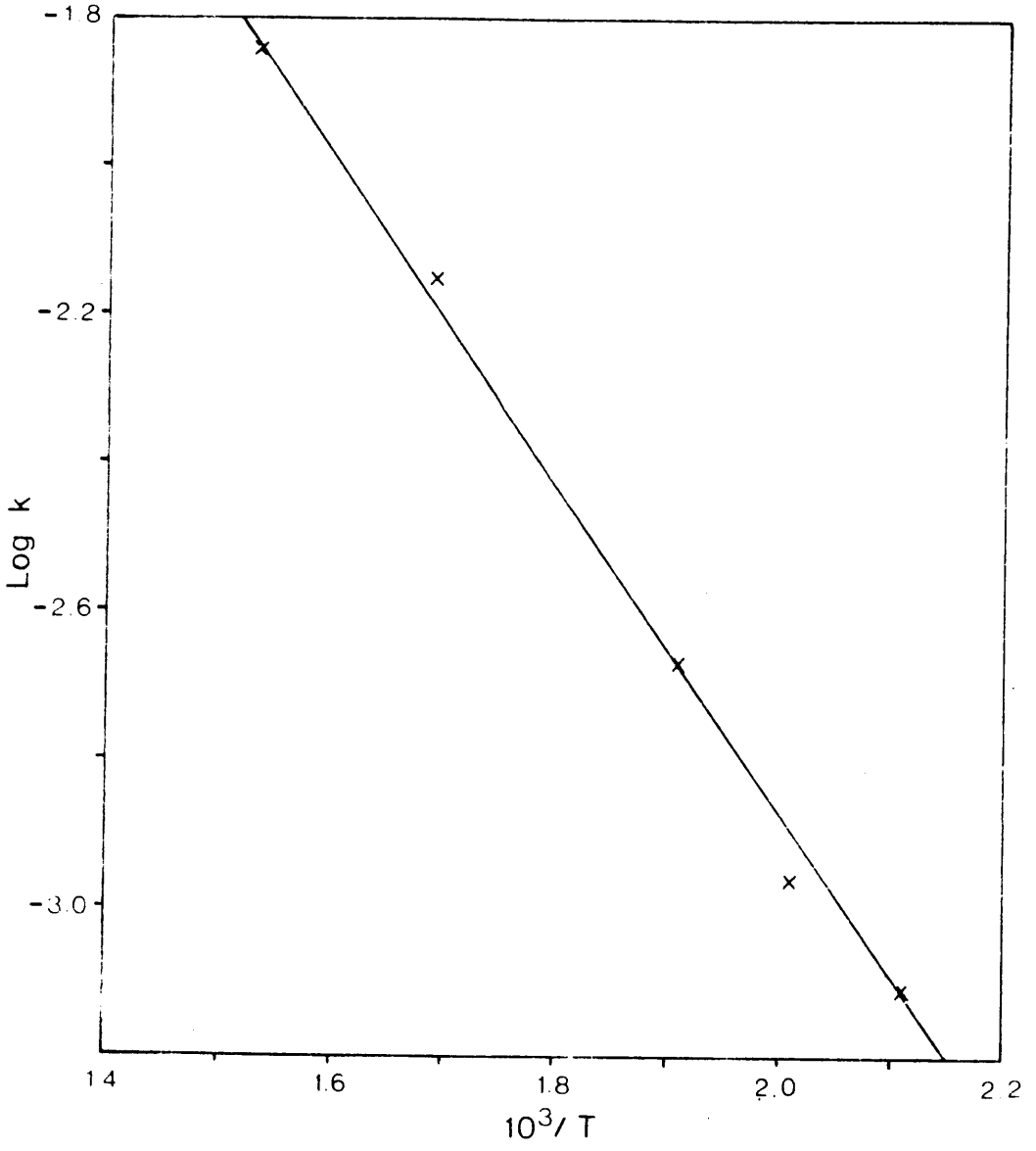


Fig. 10. ARRHENIUS PLOT OF LOG K Vs. 1/T

EXTRAPOLATION OF VAPOR PRESSURE TO LOW TEMPERATURES

The experiment carried out at 150°C showed no detectable decomposition of the pristane, suggesting that the pristane may not have been present in the vapor phase. Since the decomposition is considered to occur at a much greater rate in the vapor phase (FABUSS et al, 1962), the liquid decomposition is insignificant, and the vapor pressure of pristane must be taken into account.

In order to obtain the vapor pressures at low temperatures, the Clausius-Clapeyron equation (MOORE, 1963) is used to extrapolate measured vapor pressures at known temperatures to lower temperatures. This equation is given by

$$P = A \exp (- \Delta H/RT)$$

where P is the pressure, A is a constant, H is the heat of vaporisation, R is the gas constant, and T is the temperature.

In practice, the value of the heat of vaporisation does vary over a wide range of temperature. However, the variation is small especially when extrapolating to lower temperatures as in this experiment. LANGE (1967) states that the heat of vaporisation of nonadecane, which would have a similar value to that of pristane, is constant over the range 20 to 160°C. Hence the extrapolation in this experiment is reasonable.

From the least squares plot of log P versus 1/T (fig.11; table XVI), the slope = 4490, hence the Clausius-Clapeyron equation becomes

$$P = 1.59 \times 10^{11} \exp (-20550/RT).$$

Hence the vapor pressures of pristane at low temperatures may be calculated (table XVII).

$T^{o}C$	$T^{o}K$	$10^{3}/T$	VP torr	log VP
151.9	424.9	2.35	4.39	0.64
161.9	434.9	2.30	6.77	0.83
175.2	448.2	2.23	17.41	1.24
185.1	458.1	2.18	25.10	1.40
194.6	467.6	2.14	36.27	1.56

Table XVI. The vapor pressures for the Clausius-Clapeyron plot.

$T^{o}C$	VP (10^{-5}torr)
20	8.59
50	200.0
80	3020.0
100	14500.0
120	60000.0
150	385000.0

Table XVII. Vapor pressures of pristane at low temperatures.

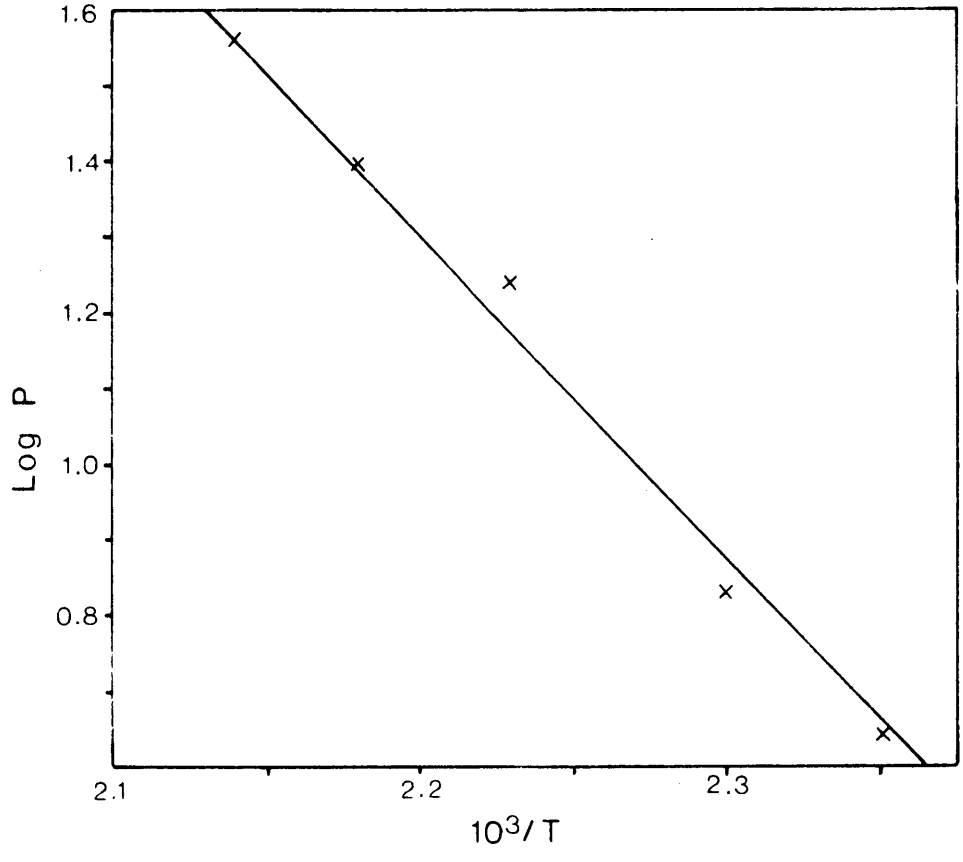


Fig.11. CLAUSIUS-CLAPEYRON PLOT OF LOG P Vs. 1/T

GEOCHEMICAL APPLICATIONS OF THESE DATA

The low value of 99 years obtained for the half life of pristane, in terms of geological time, does not explain the presence of pristane in sediments as old as 1000 million years (HAN and CALVIN, 1969). However, in all the experiments carried out all the pristane was in the vapor state (except at 150°C). In its natural state, the pristane is present in the rock as a liquid film in contact with its vapor. If the decomposition is occurring in the vapor state, then the rate of decomposition is governed by the amount of space present in which the vapor can form, and hence the rate of evaporation of the liquid. Since the rate of evaporation of the liquid is very much faster than the rate of decomposition of the vapor, the pristane vapor is continually being replenished as long as liquid pristane is present.

The equation for a first order decomposition is - d(concentration)/dt = k x(concentration), where k is the rate constant. Now, the concentration of vapor is given by the Ideal gas equation

$$n/v = P/RT$$

where n is the number of moles, v is the volume of space, P is the pressure, R is the gas constant, and T is the temperature. Thus,

the rate of decomposition

of the vapor = k x P/RT

The vapor pressure remains constant because of constant evaporation. Therefore,

the rate of decomposition

of the pristane = a constant

Thus the reaction is zero order overall and the rate of decomposition of the pristane at any temperature is given by,

rate of decomposition = k x P/RT,

where k is the rate constant for the vapor decomposition.

In its natural state, pristane coexists in parts-per-million quantity with numerous other hydrocarbons. In this situation, as has been shown experimentally, it is unlikely that the pristane would be involved in any chemisorption process. Thus the gas phase reaction involving the secondary part of the pristane decomposition curve is most useful (fig.7).

In order to calculate the rate of decomposition of pristane, the values for the rate constants (table XV) and the vapor pressures (table XVII) at low temperatures were substituted into the above equation. The results are summarised in table XVIII. The low values for the rate of decomposition show that pristane is very likely to have survived from early Precambrian times, and support its adoption as one of the biological markers.

The maximal continuous temperature was proposed as a comparative value by JONES and VALLENTYNE (1960). This is a measure of the maximum temperature that a deposit could have been subjected to continuously throughout its history. The effect that this temperature has on the decomposition rate of pristane may be illustrated by taking a typical amount of pristane found in a deposit of, for example, Cretaceous era (100 million years), and calculating the amount of pristane that would have been present in order to produce the present amount (table XIX).

T°C	Rate of decomposition in grams per million years per litre of space
20	1.15×10^{-10}
50	1.75×10^{-8}
80	6.97×10^{-7}
100	6.97×10^{-6}
120	5.63×10^{-5}
150	7.50×10^{-4}

Table XVIII. Rates of decomposition of pristane at different temperatures.

Maximal continuous temperature in °C.	Original amount in micrograms.
20	1.012
50	2.75
80	70.7
100	698.0
120	5631.0
150	75001.0

Table XIX. Amount of pristane required to produce 1 microgram at different temperatures in a 100 million year old sediment.

These calculations show that whilst a little more than 1 microgram is required to produce 1 microgram at 20°C, more than 75 milligrams is required if the maximal continuous temperature was as high as 150°C. Another illustration of the effect of different maximal continuous temperatures is shown by the decomposition of an amount of pristane contained in a Precambrian sediment (table XX).

	Geological time in millions of years							
T°C	1000	500	250	100	50	10	1	present day
20	1000	1000	1000	1000	1000	1000	1000	1000
50	1000	991	987	985	984	983	982	982
80	1000	652	477	373	338	310	304	303
100	1000	0	-	-	-	-	-	-

Table XX. Number of micrograms of pristane remaining at different times and varying temperature.

JOHNS (1966) reported the presence of pristane in Precambrian sediments in amounts greater than one percent of the branched-cyclic alkane fraction. HAN and CALVIN (1969) reported that the aliphatic hydrocarbons consisted 0.05 ppm W/W in Precambrian rocks. Assuming the branched-cyclic fraction equals the total amount of aliphatic hydrocarbons, a typical amount of pristane present in a Precambrian rock may be approximately 5 micrograms per kilogram of rock. Then, assuming a maximal continuous temperature of 20°C, for example, the original amount of pristane in the rock may be calculated to be 5.12 micrograms per kg.

CONCLUSION

It must be recognised, of course, that extrapolations of the above kind are likely to be influenced by a variety of other factors already mentioned such as oxidation reactions, the presence of water, and so on. However, the predictions are useful in that they provide comparisons if not a quantitative measure of a geological process. The calculation of the amount of pristane originally present in a sediment may provide information as to its environment of deposition. A large amount of pristane present in a particular sediment could indicate that it was deposited in a terrestrial environment rather than a marine one (POWELL and McKIRDY, 1973).

The experiments do indicate the stability of pristane and support its use as a biological marker. In sedimentary deposits, pristane is often found together with phytane (II). Work on the kinetics of the reactions of phytane may provide supporting evidence for such parameters as the maximal continuous temperatures and the environment of deposition of particular sediments.

Although the laboratory model set up for the decomposition of pristane is limited, it does provide a theoretical framework on which to base the decomposition process as it may occur in nature. A more reliable model may involve the addition of other substances to the reaction vessel, with pristane, to simulate conditions that may exist in the fossil matrix. The problem of including other compounds such as phytane, shows itself when gas chromatography analysis is attempted. The products of compounds

of higher molecular weight than pristane would interfere with the peaks from pristane in the gas chromatograms.

Some work has been done on the kinetics of amino acids, however, the saturated hydrocarbons are more stable than amino acids and, in particular, the isoprenoid alkanes are most suited for kinetic studies because of their widespread use as biological markers. The kinetics of the isoprenoid alkanes may provide information on that period of geological history when the transition from chemical evolutionary development to biological evolutionary development was made.

PART B. THE THERMAL DECOMPOSITION OF PHYTOL

EXPERIMENTAL

PREPARATION OF THE SAMPLES

Pyrex glass tubes (50 mm x 3 mm i.d.) were prepared by sealing one end and drawing the other end into a narrow neck. Phytol (Koch-Light; 10 microlitres) was added to the tubes. The tubes were evacuated and sealed in a flame, then placed in the oven preheated to the required temperature, (350°C) and single tubes removed at intervals. The products were than washed from the tubes with benzene and the washings concentrated with the aid of a nitrogen stream passing over the surface. The samples were then subjected to gas chromatography analysis followed by gas chromatography-mass spectrometry for identification of the products.

GAS CHROMATOGRAPHY

A Perkin-Elmer model F-30 gas chromatograph was used with the following settings:

Injection temperature	=	300°C;
Detection temperature	=	250°C;
Temperature program	=	80-200°C; 5 deg/min;
Hydrogen pressure	=	20 psi;
Air pressure	=	20 psi;
He flow rate	=	4 ml/min.

A wall-coated open tubular column (120 ft; 0.02 ins diameter) was prepared by passing a solution of 1% Apiezon-L in chloroform through the column under pressure (30 psi g). The column was conditioned on a temperature program of 30-250°C at one degree per minute.

The samples (0.5 microlitres) were injected with a split ratio of 12 : 1 and the gas chromatograms obtained.

HYDROGENATION

In order to obtain the pattern of the formation of the carbon skeletons of the products, the unsaturated compounds were hydrogenated so that only alkanes were present for analysis. A hydrogenator was set up as described in the previous section (fig.4) and the pressure of the hydrogen carrier gas adjusted so that 4 mls/min flowed through the gas chromatography column. Chromatograms were obtained using the same GC conditions as above.

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

A Finnigan gas chromatography-mass spectrometer Model 1015D was used for analysis of the products. The following GC conditions applied:

Injection temperature = 250°C;

Detection temperature = 200°C;

Temperature program = 60-250°C, 6 deg/min.

The previously-prepared WCOT column was used, and the method of analysis involved the injection of the sample at low temperature and under high gas flow to separate the solvent from the compounds of interest (GROB, 1972).

The samples (0.5 microlitres) were injected with the oven at room temperature and the inlet pressure on the column at 30 psi. The expulsion of the solvent was indicated by the marked rise and fall of the pressure gauge on the mass spectrometer. The column pressure was then adjusted by opening the splitter until the gauge read 14 psi. When the splitter was closed, the flow rate through

the column was 20 mls/min.

The following settings on the mass spectrometer were used:

Electron energy = 70 ev;

Ionization energy = 6 V;

Sensitivity = 10^{-7};

Filter = 3000 amu;

Scan time = 3 sec.

The mass spectra were obtained using an oscillographic recorder.

SULPHURIC ACID TREATMENT

In order to remove the unsaturated compounds contained in the sample, the products were treated with concentrated sulphuric acid. A sample of the thermal degradation products of phytol was taken and the solvent removed with the aid of a nitrogen stream passing over the surface. Concentrated sulphuric acid (0.5 ml) was added and the mixture shaken. This was then extracted with hexane several times and the extractions washed with water and subjected to gas chromatography.

The reaction involves the addition of a hydrogen ion to one side of the double bond and a bisulphate ion on the other (MORRISON and BOYD, 1973). The carbon is bonded to an oxygen and not to sulphur.

$$-C=C- + H-O-SO_3H \longrightarrow -\overset{H}{\underset{|}{C}}-\overset{OSO_3H}{\underset{|}{C}}-$$

COLUMN CHROMATOGRAPHY

In order to separate the saturated and unsaturated compounds silver nitrate/silica gel chromatography was used. The column packing was prepared by adding silica gel (10 g) and silver nitrate (AR, 1 g) to a pear-shaped flask and covering with water. Mixing was then carried out for an hour and the solvent removed with the aid of a rotary evaporator. The packing was then heated for an hour at 100°C in an oven.

The silver nitrate/silica gel was added to a column (10 cm, 1 cm diameter) containing hexane. A sample of phytol products was eluted through the column with hexane, the fractions being collected at regular intervals and then subjected to GC analysis.

RESULTS

PHYTOL DECOMPOSITION EXPERIMENTS

The gas chromatograms obtained from the phytol products (figs.12, 13) showed the formation of a homologous series of alkanes and alkenes. Peaks were noticeably absent at the C-17 and C-12 positions. The areas of the peaks relative to a coinjected standard (n-eicosane) were measured. Hence the amount of each product as a percentage of the original amount of phytol was calculated for different times. The results are shown in table XXI. As many as possible of the products were identified using the gas chromatography-mass spectrometry technique. The total quantity of alkenes and alkanes present at different times was also measured (table XXII).

