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THE FORMATION OF PRISTANE, PHYTANE AND RELATED ISOPRENOID HYDROCARBONS BY THE THERMAL DEGRADATION OF CHLOROPHYLL

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INTRODUCTION

In recent years an increasing number of isoprenoid related hydrocarbons have been isolated from crude oils and oil-shale bitumens. The first identification of 2, 6, 10, 14-tetramethylhexadecane (1) was closely followed by the characterization of the C_{14}, C_{15}, C_{16}, C_{18}, C_{19}, C_{20} and C_{21} isoprenoid hydrocarbons in an East Texas crude oil (2, 3). Recently the C_{17} isoprenoid 2, 6, 10-trimethyltetradecane, which completes the homologues series from C_{14} to C_{21}, has been reported (4). A feature common to this series is the 2, 6, 10-trimethylundecane structure which would suggest a stepwise cleavage by the loss of a methyl group from the next highest member. To date, no compounds have been reported in petroleum which typify a dual terminal cleavage as would be indicated by the compound 6, 10, 14-trimethylhexadecane; this, however, may be a reflection of the difficulties inherent in isolating individual components from such complex mixtures. The identification of isoprenoid hydrocarbons in crude petroleum has aroused considerable interest about their origin and possible geochemical significance. Undoubtedly, the symmetry and the unequivocal relationship of these materials to natural biosynthetic processes provide substantial evidence in favor of the biogenic origin of petroleum. Similarly, while it is generally accepted that the most likely precursor of pristane and phytane is the phytol component of chlorophyll, more recently squalane has been suggested as an attractive alternative. There still remains, however, much speculation about the mechanisms whereby isoprenoid hydrocarbons can be formed from these sources under geologic conditions. Most of the proposed reaction sequences require an early liberation of phytol from the chlorophyll molecule by mile acid, alkaline or enzymatic hydrolysis. According to Bendoraitis, pristane and phytane are formed from phytol in an appropriate sequence of reactions entailing reduction, oxidation, dehydration, and decarboxylation. Bogomolov (5), has pointed out the unfavorable decarboxylation step in this sequence and has proposed an alternative mechanism in which phytol is oxidized to a β-hydroxy acid which is more readily decarboxylated than is the phytanic acid. Another mechanism, proposed by Curphey (6) postulates phytol as the source of a number of petroleum hydrocarbons generated by reactions involving epoxidation and thermal cracking. Notably, none of these processes explain the formation of lower isoprenoid compounds found in petroleum. Furthermore, it seems ambiguous that free phytol has not been reported as a predominant component of recent sediments although Blumer (7) has suggested this absence as being due to the conversion of phytol to phytadiene products on catalytic dehydration of the alcohol by adsorption on clay mineral surfaces. On the other hand, it has been suggested (8) that the absence of pristane and phytane in organic rich deposits from Mud Lake, Florida, postulated as a Post Pleistocene-Recent analog of the Green River oil shale, indicates the phytyl grouping is still bound as an integral part of the chlorophyll molecule.

In view of the lack of knowledge about the preservation of organic matter in sediments, the undisputable evidence that hydrocarbons have been formed at relatively late periods in the geologic age of the sediment and the generally accepted concepts of geothermal maturation of organic matter, a further postulate would be that the bulk of the isoprenoid hydrocarbons found in crude petroleums and oil shale bitumens are formed by the geothermal cleavage of the phytol components of chlorophylls preserved in situ in the organic kerogen of the sediment. This study was an attempt to establish whether or not isoprenoid hydrocarbons, notably pristane and phytane, could be generated by the thermal degradation of chlorophyll.

EXPERIMENTAL

Extraction and Separation of Chlorophylls

Fresh-water green algae, collected during May, was homogenized and extracted with methanol. The crude product was extracted into n-hexane and the chlorophyll isolated by partition chromatography on alumina. UV spectra of the product, Figure 1, was in agreement with published data (9) with a calculated C_a:C_b 1.7. Alfalfa chlorophyll was extracted from a commercially available product (Matheson, Coleman and Bell; C_a:C_b 2.5 $\pm$ 1) and was purified in an identical manner as for the algal chlorophyll. Both products were used in this study without further purification.

Hydrogenolysis

Hydrogenolysis has been used extensively as a means of thermally degrading oil-shale kerogens (10) and of solubilizing coals into crude liquid products (11). Consequently, this method was applied in degrading the materials reported on in this paper.