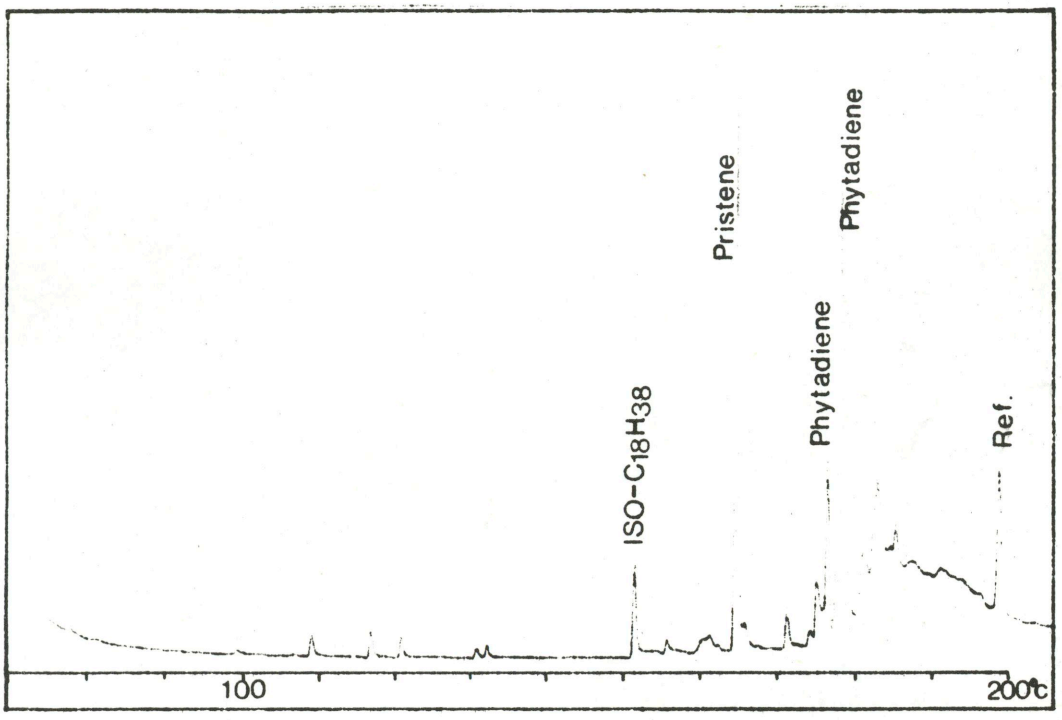


Fig. 12. G.C. OF THE PRODUCTS OF PHYTOL HEATED AT 350°c FOR 0·5 HRS

Note: iso = isoprenoid

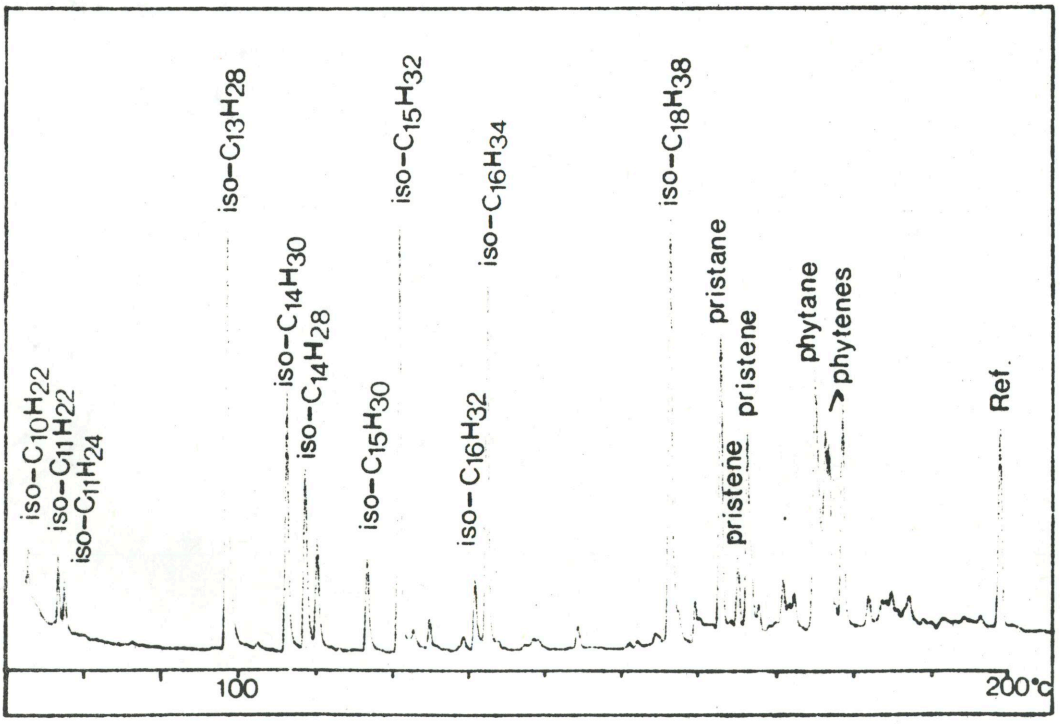


Fig. 13. PHYTOL PRODUCTS AFTER 6 HRS OF THERMAL DEGRADATION AT 350°c

t hrs	0.5	2	4	7	17	21	24	28
product(1)	% Composition							
$C_{20}H_{38}$	7.9	-	-	-	-	-	-	-
$C_{20}H_{38}$	3.2	-	-	-	-	-	-	-
$C_{20}H_{40}$	-	7.8	7.4	6.3	4.8	3.7	3.2	2.2
$C_{20}H_{40}$	-	4.1	4.3	4.2	3.6	3.1	2.2	-
$C_{20}H_{42}$	-	-	-	-	1.4	2.0	2.0	2.4
$C_{19}H_{38}$	-	1.8	2.9	4.0	4.8	4.0	3.9	1.9
$C_{19}H_{38}$	8.8	13.4	12.9	9.6	4.9	2.4	2.6	0.7
$C_{19}H_{40}$	-	0.4	0.6	1.3	2.0	2.5	2.7	2.8
$C_{18}H_{38}$	1.9	0.8	1.1	1.9	3.0	3.5	3.7	3.9
$C_{16}H_{34}$	0.3	1.0	1.1	1.8	3.1	3.8	3.5	3.5
$C_{16}H_{32}$	0.1	0.7	0.6	0.9	1.1	0.9	0.9	0.7
$C_{15}H_{32}$	0.4	1.2	1.3	2.4	0.9	4.1	3.9	4.1
$C_{15}H_{30}$	0.5	1.1	1.2	1.5	1.4	1.3	1.4	0.6
$C_{14}H_{28}$	0.4	1.6	1.4	2.7	2.7	1.1	2.8	1.8
$C_{14}H_{30}$	-	0.3	0.4	0.8	1.1	2.7	1.9	2.4
$C_{13}H_{28}$	-	-	0.8	1.9	2.7	4.6	4.1	3.9
$C_{11}H_{24}$	-	-	-	0.3	0.3	0.9	0.8	0.6
$C_{11}H_{22}$	-	0.7	0.8	1.3	0.8	1.5	1.7	0.8

(1) Peaks are in reverse order of appearance on the gas chromatograms.

Peak areas not measurable are shown as dashes.

Table XXI. The products of phytol heated at 350°C as a percentage of the original amount of phytol.

t hrs	alkene %	alkane %
0.5	21	3
2	31	4
4	32	6
7	31	10
17	24	15
21	18	24
24	19	23
28	9	24

Table XXII. Approximate percentages of alkenes and alkanes present at different times relative to the amount of phytol heated at 350°C.

HYDROGENATION EXPERIMENTS

The gas chromatograms obtained from the hydrogenation of the products of phytol heated at 350°C showed a homologous series of alkanes (fig.14). Peaks were absent at the C-17 and C-12 positions. The area of the peaks were measured relative to a coinjected standard (n-eicosane) and hence, the amount of product of a particular carbon skeleton was calculated relative to the original amount of phytol present. The results are shown in table XXIII.

	% Composition							
t hrs	C-20	C-19	C-18	C-16	C-15	C-14	C-13	C-11
0.5	35.1	25.2	3.7	0.4	0.7	0.9	-	-
2	16.4	14.1	4.7	2.8	5.8	2.7	1.2	0.7
4	14.8	14.6	3.4	3.0	3.4	2.6	1.2	0.9
7	11.9	11.2	4.1	3.5	4.4	3.9	3.2	1.2
17	10.6	9.7	6.3	3.5	4.6	3.9	4.3	2.5
21	10.3	9.3	8.4	5.2	4.7	4.3	5.9	3.1
24	7.8	7.4	4.5	3.5	3.7	3.3	3.0	2.2
28	6.4	4.3	4.6	3.2	3.0	2.5	3.0	1.2

Table XXIII. Precentages of hydrogenated products relative to the original amount of phytol heated at 350°C.

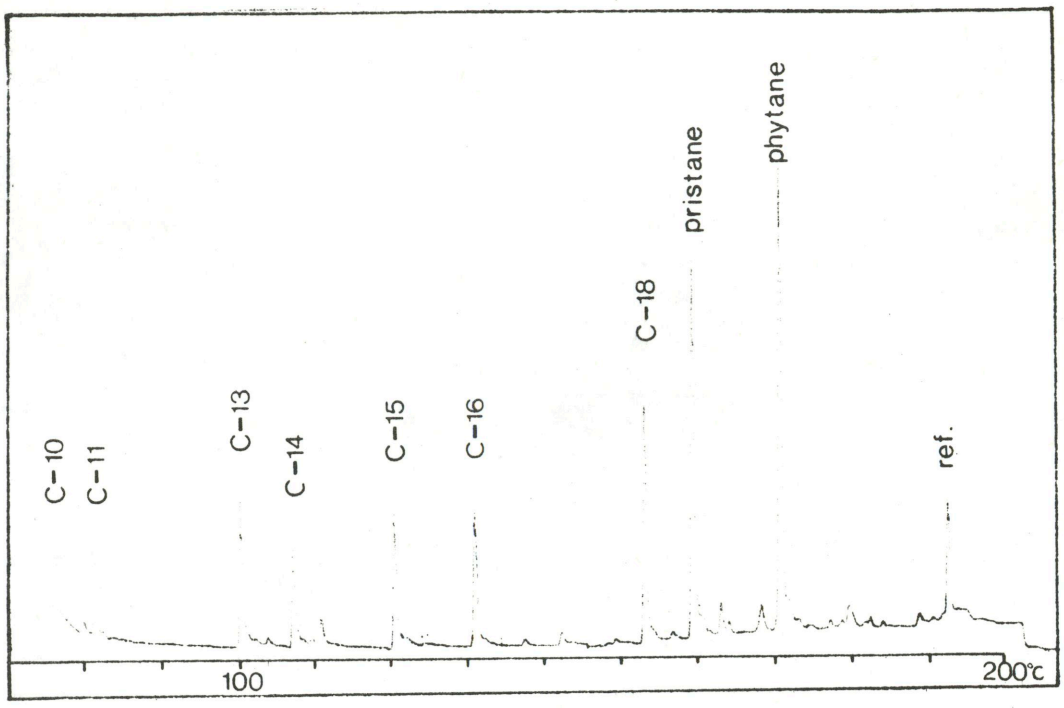


Fig. 14. HYDROGENATED PRODUCTS OF THERMALLY DECOMPOSED PHYTOL

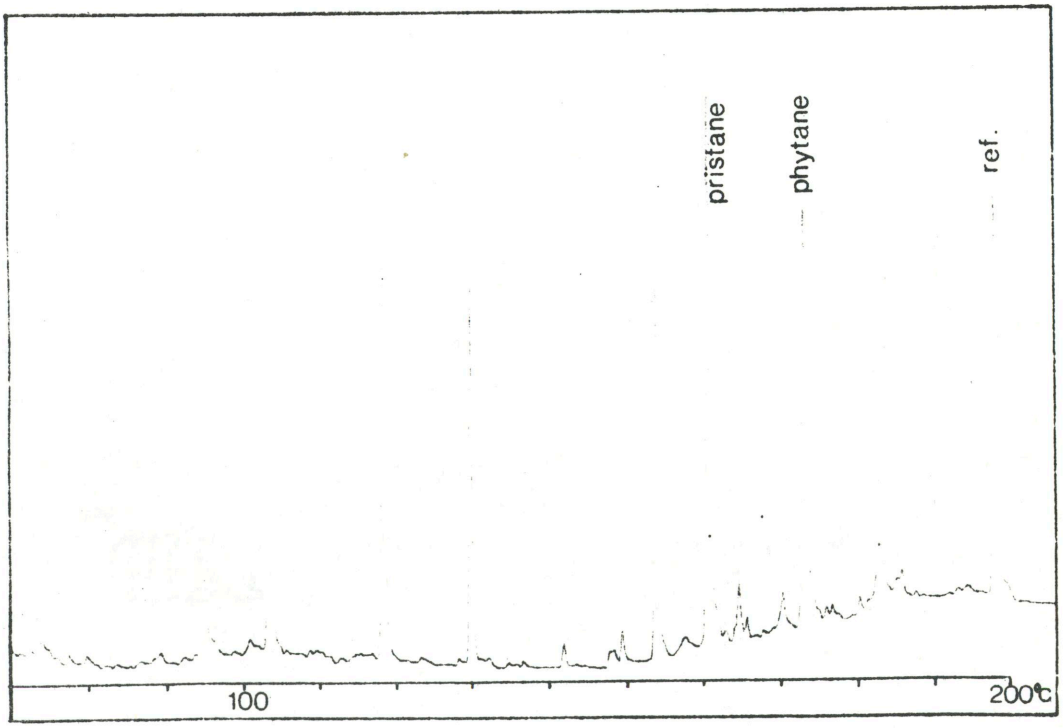


Fig. 15. PHYTOL PRODUCTS AFTER EXTRACTION WITH SULPHURIC ACID

PRODUCTS TREATED WITH SULPHURIC ACID

The gas chromatogram obtained from the sample of products treated with sulphuric acid showed the elimination of the peaks corresponding to unsaturated compounds (fig.15). This aided in the identification of the alkanes present.

SILICA GEL/SILVER NITRATE COLUMN CHROMATOGRAPHY

Gas chromatography analysis of the fractions eluted from the column showed a separation of the products into three main bands. The first consisted of the alkanes (fig.16), the second was the alkenes (fig.17) and the last consisted of the dienes, trienes, etc. The last group of compounds was not identified positively by mass spectrometry.

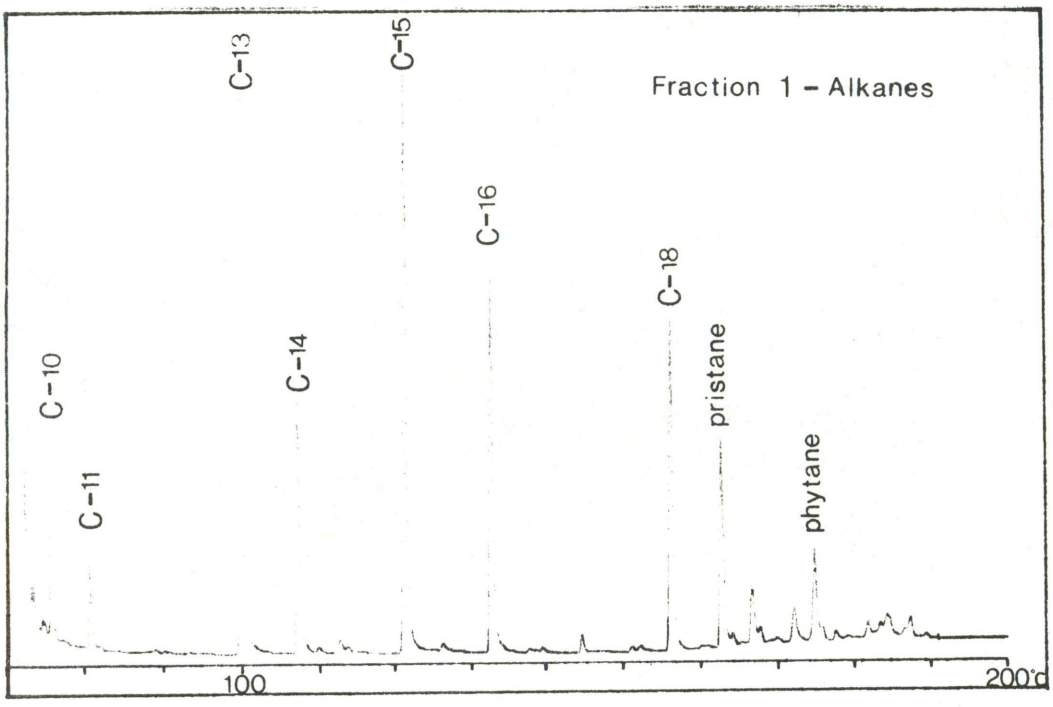


Fig.16. ALKANES SEPARATED BY $AgNO_3$/SILICA CHROMATOGRAPHY

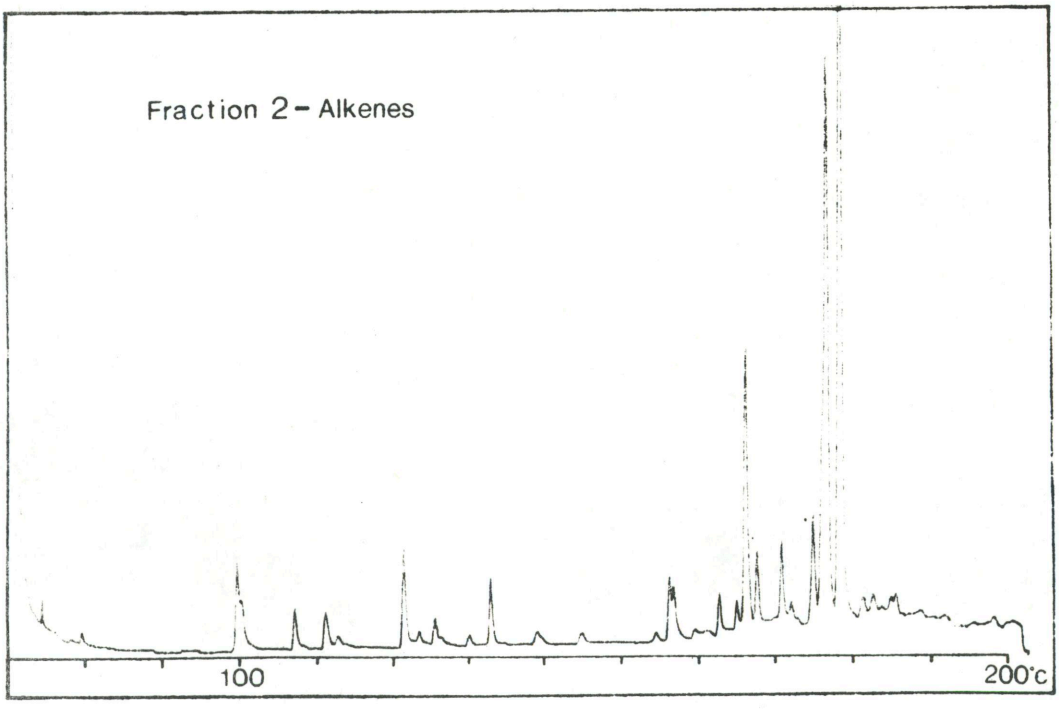


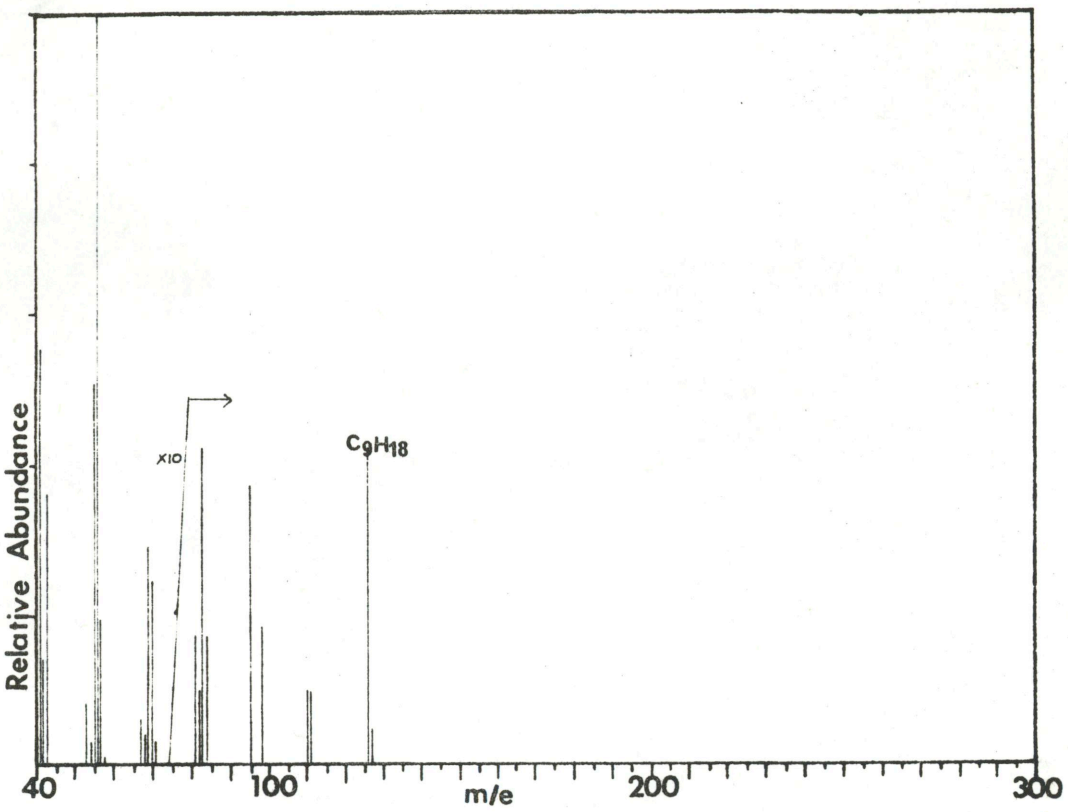
Fig.17. ALKENES SEPARATED BY $AgNO_3$/SILICA CHROMATOGRAPHY

CHARACTERISATION BY MASS SPECTROMETRY

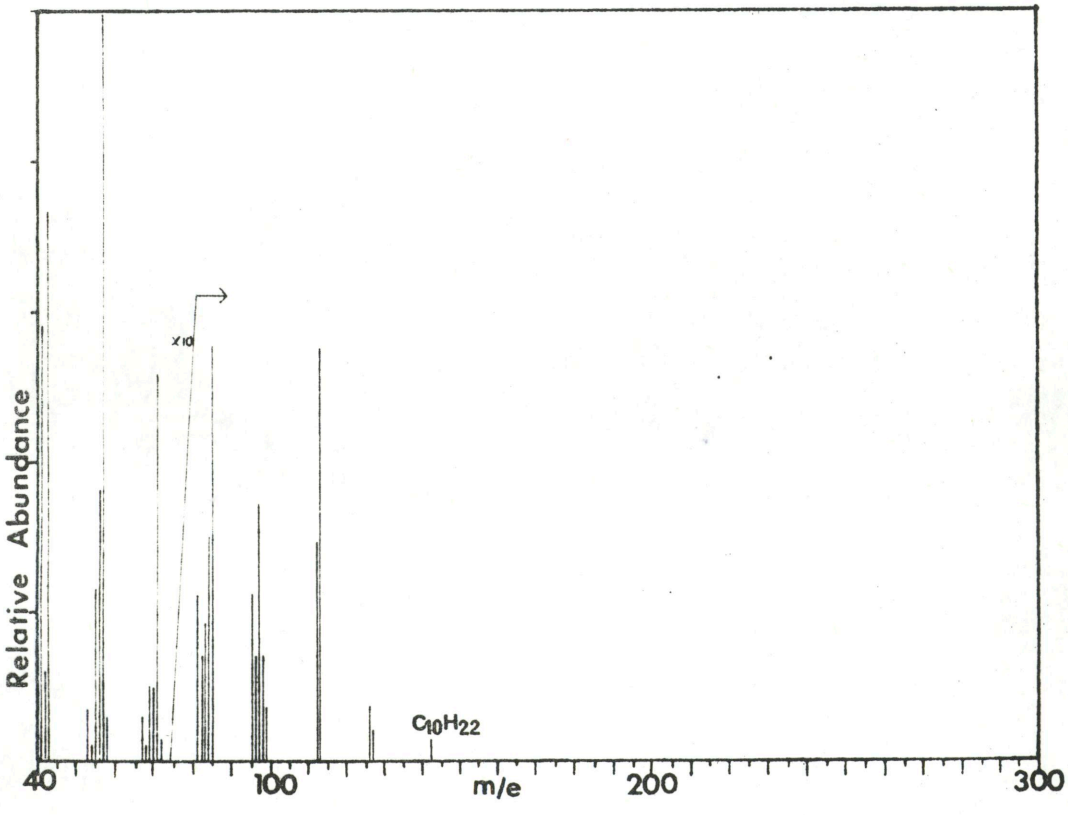
The mass spectra of isoprenoid hydrocarbons have been reported (JOHNS et al, 1966), especially those of pristane and phytane (BENDORAITIS et al, 1962; ORO et al 1965; and GELPI and ORO, 1967). All the compounds identified were saturated or unsaturated isoprenoid hydrocarbons. The fragmentation patterns followed the normal branching rule (HAMMING and FOSTER, 1972). Homologous series of peaks differing by 14 mass units and having more than one maximum were seen. For the unsaturated compounds, it was difficult to locate the position of the double bonds due to excitation of the bonds with the subsequent formation of the resonance-stabilised allylic carbonium ions (SILVERSTEIN and BASSLER, 1967).

Some peaks of interest occurred in the spectrum of the C-20 compound in spectrum 16. Peaks occurred at m/e 246 ($C_{18}H_{30}$), 175 ($C_{13}H_{19}$), 161 ($C_{12}H_{17}$), 133 ($C_{10}H_{13}$), 119 (C_9H_{11}), 105 (C_8H_9), and 91 (C_7H_7). This suggested the formation of some aromatic compounds during the thermal decomposition of phytol.

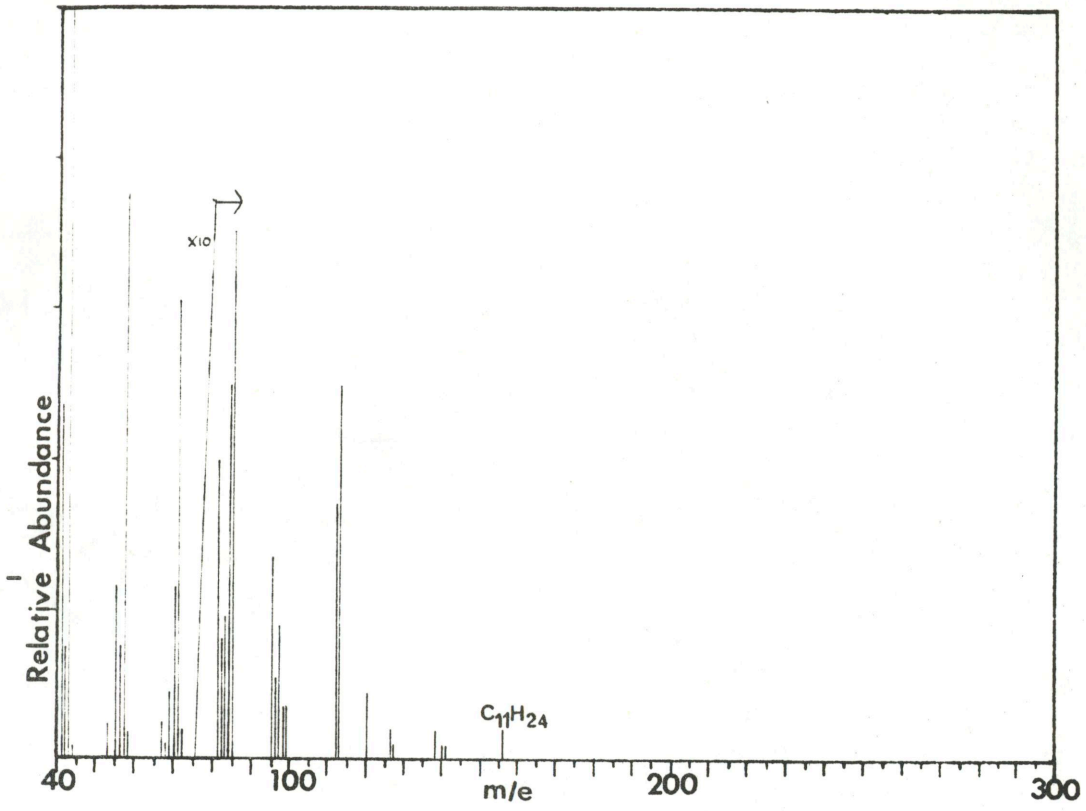
MASS SPECTRA OF THE ACYCLIC ISOPRENOID COMPOUNDS OBTAINED FROM THE THERMAL DECOMPOSITION OF PHYTOL