The isolated chlorophylls dissolved in tetralin were hydrogenolyzed in a 1 Liter Magnadrive Autoclave at 800°F for fifteen minutes in a hydrogen atmosphere. The solvent was removed from the reaction mixture by low temperature vacuum distillation. Because of solvent breakdown at the conditions of hydrogenolysis, no attempt was made to analyze products with a molecular composition less than C_{10}. For the oil shale study, shale from the Mahogany Ledge Zone, Green River Formation, was micronized and solvent extracted with a mixture of methanol, acetone and benzene in an ultrasonic tank (12). The shale had an original organic content of 14.7% of which 1.6% comprised solvent extractable bitumens. The extracted shale was hydrogenolyzed in a manner identical to that outlined for the chlorophylls.

Chromatography

The crude hydrogenolysis extracts were deasphaltened by n-pentane precipitation and the products separated into saturate, aromatic, and NSO fractions by partition chromatography on activated alumina (Alcoa F-20 Chromatographic grade alumina, 100-200 mesh; activated at 40°C for six hours). The saturate fraction was rechromatographed on activated silica gel (Davidson Chemicals, grade 923, 100-200 mesh; 40°C for one hour).

Instruments

The gas chromatograph used was an Aerograph Model 200 with a 20' 1/16" o. d., 3% Apiezon on 100-120 mesh Aeropak 30 column. The unit was temperature programmed to increase from 165° to 290°C at a rate of 4° per minute.

Mass spectrometric analyses were carried out on a Consolidated Electrodynamic Corporation Model 21-103C Mass Spectrometer fitted with a Mascot digitizer printout.

Ultraviolet spectra were recorded on a Beckmann Model DK-1 Recording Spectrophotometer.

Hydrogenolyses were run in a Standard 1-Liter Magnadrive Autoclave (Autoclave Engineers Incorporated) fitted with a Honeywell Pyro-Vane temperature control unit.

Reference Compounds

Reference isoprenoid hydrocarbons were isolated by the preparative gas chromatographic separation of a 300°C crude oil distillation cut. Each isoprenoid hydrocarbon was characterized by mass spectrometry with the spectra being in close agreement with published data (3).

RESULTS DISCUSSION

The complete thermal degradation of an alfalfa and of an algal chlorophyll extract was accomplished by high pressure, high temperature solvent hydrogenolysis. Under similar conditions greater than 90% of the organic kerogen of a Green River Oil Shale was solubilized. The hydrogenolysis products were isolated as dark brown--black tars which could be separated by absorption chromatography into asphaltene, saturate, aromatic and NSO fractions. The percentage compound-type composition of the reaction products is shown in Table I. The excellent reproducibility of the process is shown by the values quoted for three separate oil-shale hydrogenolyses. For the purpose of this study only the saturate fractions obtained from silica gel chromatography were analyzed. To achieve brevity in this report, the hydrogenolysis saturate products from the alfalfa chlorophyll, the algal chlorophyll, the oil shale kerogen 1, and the oil shale solvent extractable bitumen will be referred to as the alfalfa, algal, oil shale and bitumen saturates. Analysis of the saturate products was carried out by gas chromatography and high voltage mass spectrometry. Comparison of the gas chromatograms illustrated in Figures 2,3,4