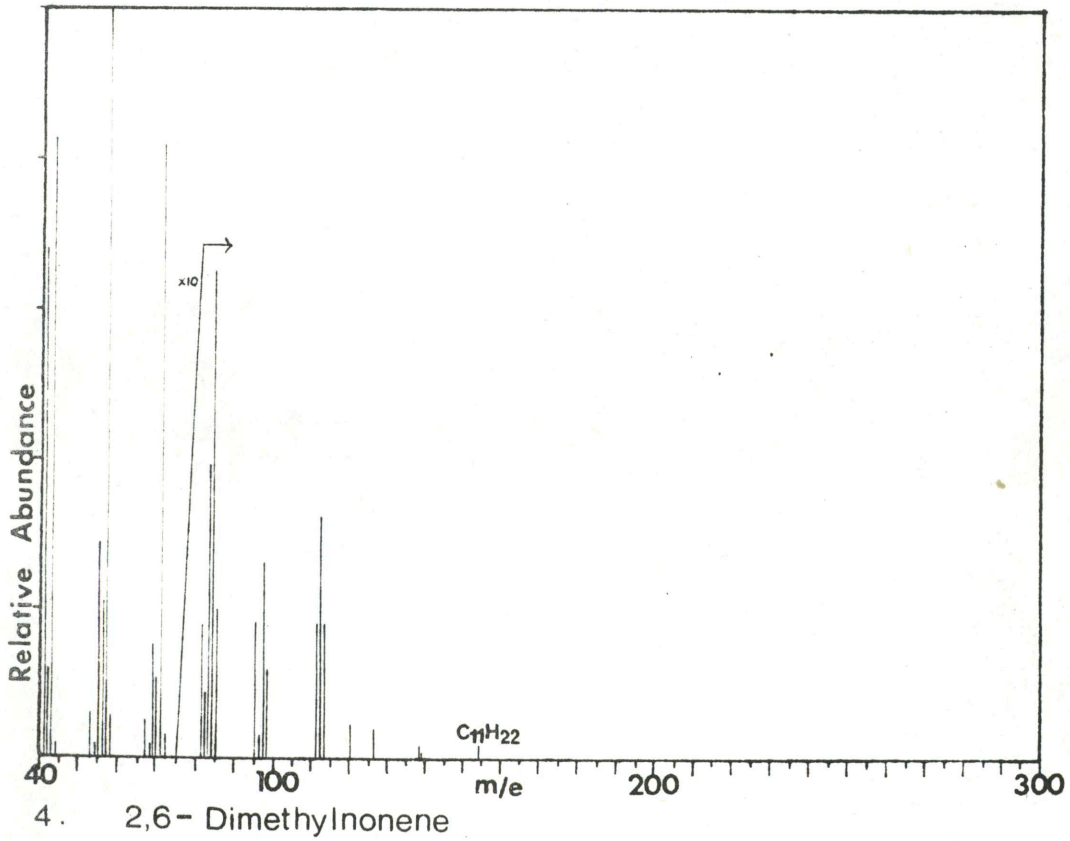
1. 2,6- Dimethylheptene



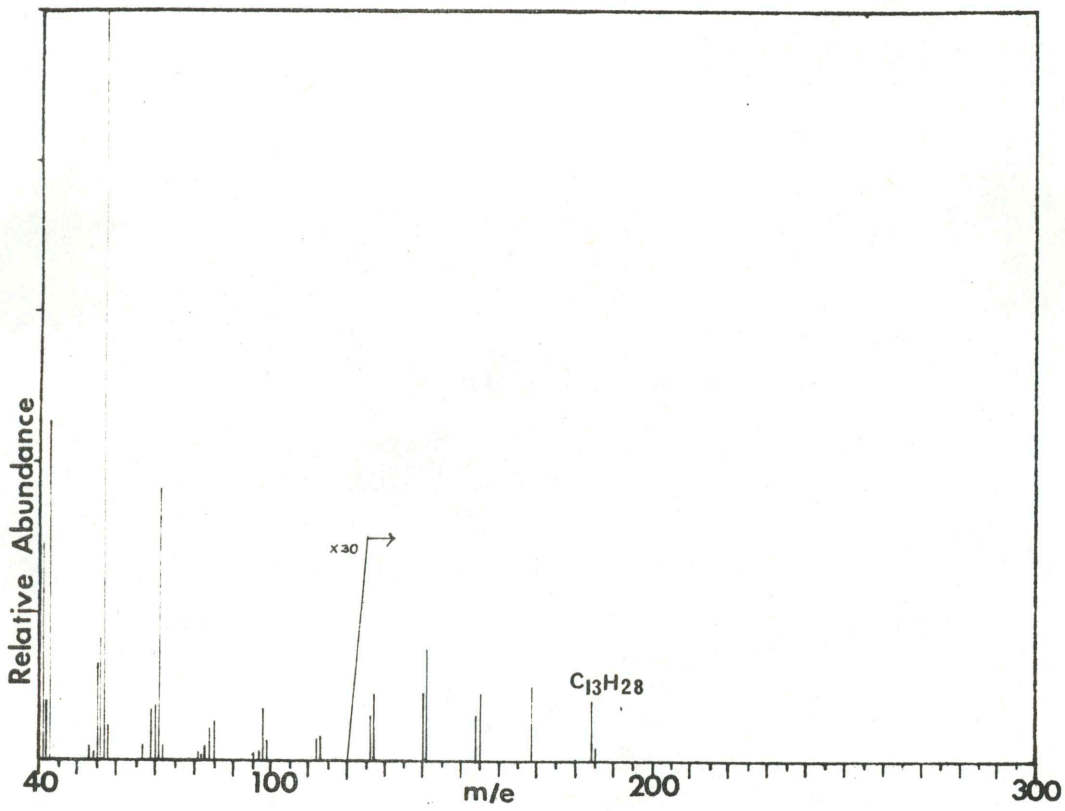
2. 2,6- Dimethyloctane



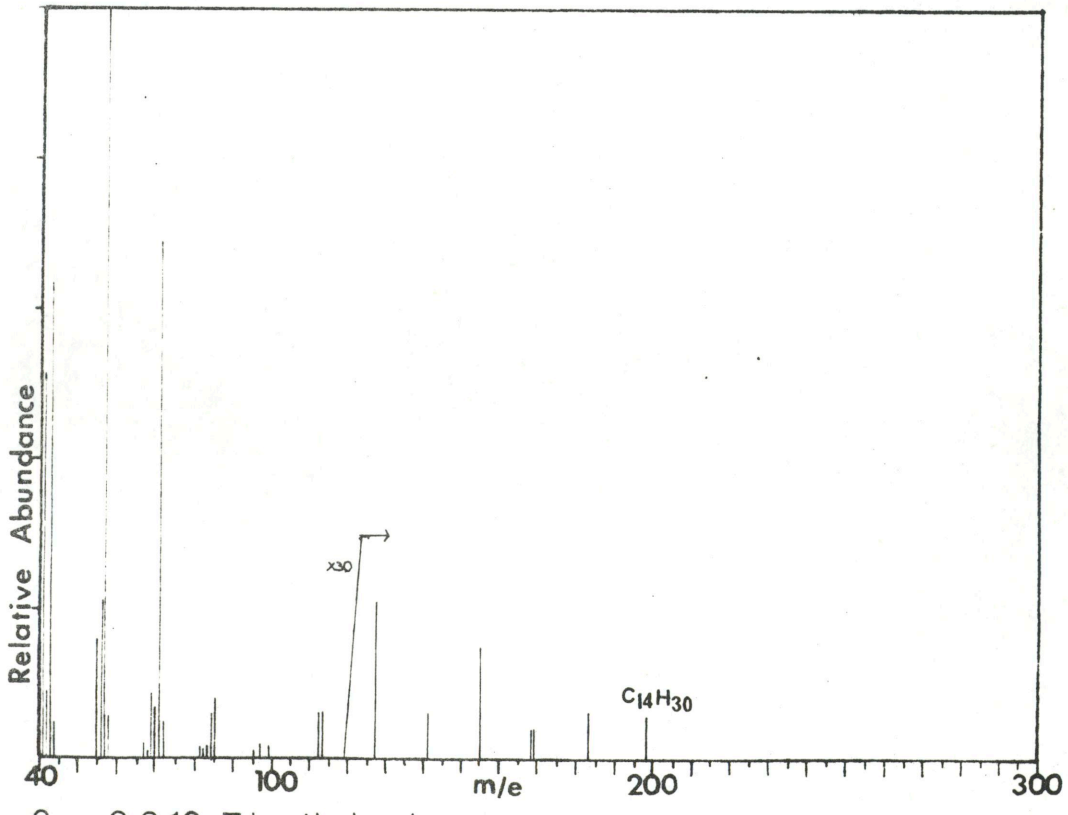
3. 2,6 – Dimethylnonane



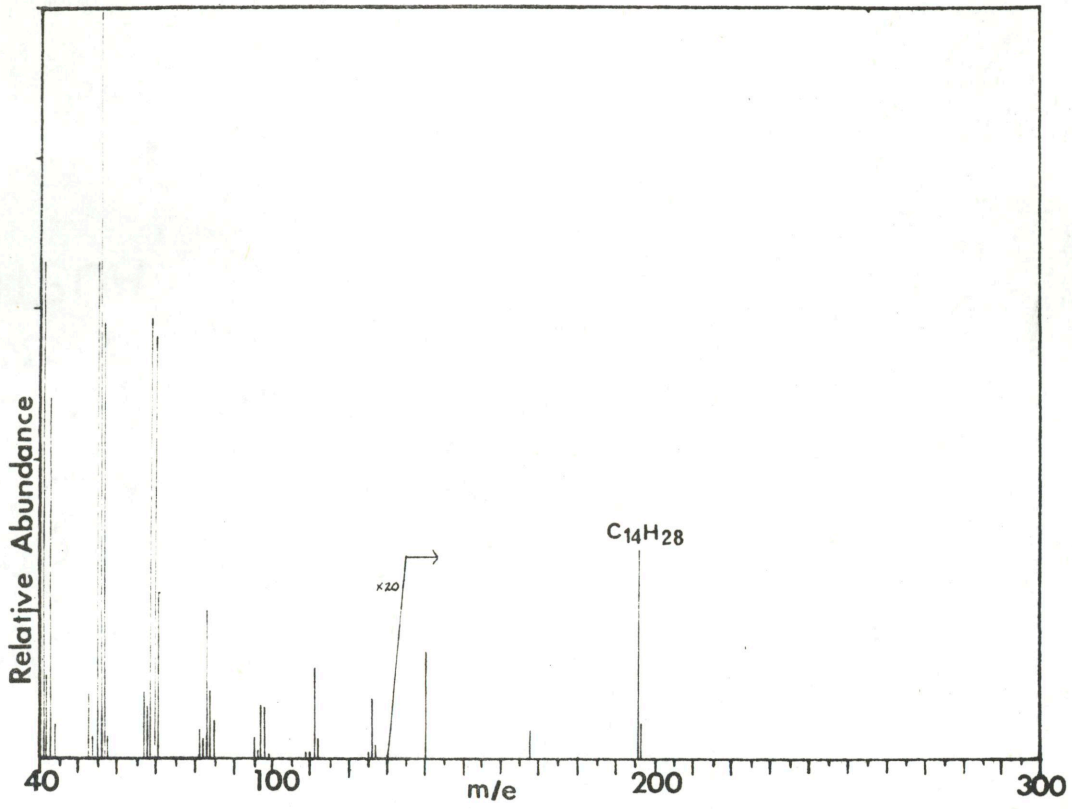
4. 2,6 – Dimethylnonene



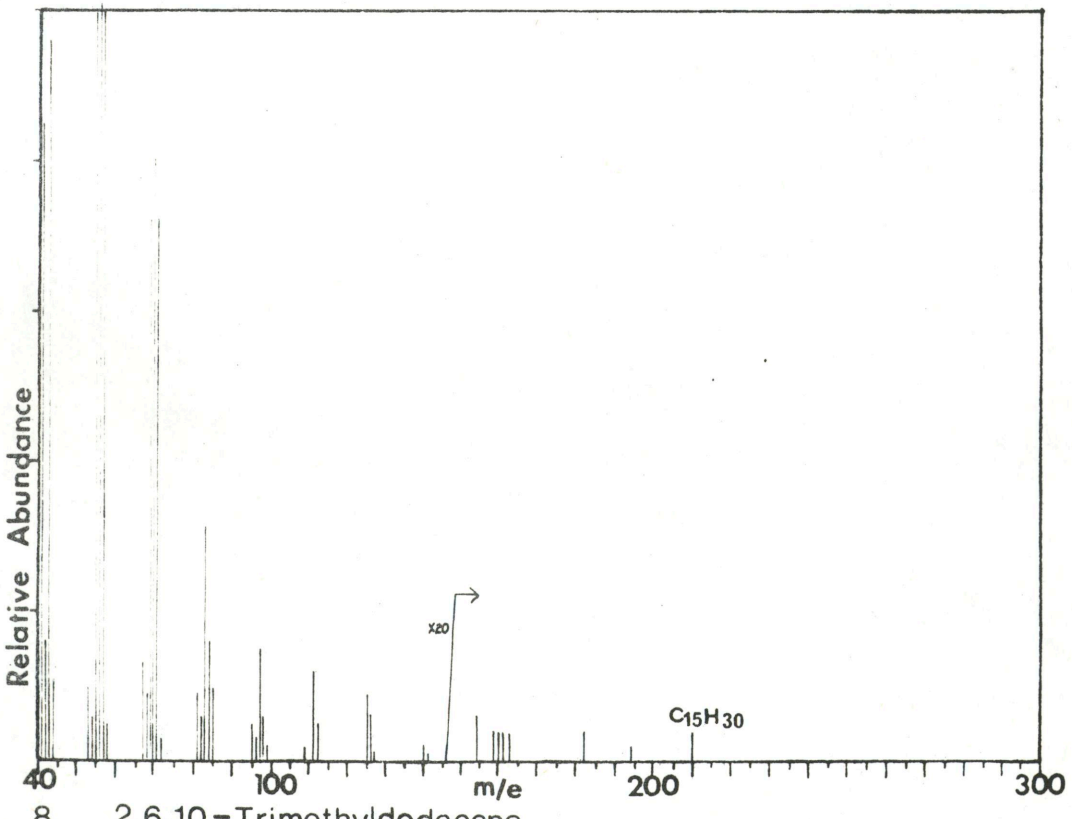
5. 2,6- Dimethylundecane



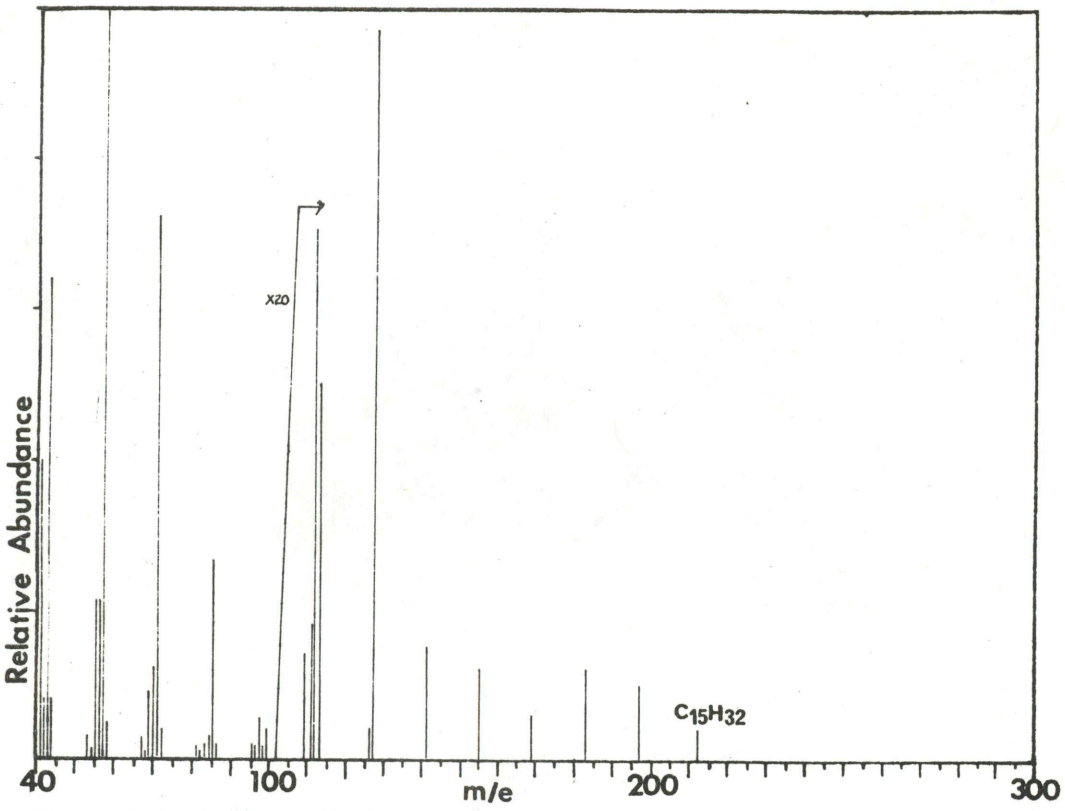
6. 2,6,10-Trimethylundecane



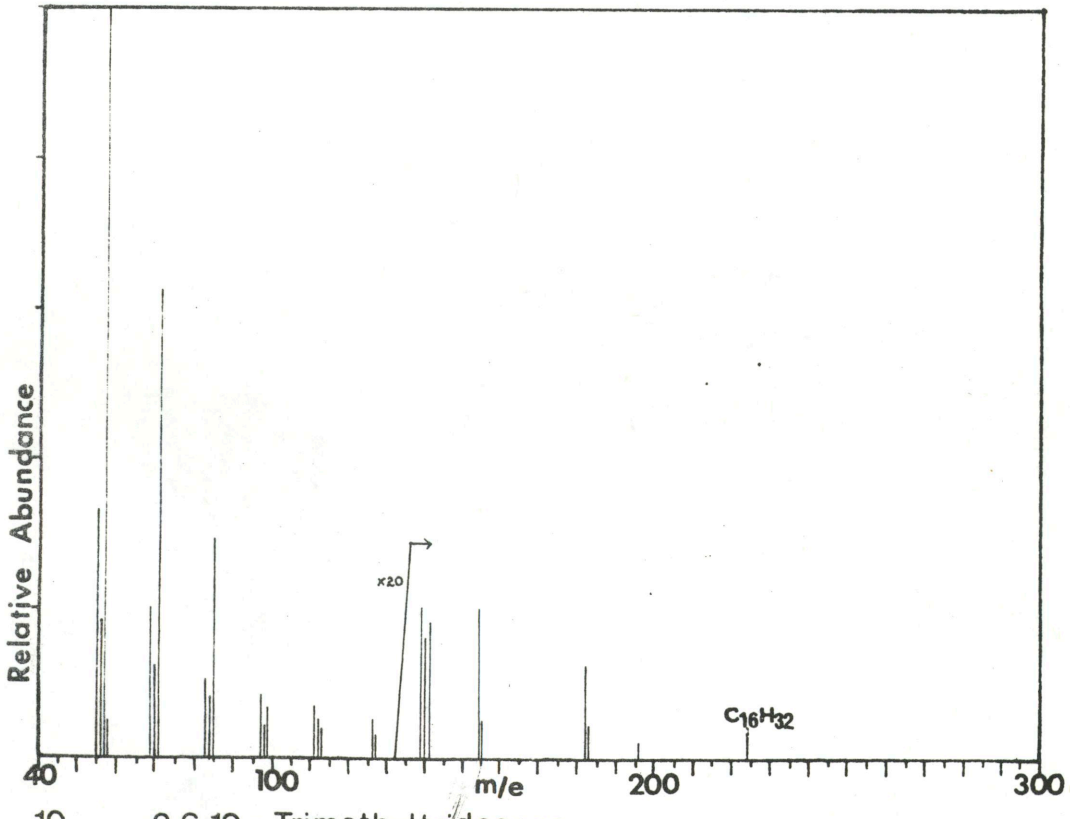
7. 2,6,10 – Trimethylundecene



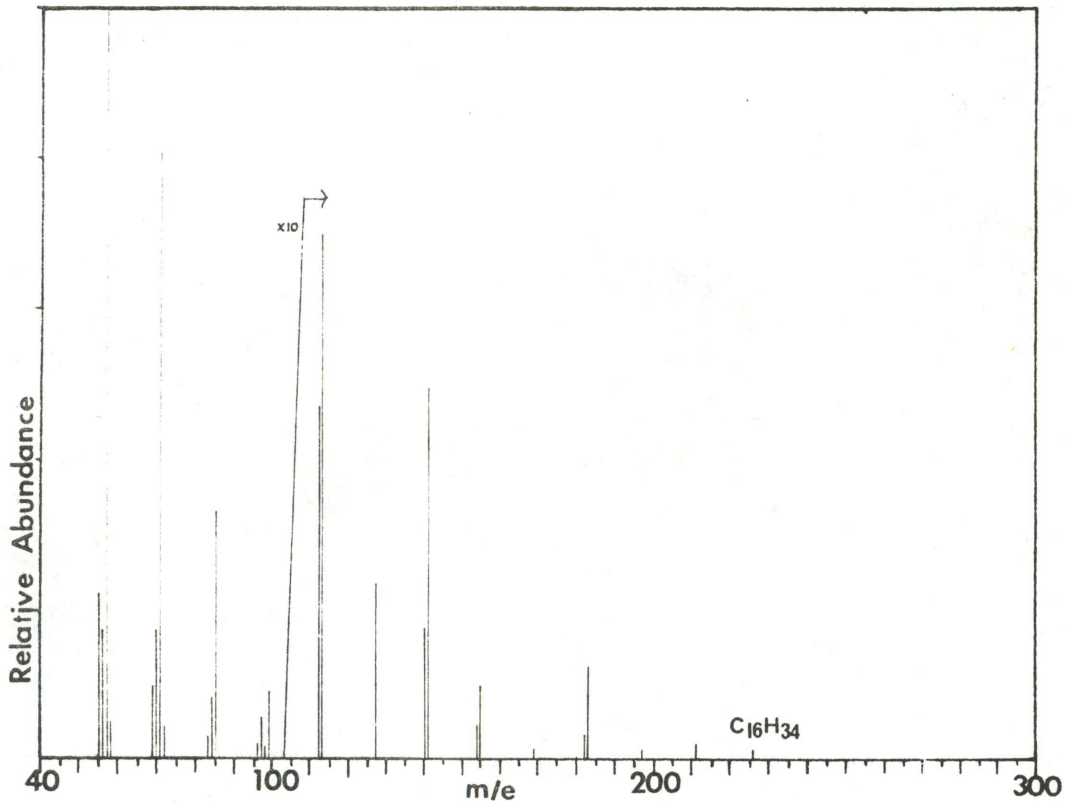
8. 2,6,10 – Trimethyldodecene



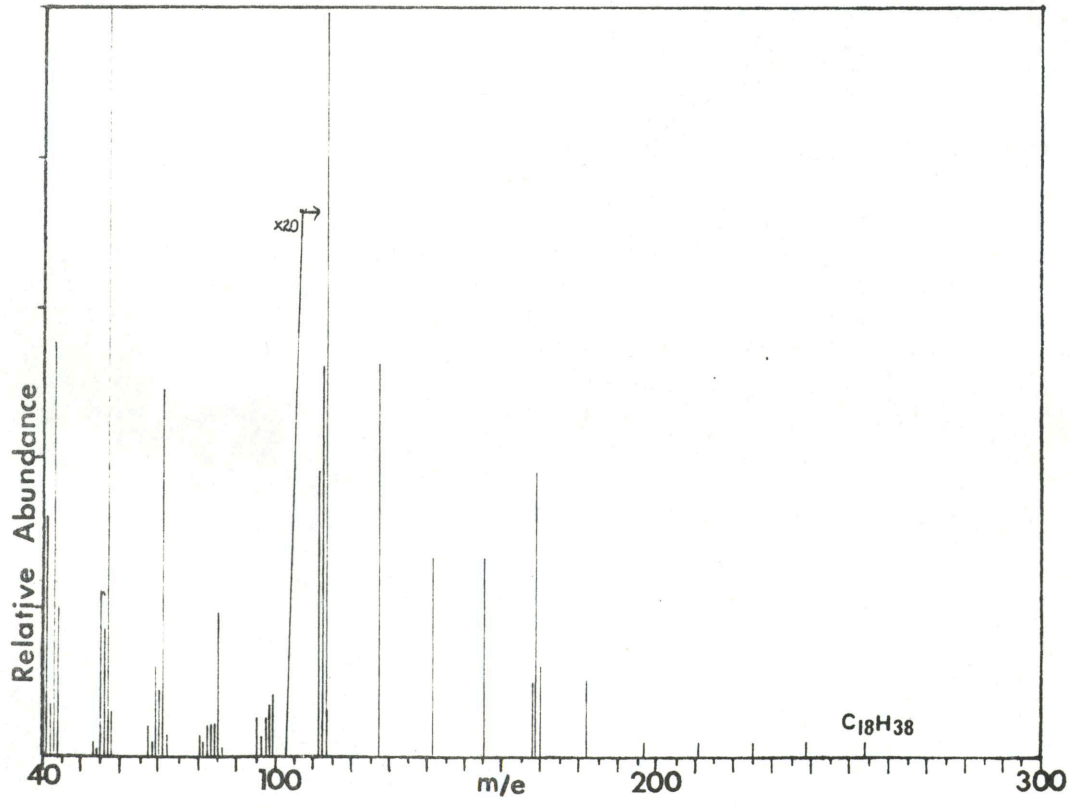
9. 2,6,10 - Trimethyldodecane



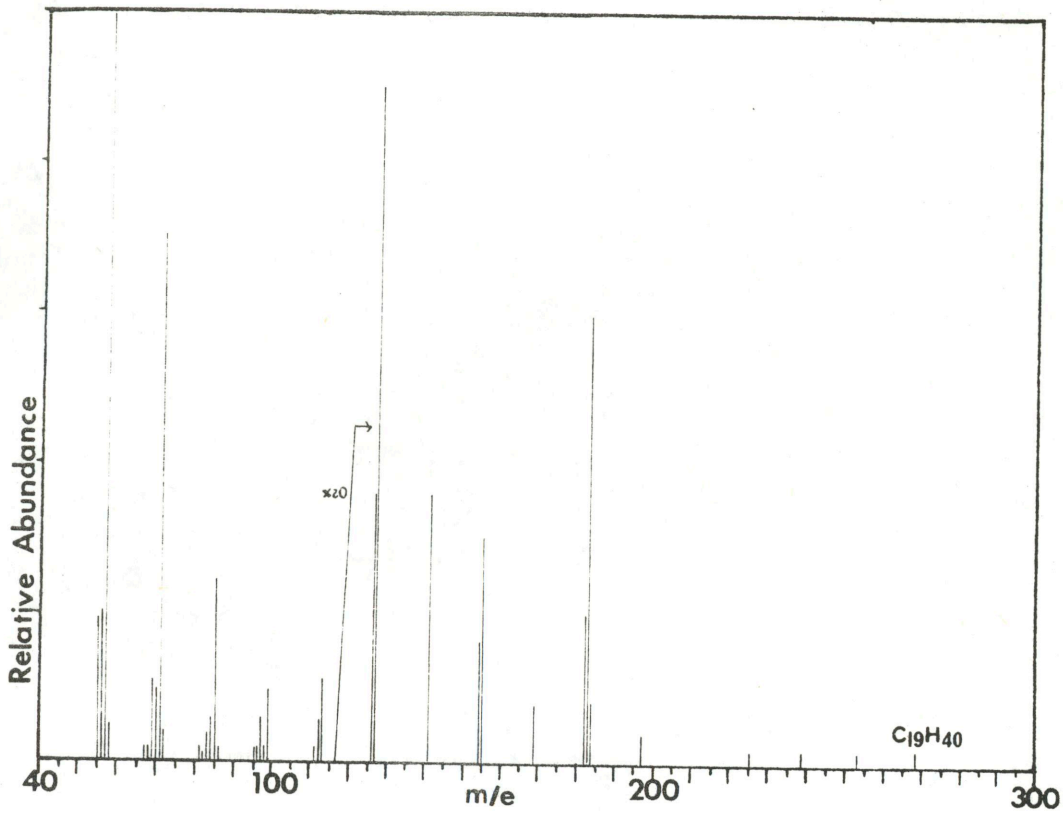
10. 2,6,10 - Trimethyltridecene



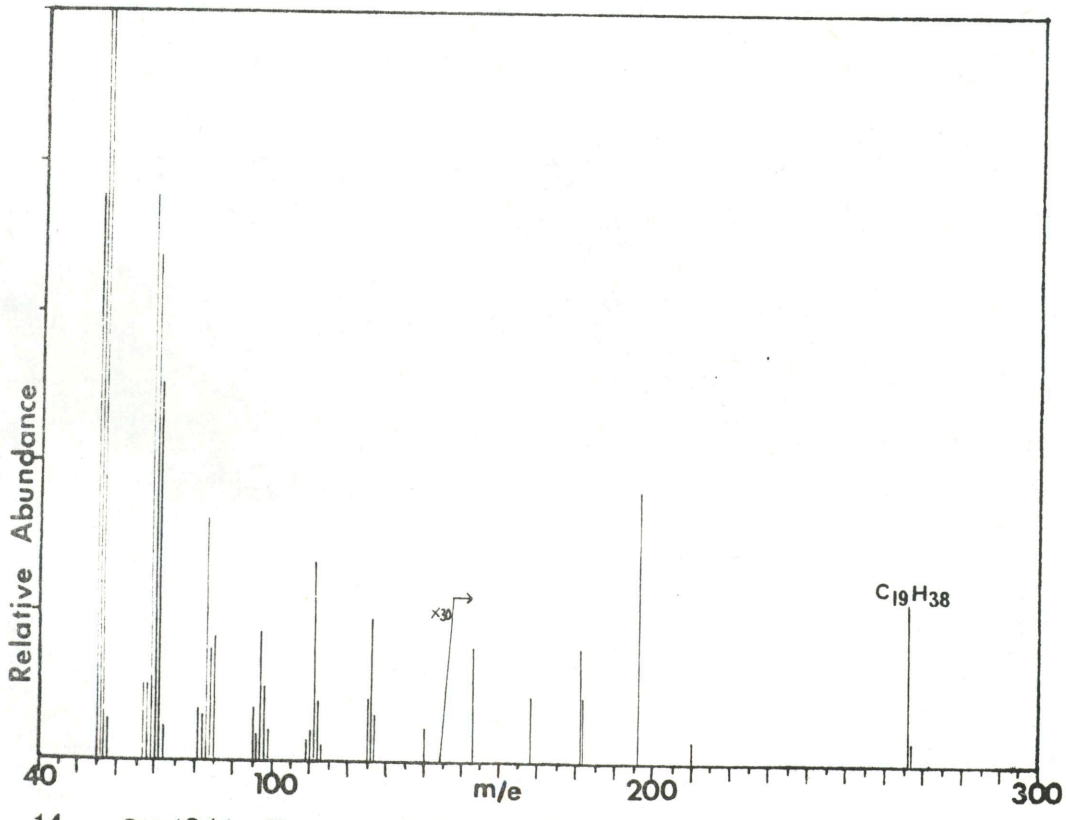
11. 2,6,10 – Trimethyltridecane



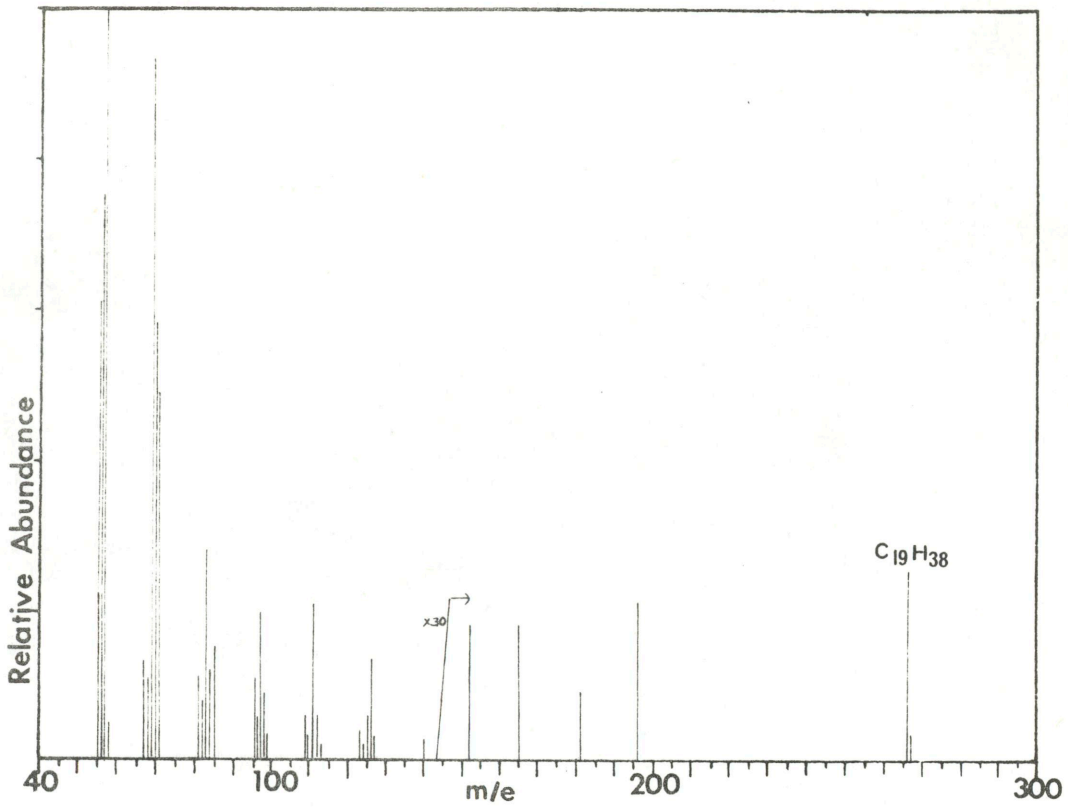
12. 2,6,10 – Trimethylpentadecane



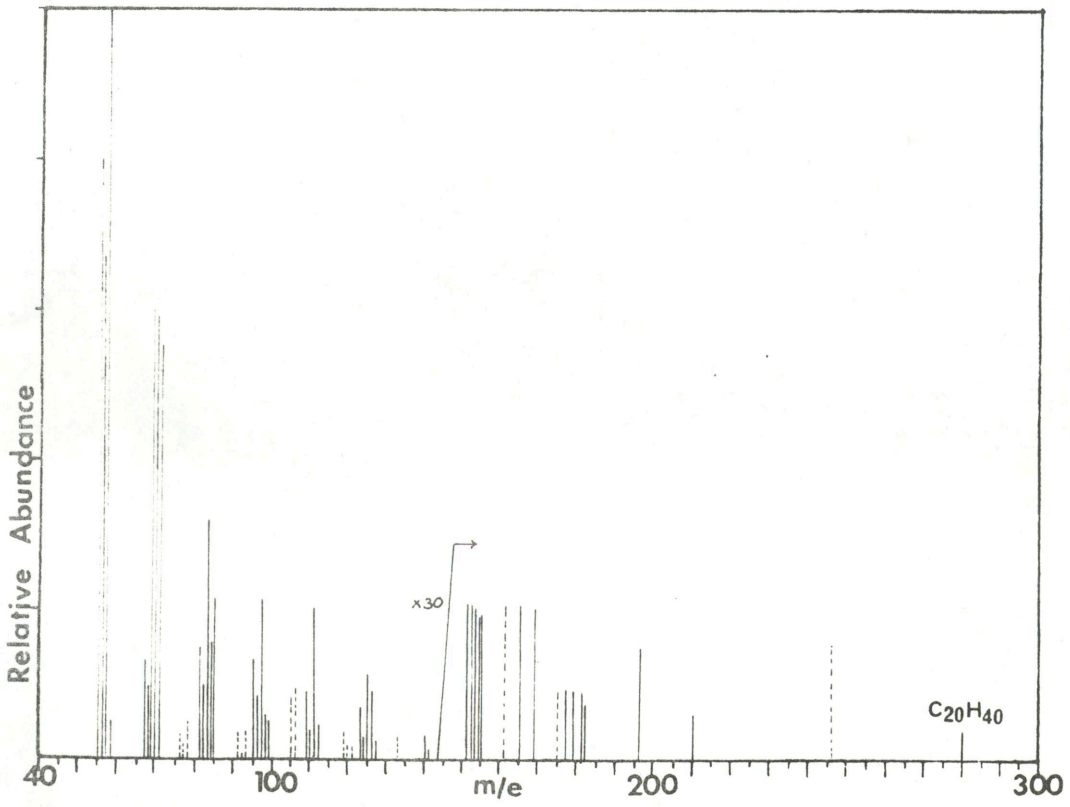
13. 2,6,10,14 – Tetramethylpentadecane (pristane)



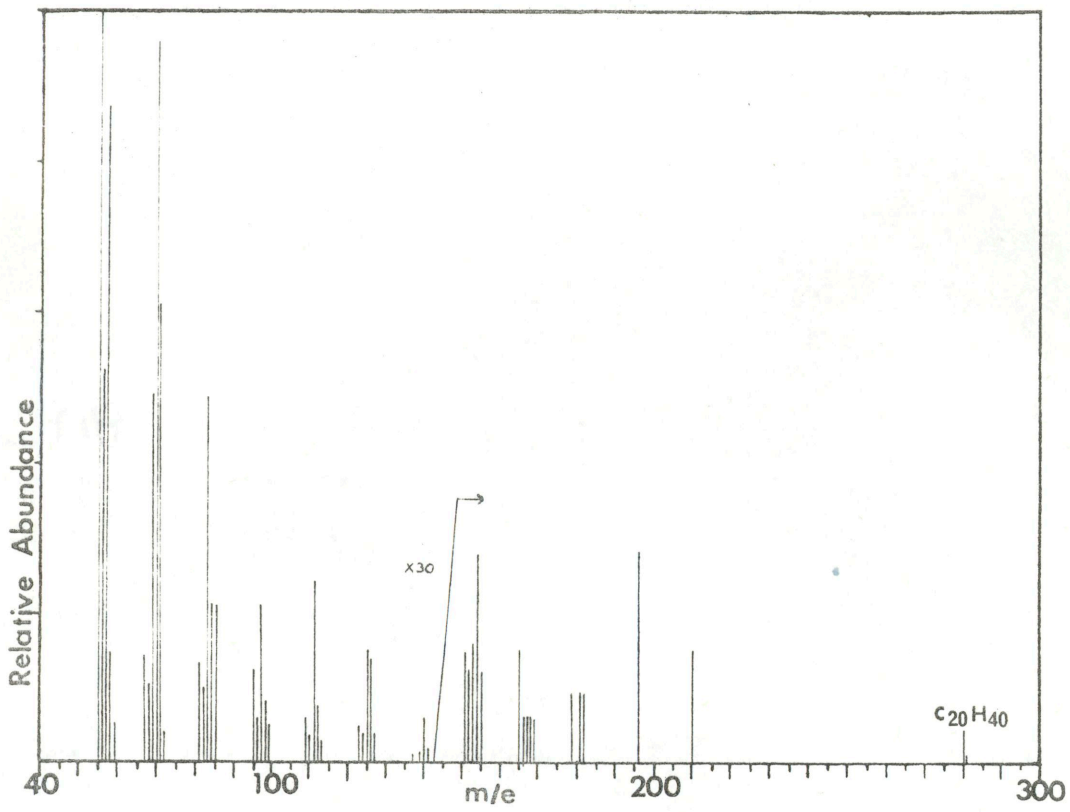
14. 2,6,10,14 – Tetramethylpentadecene (pristene)



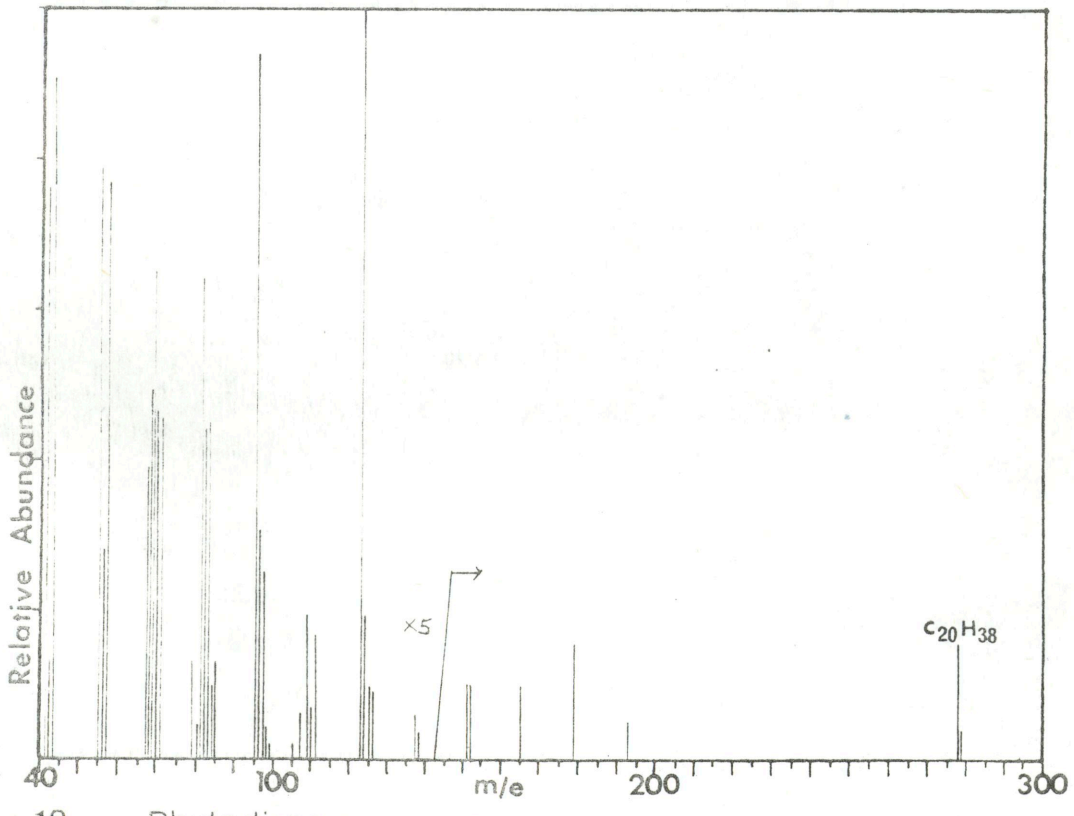
15. Pristene



16. 2,6,10,14 – Tetramethylhexadecene (phytene)



17. Phytene



18. Phytadiene

DISCUSSION

GENERAL

Pristane (I) and Phytane (II) have been detected in sediments of all ages (EGLINTON et al, 1966; ORO et al, 1965), coal (BROOKS et al, 1969) and petroleum (DEAN and WHITEHEAD, 1961; BENDORAITIS et al, 1962). Other isoprenoid hydrocarbons in the homologous series from C-10 to C-20 (XI to XVII) are also found. The isoprenoids C-17 and C-12 are usually absent in sediments though the C-17 isoprenoid alkane has been isolated from shale (McCARTHY and CALVIN, 1967a). It is postulated that the series of isoprenoids from C-10 to C-20 originates from the phytyl side chain of chlorophyll (VII), the phytol (IX) being cleaved from the chlorophyll by hydrolysis. Stereochemical studies of these compounds and their possible intermediates support this postulate (KATES et al, 1967; COX et al, 1970).

Dihydrophytol (XVIII) has been found in Recent and Ancient sediments (SEVER and PARKER, 1969) and may be the precursor of phytane and phytanic acid (X). Both phytanic and pristanic (XIX) acids have been found in Recent sediments (BLUMER and COOPER, 1967), however, pristane is found in Recent sediments whilst phytane is not. Most of the schemes for the diagenesis and maturation of phytol involve such processes as oxidation, hydrogenation, decarboxylation and thermal cracking. It is conceivable that such processes as oxidation and reduction would occur by biological means during early diagenesis. Decarboxylation and thermal cracking could occur as slow processes

over a long period of time during maturation.