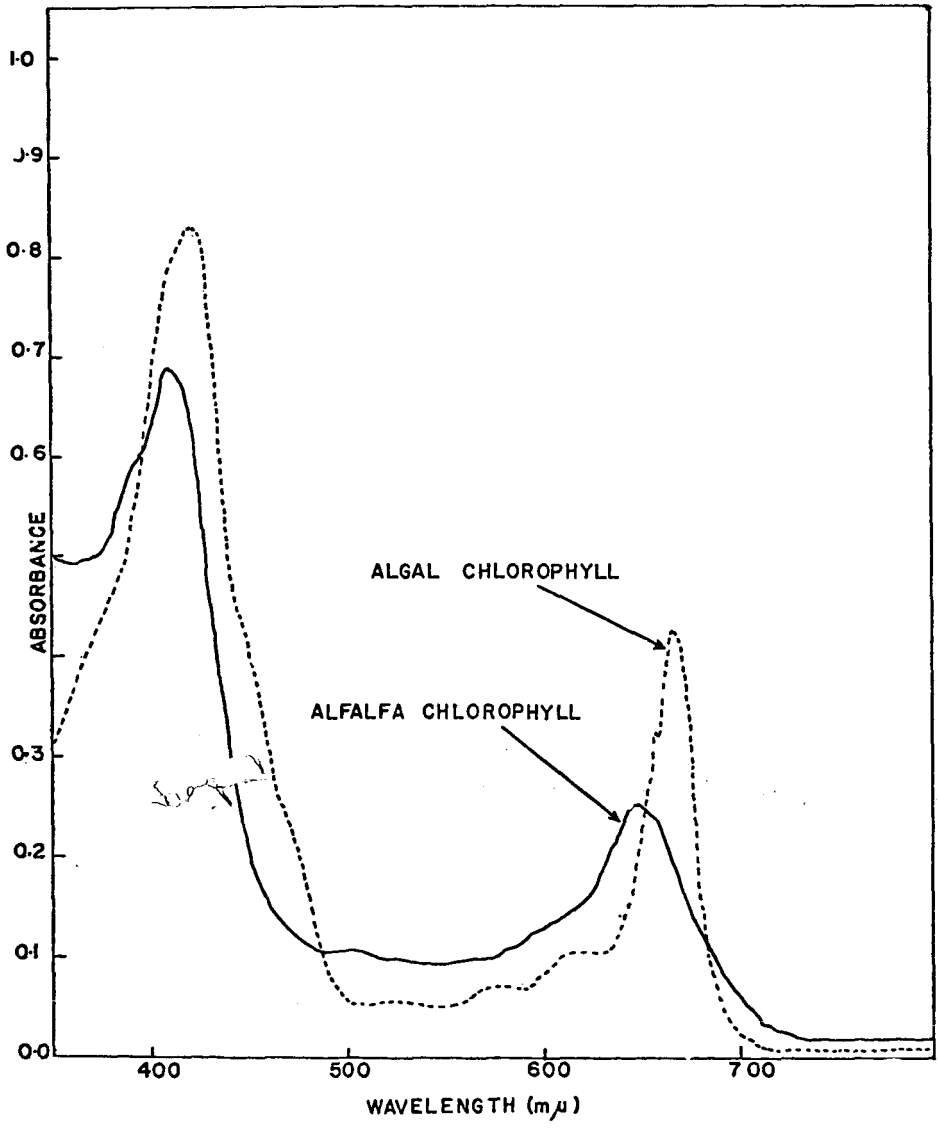
TABLE I

HYDROGENOLYSIS AND CHROMATOGRAPHY DATA

	Alfalfa Chlorophyll	Algal Chlorophyll	Oil-Shale Bitumen	Oil-Shale Kerogen 1	Oil-Shale Kerogen 2	Oil-Shale Kerogen 3
Weight Hydrogenolysed	2.561	0.278		6.58	6.58	6.58
Weight Recovered	2.548	0.269		6.21	6.27	6.23
Alumina Chromatography						
Weight % Asphaltenes	2.4	1.0	21.3	30.3	32.3	35.1
Weight % Saturates	29.4	26.9	11.2	17.9	14.9	14.8
Weight % Aromatics and and Eluted Non-hydrocarbons	49.3	30.0	50.0	36.2	38.0	39.1
Weight % Nonrecovered	18.9	42.1	17.5	16.6	14.8	11.0
Silica Gel Chromatography						
Weight % Saturates	7.6	3.7	7.9	5.2	6.3	6.5

FIGURE 1

ULTRAVIOLET SPECTRA OF CHLOROPHYLL EXTRACTS



and 5, shows varying degrees of complexity, with the differences being mainly in relative peak intensities rather than in compound types. The bitumen saturates contained pristane and phytane (1:3) as the major isoprenoid hydrocarbons along with another notable response at a retention time coincident with that for the normal C_{17} hydrocarbon. Analysis of the oil shale saturates showed several differences, particularly the predominant amount of pristane formed from the kerogen by this process. The overall complexity of the oil shale saturate products was as expected and in fact suitable attenuation of the detector response for the bitumen analysis gave a chromatogram similar for the two fractions. In a comparable analysis of the alfalfa saturates, the most notable features were that the complexity of the compound types increased and that there was about three times as much pristane as phytane. An appreciable quantity of the C_{15} isoprenoid was also present although the C_{18} and the C_{16} isoprenoid hydrocarbons were only present in trace amounts. In contrast, analysis of the algal saturates showed there was about three times as much phytane as pristane. Lower isoprenoid hydrocarbons were undetectable in this extract. A compound at RT 9 minutes was present in both chlorophyll saturates but this has not yet been identified.

These saturate fractions were further characterized by mass spectrometry. Partial mass spectra data for each of the samples is represented in a plot of the relative peak intensity (m/e 71 = 100) for the C_nH_{2n-1}, C_nH_{2n}, C_nH_{2n+1}, and the C_nH_{2n+2} series of molecular and fragment ions. The values are reported by the diagrammatic presentation for the series, n = 10 through 20, in Figures 6, 7, 8, 9, 10, 11, 12 and 13.