Work on the kinetics of the degradation of phytol may elucidate the reaction pathways involved in the formation of lower isoprenoids in the homologous series, including pristane. Experiments carried out in the laboratory must attempt to simulate those conditions which would exist under geologic situations. It must be emphasised that there are limitations involved in setting up a laboratory model which have been discussed earlier. However, the results obtained justify the model in that they show the formation of a series of products in a similar pattern to that found in sediments. The kinetics of the formation of these individual products may provide the answers as to why different products are more preferred than others.

FORMATION OF CARBON SKELETONS

The hydrogenation experiments enable a kinetic study to be done on the formation of the carbon skeletons of the products. Figure 18 shows that the C-19 and C-18 compounds are formed early in the reaction. The lower compounds in the series begin to appear as the amount of C-19 and C-20 compounds is lessened. The absence of the C-17 and C-12 compounds is consistent with that found in sediments. The formation of the individual products is not generally uniform with increase in time, though the decomposition of the C-19 and C-20 structures is occurring continuously (fig.19).

These results show that the formation of the lower products of the series and the decomposition of the higher compounds do not follow simple kinetic laws, and many more

experiments are required in order to establish the kinetic order of the reactions. Experiments carried out at the same temperature establish the order of the reaction whereas those carried out at different temperatures enable the calculation of the activation energies.

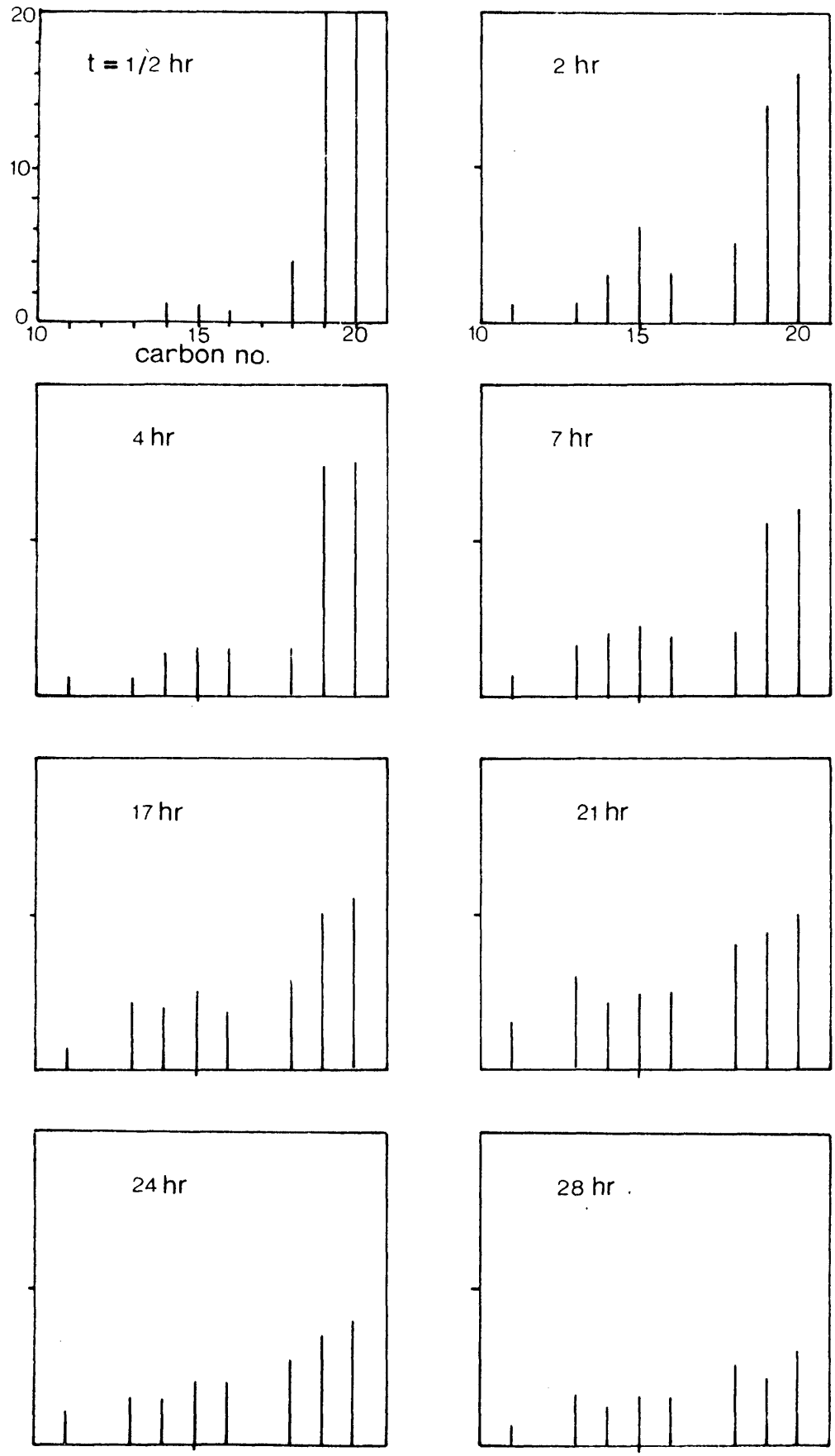


Fig.18. PLOT OF THE HYDROGENATED PRODUCTS OF PHYTOL Vs. TIME

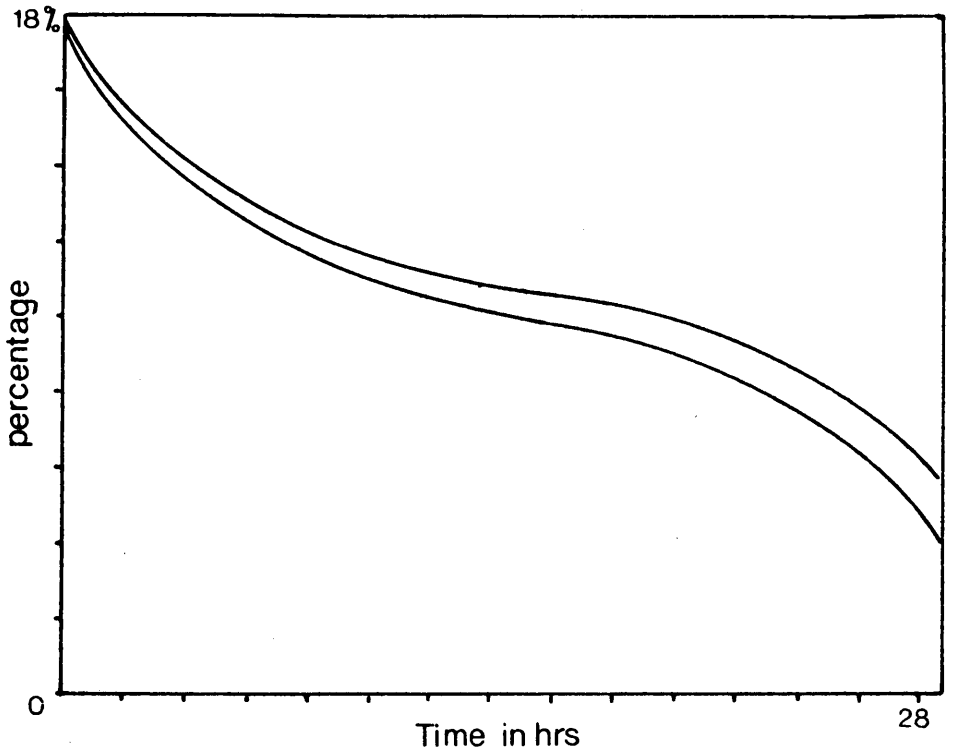


Fig.19. DECOMPOSITION OF THE C-19 & C-20 SKELETONS

FORMATION OF PHYTOL DECOMPOSITION PRODUCTS

Possible pathways for the formation of the phytol decomposition products may involve the following:

(a) Dehydration of phytol to form phytadienes which are hydrogenated to monoenes, which undergo oxidative cleavage at the double bonds to form C-19, C-18 and C-16 isoprenoids (JOHNS, et al, 1966);

(b) Oxidation of phytol to the acid which loses CO_2 to form an intermediate which reacts to give a paraffin and an acid, each product having one less carbon than the original acid, and so on (based on the mechanism of COOPER and BRAY (1963) for n-alkanes); or

(c) Oxidation of phytol to the ketone, followed by formation of the C-18 alkene which forms the lower isoprenoids by thermal and catalytic cracking (fig.22; COX et al, 1972).