In the case of the bitumen saturates the predominant isoprenoid character is shown by the large m/e 183, m/e 253 and m/e 267 responses in the C_nH_{2n+1} series. Presence of the normal C_{17} hydrocarbon is also confirmed by the intensity of the m/e 240 molecular ion in the C_nH_{2n+2} series. Comparison of this spectra with the partial mass spectra of the oil shale saturates shows a close agreement between the two sets of data. The high concentration of isoprenoid compounds is again reflected in the m/e 183 fragment ion, but in this instance the comparative unimportance of the normal C_{17} hydrocarbon is shown by the absence of peaking in the C_nH_{2n+2} series. Notably, the C_nH_{2n} and the C_nH_{2n-1} species are identical with a predominant fragmentation being recorded at m/e 181 and 195.

Similar evaluation of the partial mass spectra for the algal and alfalfa saturates shows fragment ions at m/e 183 and m/e 239; whereas the C_nH_{2n+2} series is characterized by the molecular ion peaks for values of n = 13, n = 15, and n = 17. It is of note that the relative intensities for these ions is greater than that expected for the parent ions of isoprenoid hydrocarbons, being intermediate between that for the parent ion of a branched hydrocarbon and that for the n-paraffin of similar molecular weight. The most outstanding difference shown in the formation of hydrocarbon products from the thermal degradation of the chlorophylls is illustrated in the partial mass spectra of the relative intensities of the C_nH_{2n-1} and the C_nH_{2n} series. In the C_nH_{2n} series for the alfalfa saturates, a large relative response is shown for the molecular ion m/e 238 which would be consistent with that expected for a C_{17} mono-olefin. Other olefinic molecular ions were also indicated by peaking at n = 13 and n = 15 although these responses were much less intense. In contrast, the partial mass spectra of the algal saturates showed a predominant response for an olefinic molecular ion, m/e 210, which would indicate a C_{15} mono-olefinic hydrocarbon. Again, other olefinic species were indicated n = 13, n - 17 and n = 19.

Such differences in the isoprenoid hydrocarbons formed by the thermal degradation of the chlorophylls suggest a fundamental difference in the molecular structure of the phytyl component. The location of the olefinic bond and the possible stereochemical characteristics of the molecule are two possibilities. These features would undoubtedly influence the point at which preferential cleavage of the hydrocarbon chain could occur. Several schemes are outlined (Figure 14) to explain the predominant amounts of pristane and of phytane in the hydrogenolysis products.

In scheme I, the preferred cleavage is postulated to occur between the C_{19}-C_{20} bond in a non-olefinic saturate hydrocarbon chain. This is applicable to the oil-shale kerogen products since the absence of olefinic compounds, shown by the relative low response in the C_nH_{2n} series, indicates the phytyl isoprenoid precursor in the kerogen may have been hydrogenated under geologic conditions. Subsequent cleavage during hydrogenolysis gives pristane as the major hydrocarbon product.

To explain the results for the bitumen and the chlorophyll saturates, a process such as illustrated in scheme II would be necessary. Scheme II (a) would explain the relatively greater abundance of phytane in these products, whereas scheme II (b) would account for the predominance of pristane. The cleavage at the points indicated is based on the preferred electron impact fragmentation of myrecene (13). Such mechanisms may reflect possible isomerization processes participating in the early diagenesis of organic matter in sediments.

One other explanation for the preferred formation of pristane and phytane from the alfalfa and the algal chlorophylls is that hydrogenation of the olefinic bond may occur before cleavage.

FIGURE 2

GAS CHROMATOGRAM OF ALFALFA CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