However, all these pathways involve the presence of oxidising conditions which are absent in the laboratory model, and the decomposition must be occurring by a purely thermal process such as in free-radical thermal cracking of hydrocarbons (EISMA and JURG, 1969).

Phytadienes predominate in the initial stages of the phytol decomposition and their disappearance corresponds with an increase in the lower isoprenoids, designating the dienes as precursors of the lower compounds. Also the experimental results show that the decrease in the total quantity of alkenes corresponds with an increase in the total alkanes (fig.20), indicating that the alkanes are being formed via alkene intermediates.

The positions of the double bonds in the dienes were not established but phytadienes (XX to XXII) have been synthesised in the laboratory from phytol (JOHNSTONE and QUAN, 1963), and the structure of the dienes obtained experimentally may be similar. Phytadienes XX to XXII have also been found in biological sources (BLUMER and THOMAS, 1965; BURRELL et al, 1966).

Aromatic compounds have been found in hydrocarbon thermal cracking reactions, and the peaks found in the spectrum of the C-20 isoprenoid (spectrum 16) suggest that aromatic compounds are formed during the thermal decomposition of phytol. The peaks in this mass spectrum may correspond to the compound shown in fig.23. A possible pathway for the formation of this aromatic compound may involve electrocyclic addition in a C-19 triene followed by the loss of methane to form an aromatic $C_{18}H_{30}$. Other possible pathways exist, such as the electrocyclic addition of a C-18 triene which would form an aromatic compound without loss of methane.

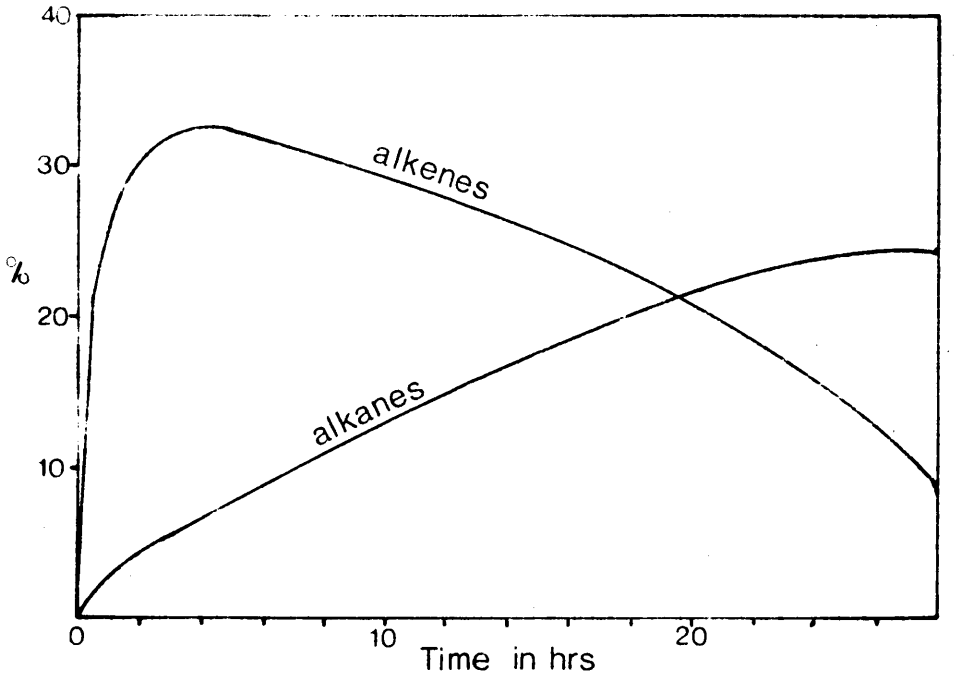


Fig. 20. FORMATION OF ALKANES & ALKENES WITH TIME

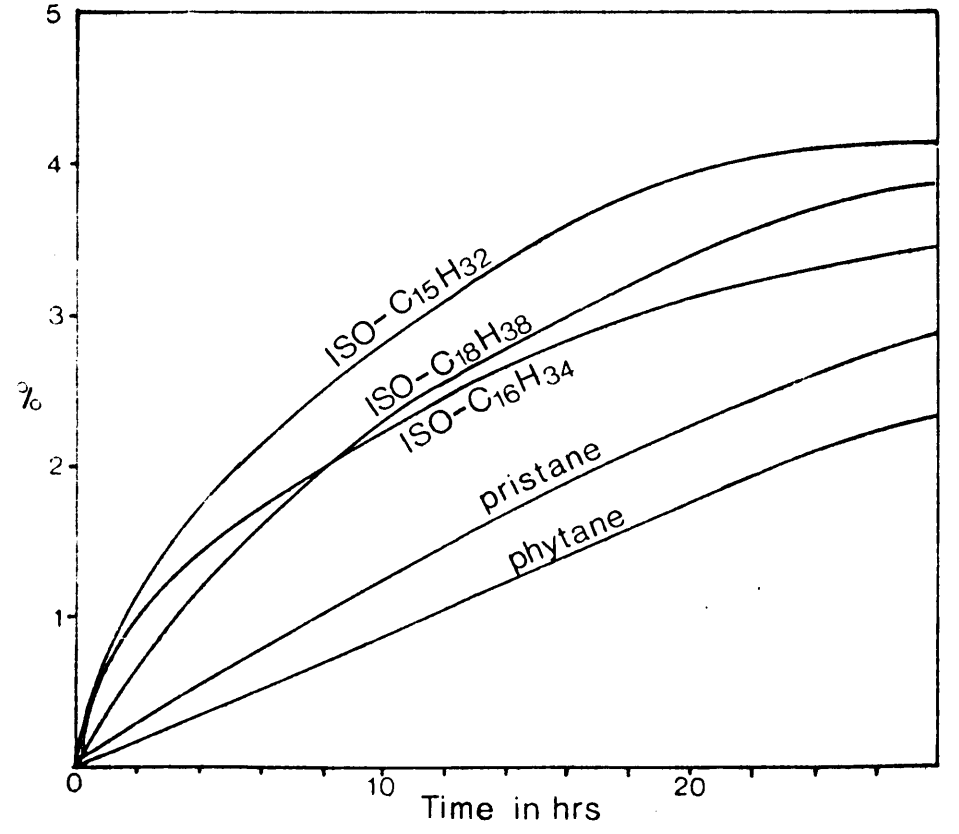


Fig. 21. FORMATION OF SOME ALKANES WITH TIME

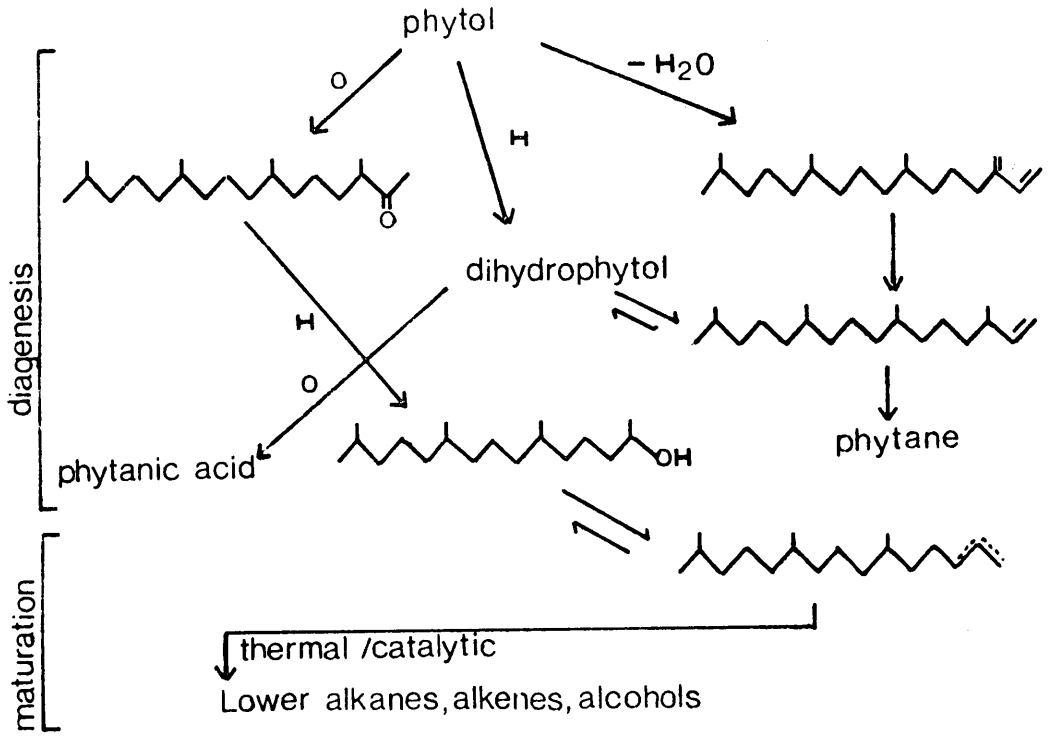


Fig. 22. A mechanism for the decomposition of phytol (after COX et al, 1972)

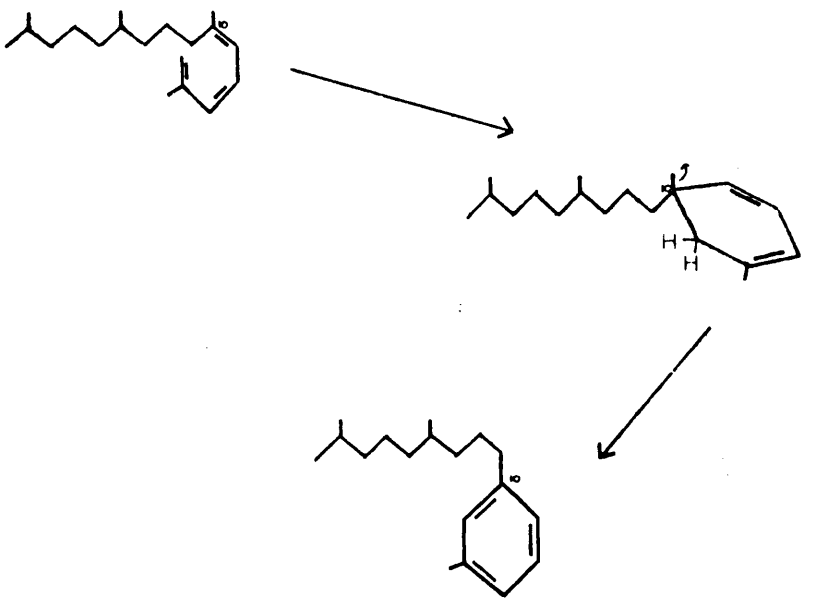


Fig. 23. Scheme for the formation of $C_{18}H_{30}$.

FORMATION OF PRISTANE

It is postulated that in sediments, phytol is hydrogenated to dihydrophytol (XVIII), which is oxidised to phytanic acid (X), followed by decarboxylation to pristane (fig.25, MEINSCHEIN, 1969). The first two stages of this reaction may occur during early diagenesis and the decarboxylation at a later stage over a long period. Pristanic acid (XIX) has been ruled out as a precursor of pristane by AVIGAN and BLUMER (1968), who investigated the conversion of phytol to pristane by zooplankton copepods. Base-catalysed dehydration of phytol yields pristenes (JOHNSTONE and QUAN, 1963), but it is unlikely that the conditions required for this reaction would be present in either the laboratory model or the geological situation. Various pristenes have been isolated from marine zooplanktons (BLUMER et al, 1969), but the quantities are such that they are not likely to be major contributors to organic geochemicals.

Pristenes are formed almost immediately in the phytol decomposition reaction and in comparable amounts to the C-20 alkenes. This suggests that the pristene may be formed directly by a thermal mechanism from the phytol or one of the unsaturated C-20 compounds, and that pristene is the intermediate in the conversion of phytol to pristane. This process may involve a free-radical mechanism such as that proposed for petroleum hydrocarbons (EISMA and JURG, 1969). A pathway for the formation of pristane from phytol which involves the isomerisation of phytol to phytaldehyde, followed by the loss of CO, has been suggested (TARDIF, 1974, fig.24).

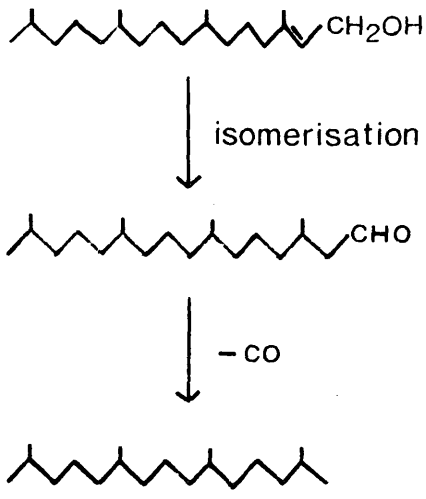


Fig.24. Possible formation of pristane from phytol by thermal reactions (after TARDIF, 1974).

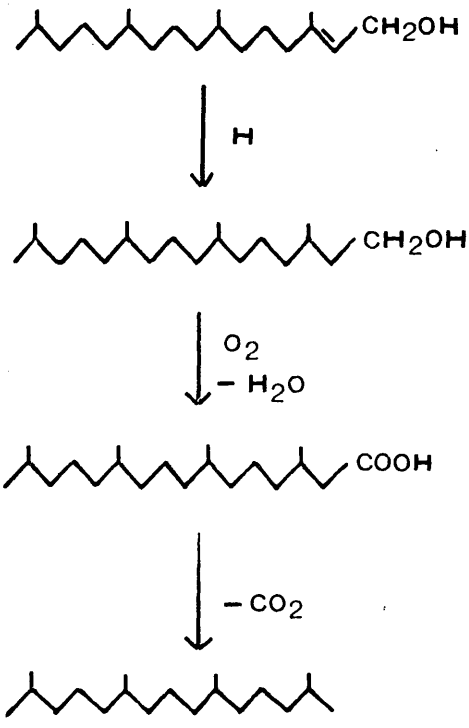


Fig. 25. Suggested formation of pristane from phytol in early diagenesis (after MEINSCHEIN, 1969).

A MECHANISM FOR THE FORMATION OF PHYTOL PRODUCTS

The results show that the following events are occurring in the decomposition of phytol:

(a) phytadienes are formed early and rapidly decompose;

(b) phytenes and pristenes are formed early and slowly decompose;

(c) the formation of the shorter chain compounds coincides with a decrease in the longer chain compounds;

(d) the formation of the alkanes occurs slowly coinciding with a decrease in the alkenes.

A mechanism to explain the decomposition reactions of phytol must take into account the following:

(1) No irregular isoprenoid compounds are formed (i.e. all the compounds have methyl side-chains in the 2,6,(10,14) positions). This implies that the cleavage of the phytol molecule cannot be a random process since compounds with methyl side-chains in the 3,7,(10) position or compounds lacking one or more methyl side-chains are not found;

(2) The C-12 and C-17 isoprenoid compounds are not formed. Hence, more than one carbon atom is being cleaved each time from the phytol molecule except in the case of C-19, and cleavage must be occurring from the functional group end of the phytyl chain in a stepwise manner;

(3) The formation of the shorter chain compounds coincides with a decrease in the phytenes. Hence, the phytenes are the major precursors of the shorter chain compounds;

(4) The C-15 isoprenoid forms more rapidly than other short chain compounds. This implies that a C-5 isoprene

unit is cleaved early in the reaction from the phytene molecule;

(5) The formation of alkenes precedes the formation of the alkanes generally. Also, after cleavage, the isoprenoid molecule appears to either undergo another cleavage or form a more stable compound with an unchanged carbon skeleton.

A mechanism for the thermal cracking of alkanes involving free radicals has been devised for petroleum hydrocarbons (EISMA and JURG, 1969), though the thermal reactions of alkenes are much less understood (BOYD et al, 1967). This mechanism involves the formation of an alkyl free radical due to loss of a hydrogen atom initiated by a collision, followed by the cracking of this radical at the C-C bond located in the beta-position to the carbon atom lacking the hydrogen. This mechanism does involve the cleavage of two carbon atoms and may involve three if a side-methyl is located at the alpha position to the position of the free radical. Cleavage of the side methyl does not occur since no irregular isoprenoid compounds were found.

Based on the above observations and the free radical cracking mechanism, the cleavage sequences which may occur in the phytol skeleton are shown in figure 26. The formation of the C-16, C-14, C-11, etc. isoprenoids would occur by cleavage of the phytol molecule in a stepwise manner commencing at the C-C bond adjacent to the side methyl closest to the functional group end of the molecule. The C-18, C-15, C-13, C-10 etc. isoprenoids would result from a stepwise cleavage from the bond located at the 2-position.

The C-19 isoprenoid must be formed by cleavage of a single carbon atom from the phytol molecule, and, as shown later, decomposition of the C-19 molecule may result in the formation of the C-15, C-13, etc. isoprenoids.

Figure 27 shows the adaption of a free radical thermal cracking mechanism to the decomposition of the phytol molecule. The most stable free radical formed from the phytene molecule would undergo beta-scission to form a C-15 isoprenoid, a C-5 group being cleaved. The C-15 free radical may then undergo cleavage again or form a more stable compound of the same carbon skeleton.

Based on this mechanism and the cleavage sequences proposed, an outline of the pathway for the decomposition of phytol is shown in figure 28. The C-20 and C-19 free radicals are formed early in the reaction which undergo thermal cracking to form the pattern of isoprenoid products found in the experiments and in sediments, the C-17 and C-12 isoprenoids being absent.

A more detailed mechanism for the formation of the lower isoprenoids from phytol is shown in figures 29 to 31. Dehydration of phytol results in the formation of phytadienes producing monoenes which may form C-20 molecules with free radicals at one of the following positions:

(a) The 2-position — Beta-scission of this free radical would result in the formation of the C-16, C-14, C-11, etc. isoprenoids (fig.29);

(b) The 3-position — This would be the most stable free radical, and beta-scission would result in the formation of the C-15, C-13, C-10, etc. isoprenoids (fig.30)

and the C-19 molecule (pristane), as shown in figure 31. The most stable free radical formed from the C-19 molecule would have the free radical at the 2-position, which on undergoing beta-scission would form the C-15, etc. compounds. This may be another reason why C-15 is formed more rapidly than the other shorter chain compounds; or

(c) The 4-position — Beta scission of this free radical may result in the formation of the C-18 (fig.30) or C-14 isoprenoid (fig.29).

The phytenes shown in the above schemes are considered to be the most likely, since the assumed phytadiene structures (XX to XXII) would form stable allylic free radicals producing the monoenes, as shown in figure 32. The mass spectra of the phytenes also support this structure since an intense peak appears at the M-69 position.

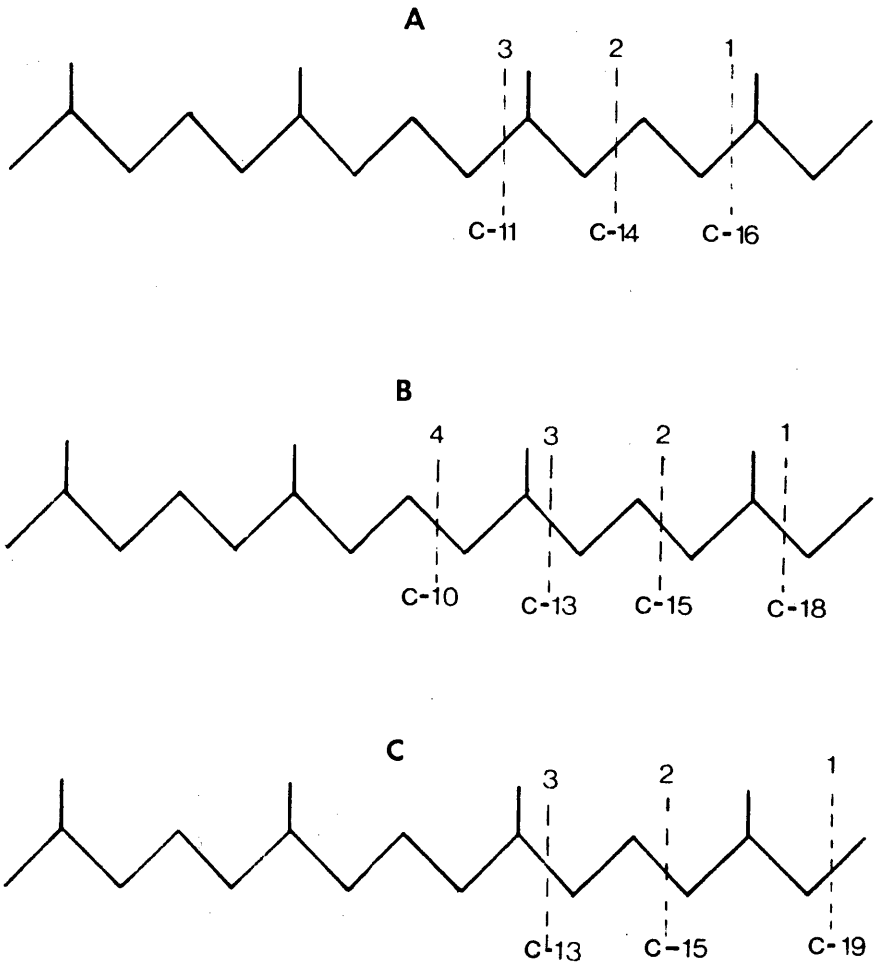


Fig. 26. Cleavage sequences of the phytol skeleton.

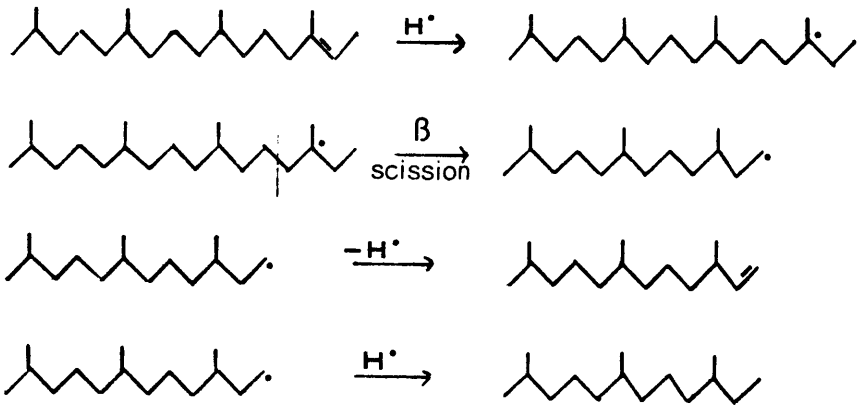


Fig. 27. Free radical thermal cracking mechanism.

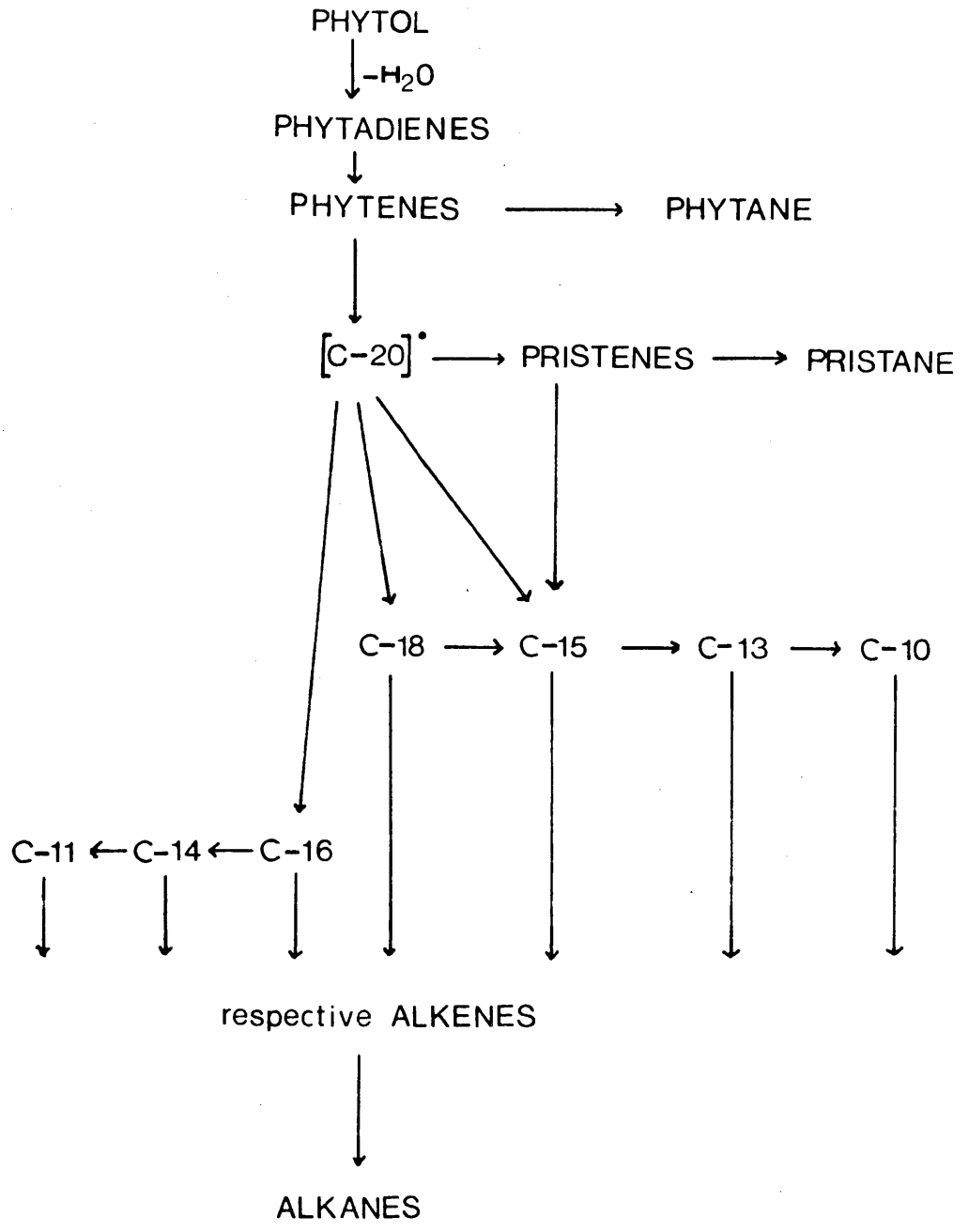


Fig. 28. Reaction pathway for the decomposition of phytol.

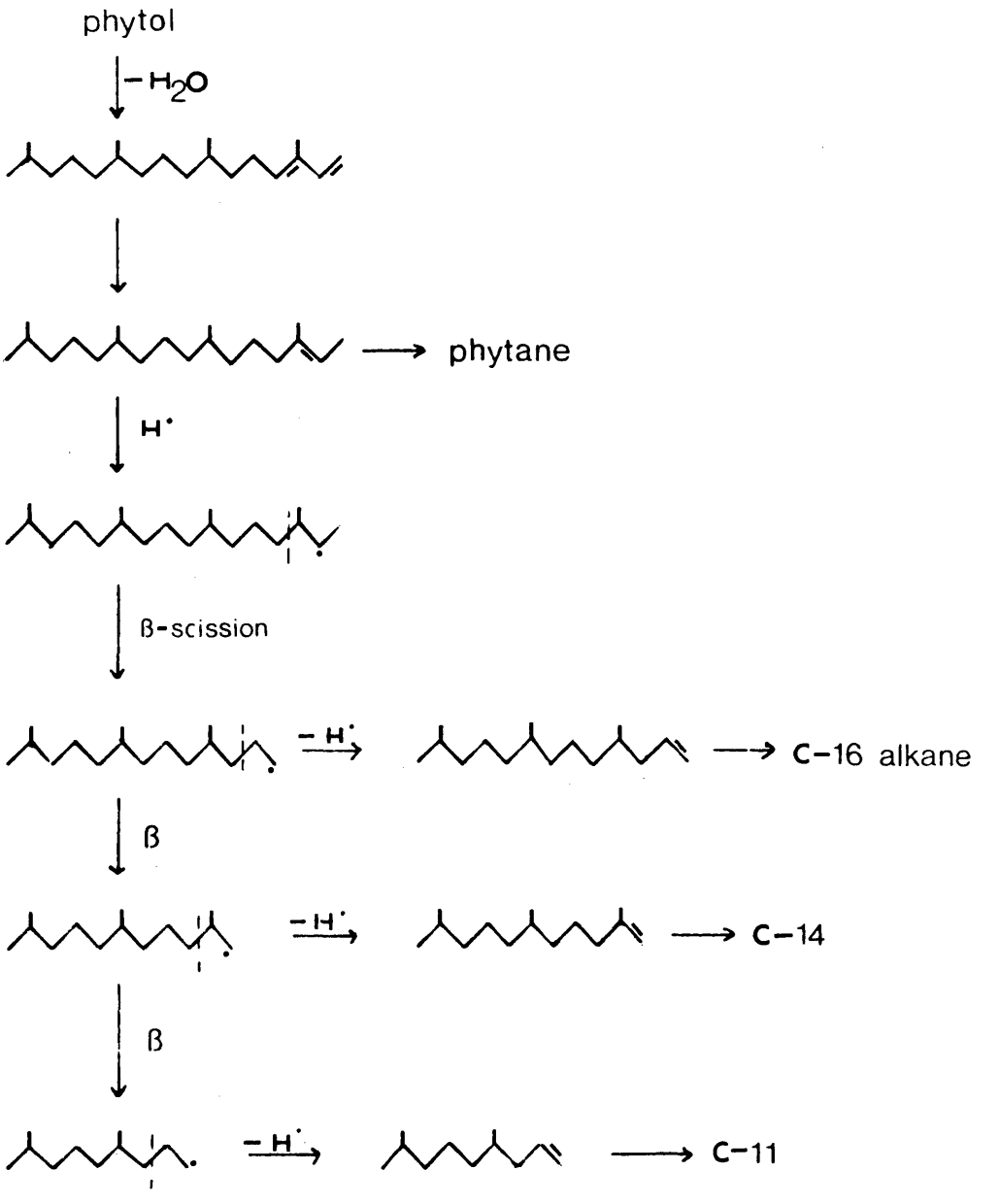


Fig. 29. PATH A – Formation of C-16, C-14 & C-11 isoprenoids.

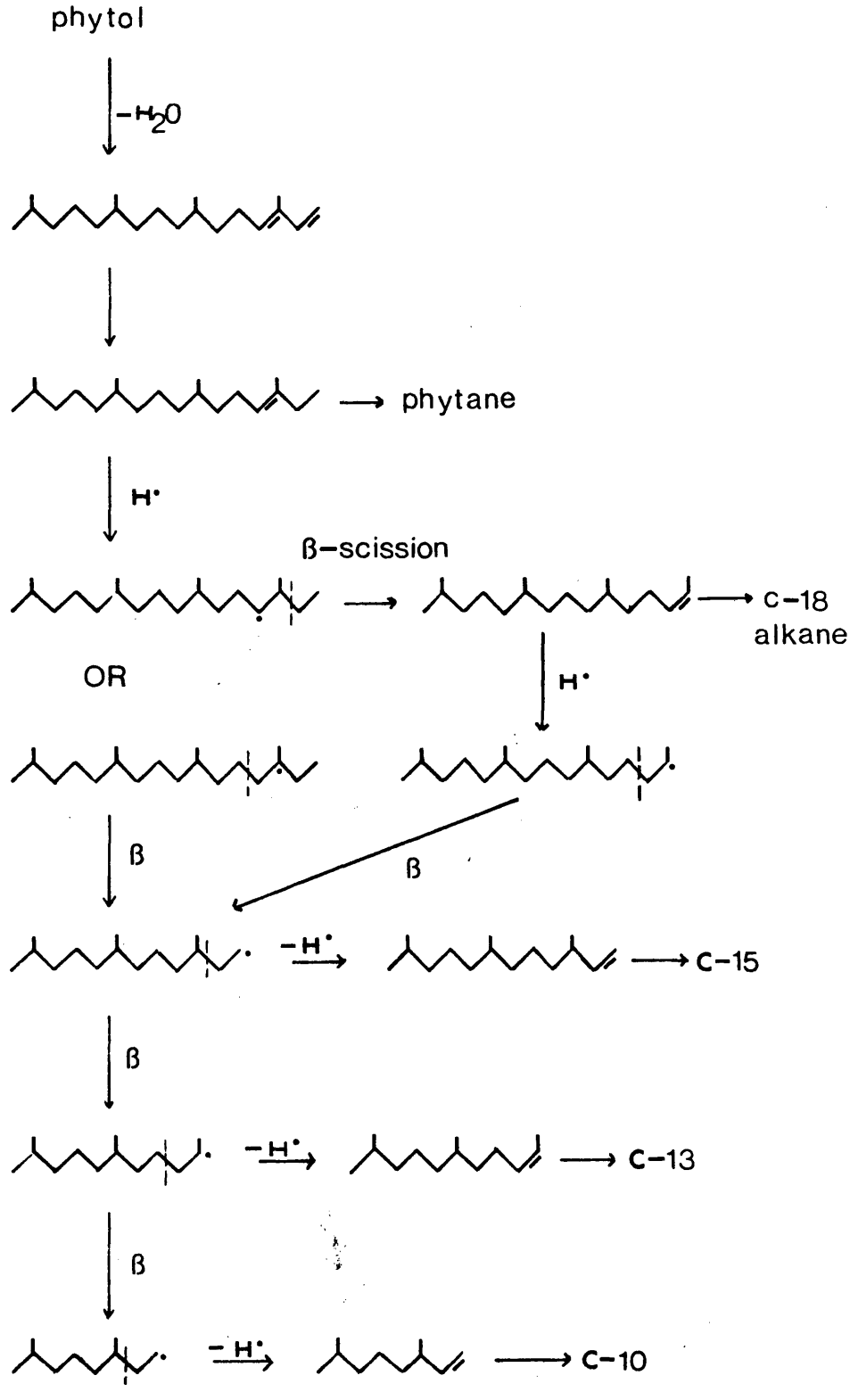


Fig. 30. PATH B- Formation of C-18, C-15, C-13 & C-10 isoprenoids.

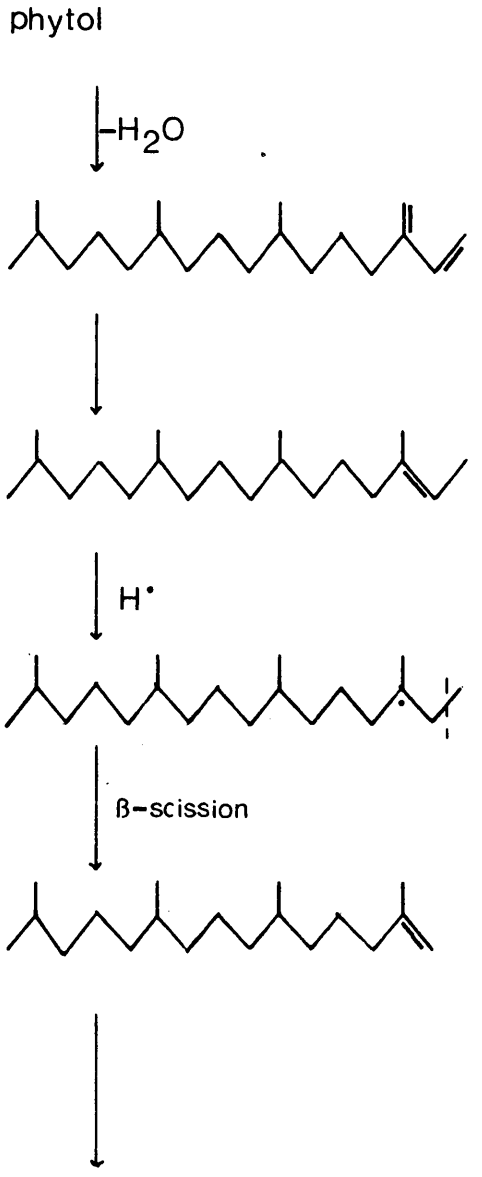


Fig. 31. PATH C - Formation of the C-19 isoprenoid.

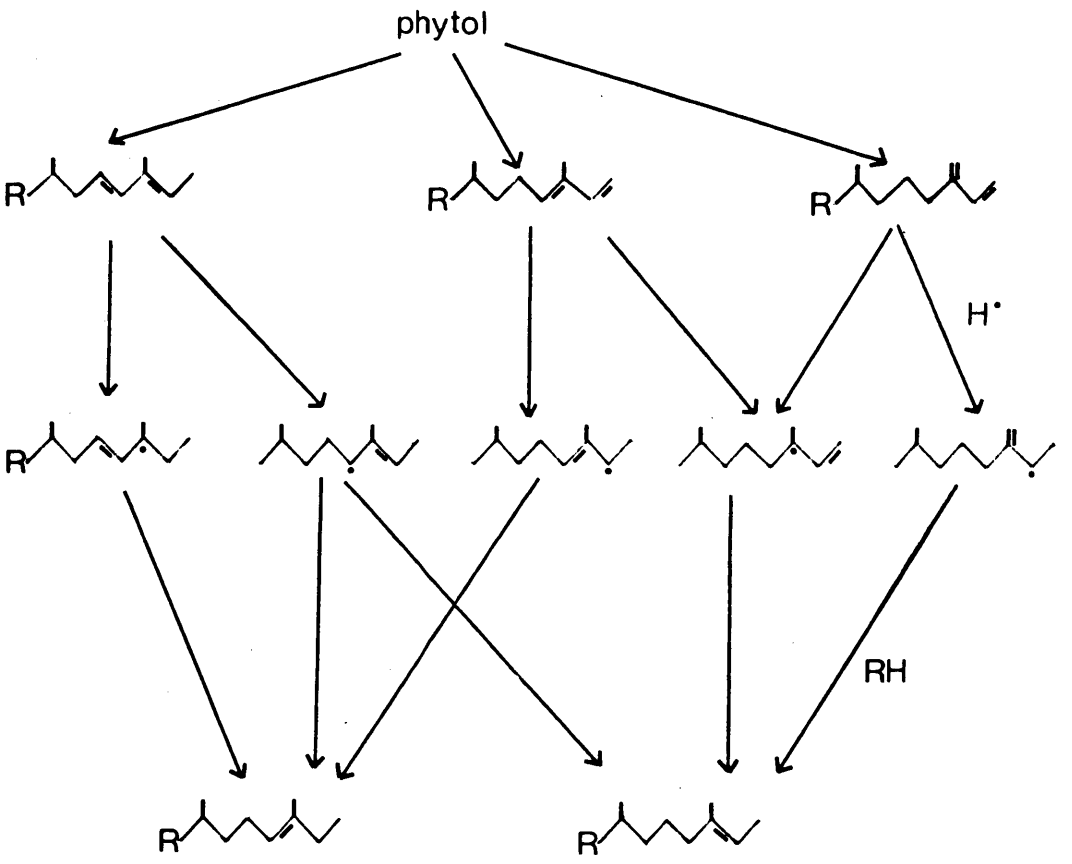


Fig. 32. Scheme for the formation of the most-likely alkenes from phytol.

CONCLUSION

The experiments show the formation of a series of isoprenoids in reasonable yields by a purely thermal mechanism. Catalytic or oxidising conditions were not present in the laboratory model, however, the same pattern of compounds as that occurring in sediments was found. The mechanism suggested is a preliminary one based on only one experiment. Many more experiments are required for any mechanism to be proved.

Experiments on the thermal decomposition of normal 1-alkenes may aid in the verification of the mechanism. The products obtained should be contained in a homologous series of compounds differing by two carbons. Experiments may also be carried out to compare the rate of decomposition of substances such as phytene, with the rate of formation of its supposed product.

In order to look at the kinetics of the decomposition of the phytadienes and phytenes, it is necessary to measure the peak areas accurately. Although the optimum gas chromatography conditions may have been obtained, a problem arises in measuring the peak areas in that there are many compounds emerging from the gas chromatography column concurrently, with the result that the peaks overlap. The following section of this thesis describes the formulation of a computer program to resolve two overlapping peaks using a least-squares technique.

The isoprenoids are important constituents of sediments and their presence is taken to be indicative of life processes at the time of deposition. The study of

the kinetics of the reactions of these compounds may provide valuable information on the reaction pathways involved in the decomposition and formation of organic geochemicals. The mechanism does have some general rules in common with those proposed by TARDIF (1974):

i. cleavage is not random;

ii. the side methyls are not cleaved;

iii. more than one carbon is cleaved each time;

iv. cleavages are successive from one end; and

v. after cleavage, the molecule has the choice of another cleavage or the formation of a more stable compound with an unchanged carbon skeleton.

PART C. A COMPUTER PROGRAM TO RESOLVE OVERLAPPING GAS CHROMATOGRAPHY PEAKS

EXPERIMENTAL

THE PROBLEM

In order to obtain the quantities of particular phytenes and phytadienes present at any time during the decomposition of phytol, it is necessary to be able to measure the areas of the individual peaks of a complex set of overlapping peaks. The analysis of two overlapping peaks was attempted initially, with the intention of expanding this to include a number of peaks.

The determination of the areas of overlapping chromatographic peaks has been approached (BARTLETT and SMITH, 1960; TURINA et al 1970; LITTLEWOOD et al, 1969; ROBERTS et al, 1970). Some of these methods include:

(a) The assumption is made that the overlapping peaks closely approximate a normal or gaussion distribution. The method may be applied to peaks where the maxima are distinct or where one peak appears only as a shoulder on the other. A disadvantage is that very few chromatographic peaks are gaussion in shape and a substantial area of the peak is contained under that section caused by excessive tailing;

(b) When the peaks are asymmetric or skewed it is assumed that the peaks still have some of the properties of a normal distribution. Thus the areas are determined in a similar manner to that for a Gaussion distribution, however, this method still does not compensate for the tailing effect;

(c) A substance which is chemically similar to the compounds in the complex mixture is injected into the gas chromatograph and its peak shape recorded. This provides a standard peak shape and the complex set of overlapping peaks is assumed to consist of a number of peaks of the same shape as the standard. A set of standard peaks is set up so that the sum of all the peaks corresponds to the complex set of experimentally obtained peaks. The method of least squares is used in the iteration process.

Method (c) was adopted in this work because the standard peak is experimentally determined and does not depend on known functions for the shape of the curves.

METHOD USED

A digital voltmeter coupled with a printer was connected to the output from the detector of the gas chromatograph. Voltage readings were printed at the rate of three per second, the base-line of the chromatogram being maintained at zero voltage by the detector control. The standard compound used was a closely related substance to one of the compounds of the mixture, having a similar retention time and peak shape.

The program was written in FORTRAN IV (table XXV) for a DDP-516 Honeywell computer. A least-squares treatment was used for the fitting of the standard-shaped curve to the experimentally obtained overlapping curves, which were arranged in an array (table XXIVa). The standard array (table XXIVb) was then moved so that it was positioned at the leading edge of the experimental peaks, at the reading which is close to 70% of the first maximum. The Lagrange

method was used for the interpolation (SWINBOURNE, 1971). The standard array was then adjusted so that the peak heights were coincident with the leading experimental peak.

A second peak was set up by aligning the standard array similarly with respect to location and height at the trailing edge of the experimental peaks. The ratio of the areas of each peak was obtained by taking the ratio of the sums of all the values in each array.

A mixture of n-hexadecane and n-hexadecene (60.40) was injected into the gas chromatograph and the arrays of the overlapping peaks obtained. The standard-shaped peak was obtained by using n-hexadecane alone.

RESULTS

The results showed an array of two peaks with the ratio of the areas 64:36 (fig.33).

DISCUSSION

The method is approximate because it assumes that when each peak is aligned it is free from interference from the other. This limitation imposes the condition that in the separation of a two-component mixture, two maxima must be discernible, which is not always possible in experimental gas chromatography.

After this program was written, a program was published (FRASER and SUZUKI, 1974) which will separate a twelve-component mixture by a least-squares technique. However, this program was too large for a DDP-516 Honeywell with 16K memory. On transcribing, the program was found to

be unworkable when using the combined Gaussion-Cauchy function, but yielded similar results to the above program (table XX), when used with a standard-shape function.

The program written does resolve two overlapping peaks with an approximate solution. A more accurate iteration process may involve the use of a multi-dimensional Newton-Rhapsom process (HARTREE, 1958). The measurements of the areas of a complex set of peaks lies in a workable program to resolve a multi-component mixture. The program of FRASER and SUZUKI may separate up to a four-component mixture on a DDP-516 Honeywell but has yet only been tested for a two-component mixture.

Table XXIV. Input for program.

(a) Experimental array.

5	8	11	23	63	143
236	308	347	358	351	337
317	299	277	255	237	217
198	184	170	164	162	168
186	218	252	282	302	316
315	310	300	287	272	254
237	223	208	192	177	167
153	141	131	120	110	103
95	86	79	73	67	61
58	53	48	44	41	38
34	31	30	27	25	24
21	19	19	18	17	14
14	14	12	12	11	11
10	10				

(b) Standard array

0	1	8	18	32	54
92	178	314	445	528	566
554	527	494	464	431	404
374	344	322	297	272	253
231	214	196	183	168	154
142	128	122	121	100	94
84	80	72	65	61	56
51	47	43	38	36	32
31	28	26	23	23	20
18	17	16	14	14	13
11	11	11	10	9	9
8	8	0	0		

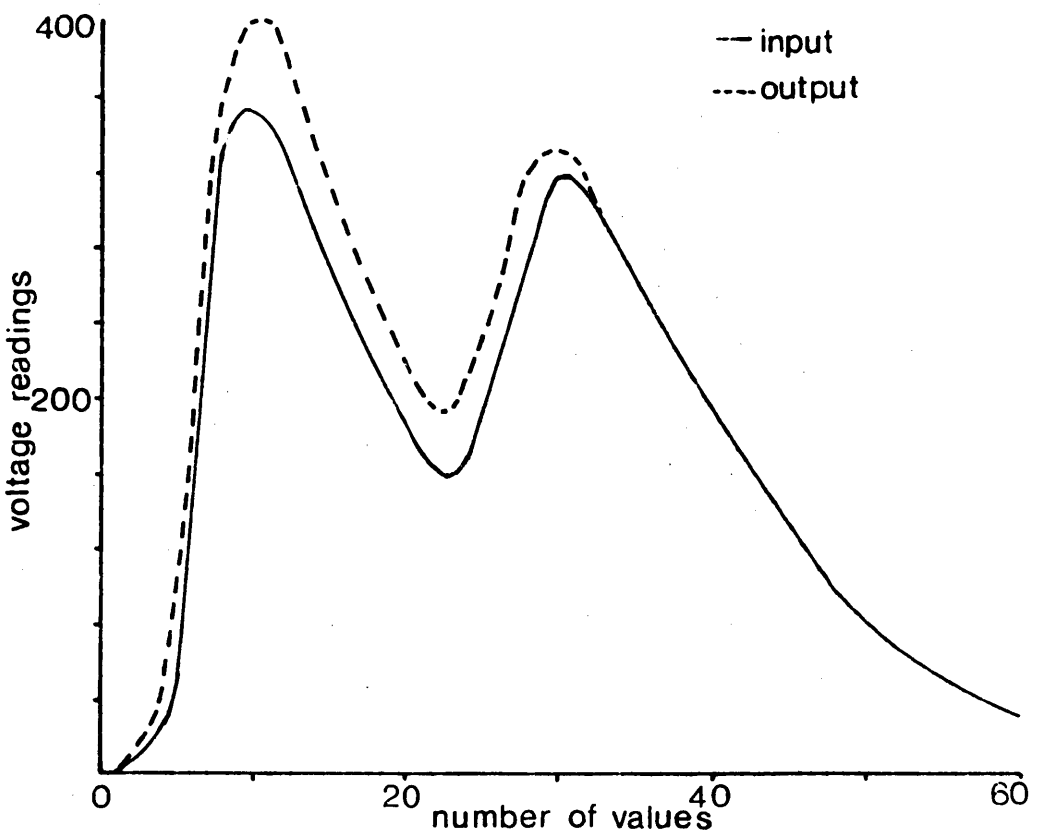


Fig. 33 . Comparison of the input and output arrays from the program.

Table XXV. Program for the resolution of two overlapping GC peaks.

```
C   OVERLAPPING PEAKS
C   A PROGRAM TO DETERMINE THE RELATIVE AMOUNTS OF A COMPOUND IN 2
C   OVERLAPPING PEAKS OBTAINED IN GAS CHROMATOGRAPHY.
C
C   THE STANDARD PEAK IS LINED UP WITH THE EXPERIMENTAL PEAK USING THE
C   70 PERCENT POINT ON THE LEFT EDGE OF THE CURVE. THE STANDARD IS
C   DECREASED UNTIL THE SUM OF THE DIFFERENCES SQUARED IS A MINIMUM.
C   A NEW PEAK IS SET UP BY MOVING THE STANDARD RIGHT AND ALTERING IT BY
C   A FACTOR UNTIL THE SUM OF THE DIFFERENCES BETWEEN THE VALUES OF THE
C   EXPERIMENTAL,STANDARD,AND NEW PEAK,SQUARED,IS A MINIMUM.
C
      DIMENSION A(100),B(100),C(100),D(100)
      DIMENSION RAT(10)
      READ(3,100)N,M
  100 FORMAT(2I10)
      READ(3,101)(A(I),I=1,N)
  101 FORMAT(8F10.0)
      READ(3,101)(B(K),K=1,M)
      WRITE(4,117)
  117 FORMAT(/,14H STANDARD PEAK)
      WRITE(4,101)(A(I),I=1,N)
      WRITE(4,118)
  118 FORMAT(18H EXPERIMENTAL PEAK)
      WRITE(4,101)(B(K),K=1,M)
C
      NI=N+1
      DO 114 I=NI,100
      A(I)=0.
  114 CONTINUE
C
C   FIND 1ST MAX ON EXPERIMENTAL PEAK
C
      DO 1 K=1,M
      IF(B(K).GT.B(K+1))GO TO 19
    1 CONTINUE
   19 BMAX=B(K)
C
C   FIND 70 PERCENT POINT
C
      PT70=BMAX*0.7
      DO 2 KJ=1,M
      IF(B(KJ).GT.PT70)GO TO 29
    2 CONTINUE
   29 CONTINUE
      WRITE(4,106)
  106 FORMAT(//,10H  1ST FACT,10H  2ND FACT,5X,5H SEPN,13X,7H PEAK A,13X
     A,7H PEAK B,9X,11H TOTAL AREA,8X,21H RATIO PEAKA TO TOTAL)
C
      DO 500 KOUNT=1,10
C   MOVE STANDARD PEAK TO 70 PERCENT POINT
C
C     INTEGER INCREMENTS
   99 SUMT=1.E15
```

```
      DO 3 KX=1,50
      SUMS=0.0
      DO 4 I=1,KJ
      K=I+KX-1
      SUMS=SUMS+(B(I)-A(K))**2
    4 CONTINUE
      IF(SUMS.GT.SUMT)GO TO 39
      SUMT=SUMS
    3 CONTINUE
   39 CONTINUE
C
C     NONINTEGER INCREMENTS
      X=0.0
      XK=0.2
   17 SUMS=1.E15
   15 SUMT=SUMS
      X=X+XK
      CALL INTERP(X,A,N)
      SUMS=0.0
      DO 6 I=1,KJ
      K=I+KX-1
      SUMS=SUMS+(B(I)-A(K))**2
    6 CONTINUE
      IF(SUMS.LT.SUMT)GO TO 15
      X=X-2.0*XK
      XK=XK/2.0
      IF(XK.GT.1.E-2)GO TO 17
      X=X+XK
      Z=KX
      DIST=Z+X
C
C   FIND FACTOR TO CHANGE CURVE
C
      FACT=0.1
      XK=0.2
   27 SUMS=1.E30
   25 SUMT=SUMS
      FACT=FACT+XK
      SUMS=0.0
      DO 8 I=1,M
      K=I+KX-1
      SUMS=SUMS+(B(I)-A(K)*FACT)**2
    8 CONTINUE
      IF(SUMS.LT.SUMT)GO TO 25
      FACT=FACT-2.0*XK
      XK=XK/2.0
      IF(XK.GT.1.E-2)GO TO 27
      FACT=FACT+XK
C
      DO 9 K=1,M
      A(K)=A(K)*FACT
    9 CONTINUE
C
C   SET UP NEW CURVE
C
```

```
      DO 11 I=1,M
      C(I)=A(I)
   11 CONTINUE
C
C  MOVE CURVE RIGHT
C
C     INTEGER INCREMENTS
      SUMT=1.E15
      DO 12 KM=1,50
      SUMS=0.0
      DO 13 I=1,M
      J=I+KX-1
      K=I+KX-KM
      SUMS=SUMS+(B(I)-A(J)-C(K))**2
   13    CONTINUE
      IF(SUMS.GT.SUMT)GO TO 49
      SUMT=SUMS
   12 CONTINUE
   49 CONTINUE
C
C     NONINTEGER INCREMENTS
      XY=0.0
      XK=0.2
   47 SUMS=1.E15
   55 SUMT=SUMS
      XY=XY+XK
      CALL INTERP(XY,A,N)
      SUMS=0.0
      DO 14 I=1,M
      J=I+KX-1
      K=I+KX-KM
      SUMS=SUMS+(B(I)-A(J)-C(K))**2
   14    CONTINUE
      IF(SUMS.LT.SUMT)GO TO 55
      XY=XY-2.0*XK
      XK=XK/2.0
      IF(XK.GT.1.E-2)GO TO 47
      XY=XY-XK
      Z2=KM
      DIST2=XY+Z2
C
C  FIND FACTOR TO CHANGE NEW CURVE
C
      FACT1=0.1
      XK=0.2
   37 SUMS=1.E30
   35 SUMT=SUMS
      FACT1=FACT1+XK
      SUMS=0.0
      DO 16 I=1,M
      K=I+KX-1
      J=I+KX-KM
         SUMS=SUMS+(B(I)-A(K)-C(J)*FACT1)**2
```

```
   16     CONTINUE
          IF(SUMS.LT.SUMT)G 35
          FACT1=FACT1-2.0*XK
          XK=XK/2.0
          IF(XK.GT.1.E-2)GO TO 37
          FACT1=FACT1+XK
C
          DO 22 K=1,M
          C(K)=C(K)*FACT1
   22     CONTINUE
C
          SUM=0.0
          DO 61  J=1,M
          SUM=SUM+A(J)
   61     CONTINUE
          SUMA=0.0
          DO 62 K=1,M
          SUMA=SUMA+C(K)
   62     CONTINUE
          SUMB=SUMA+SUM
          RAT(KOUNT)=SUM/SUMB
C
          WRITE(4,115)FACT,FACT1,DIST2,SUM,SUMA,SUMB,RAT(KOUNT)
  115     FORMAT(3F10.2,3F20.5,F29.5)
C
          IF(KOUNT.LE.2)GO TO 500
          IF(RAT(KOUNT).GT.RAT(KOUNT-1))GO TO 199
C         RAT(KOUNT-1) IS THE REQUIRED ANSWER
  500     CONTINUE
  199     STOP
          END
C
          SUBROUTINE INTERP(X,A,N)
          DIMENSION A(N)
          X=-X
          X1=(1.0-X)*A(1)+X*A(2)
          KN=N-2
          DO 1  I=1,KN
          X2=X*(X-1.0)*A(I)/2.0+(1.0-X*X)*A(I+1)+(X+1.0)*X*A(I+2)/2.0
          A(I)=X1
          X1=X2
     1    CONTINUE
          A(N-1)=X1
          A(N)=(1.0+X)*A(N)-X*A(N-1)
  200     RETURN
          END
```

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