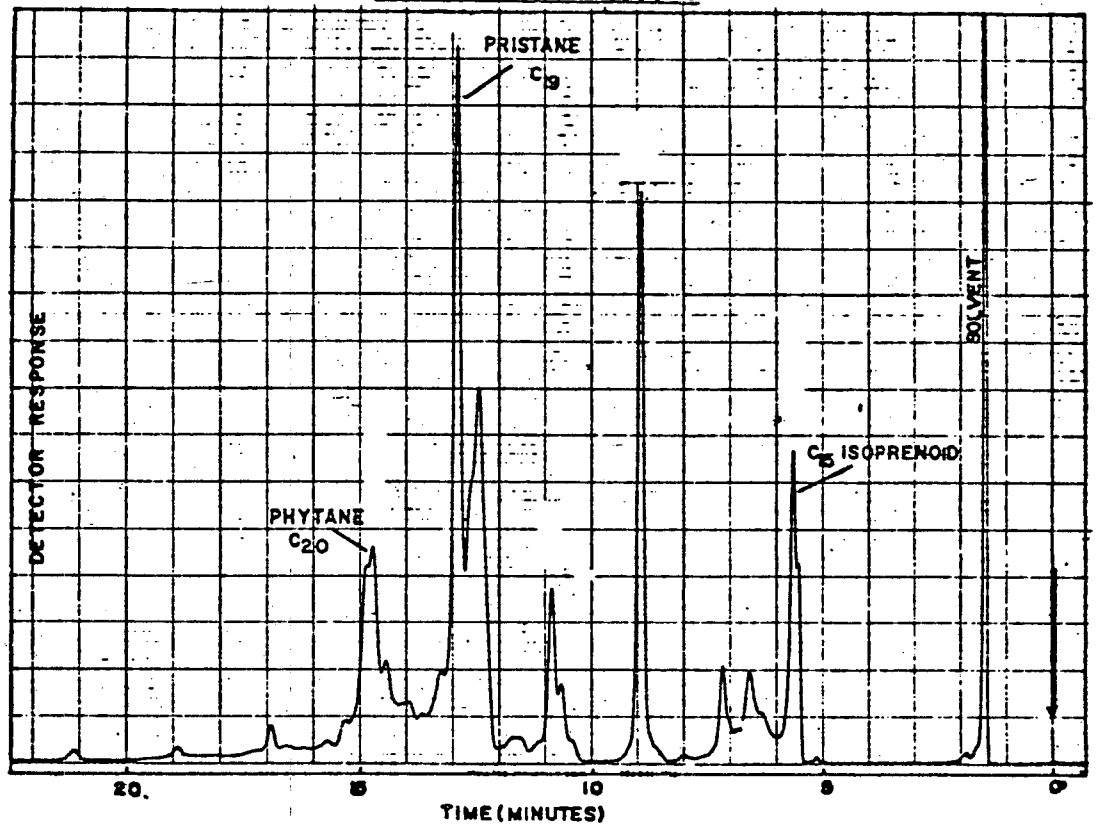


FIGURE 3

GAS CHROMATOGRAM OF ALGAL CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

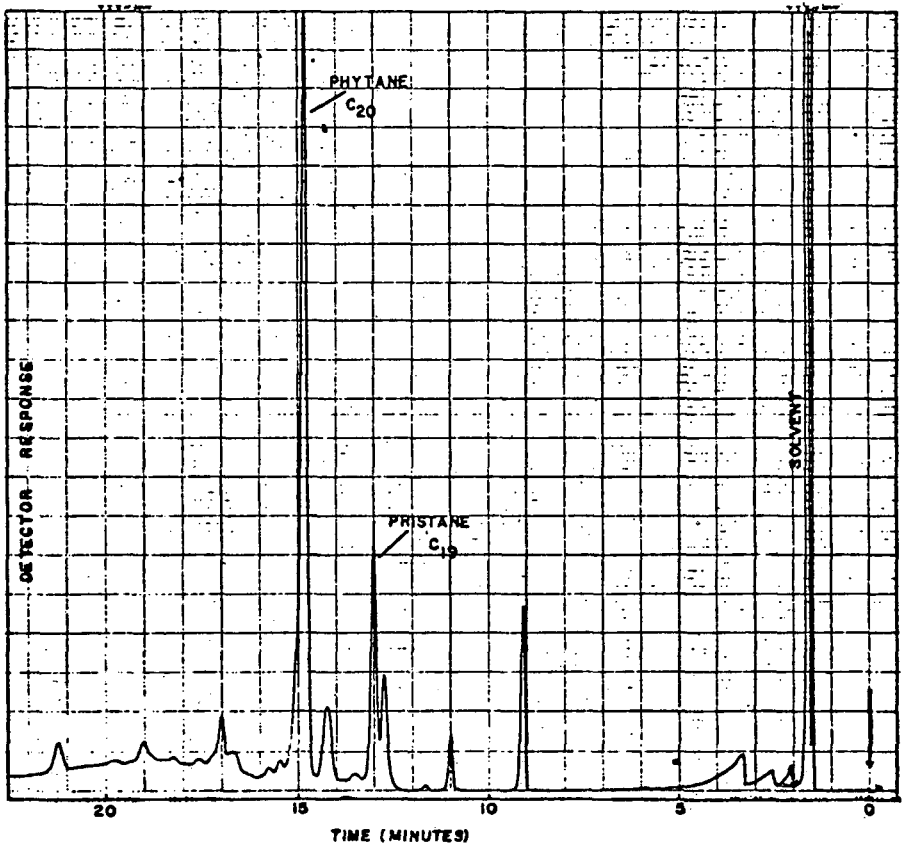


FIGURE 4

GAS CHROMATOGRAM OF OIL-SHALE BITUMEN

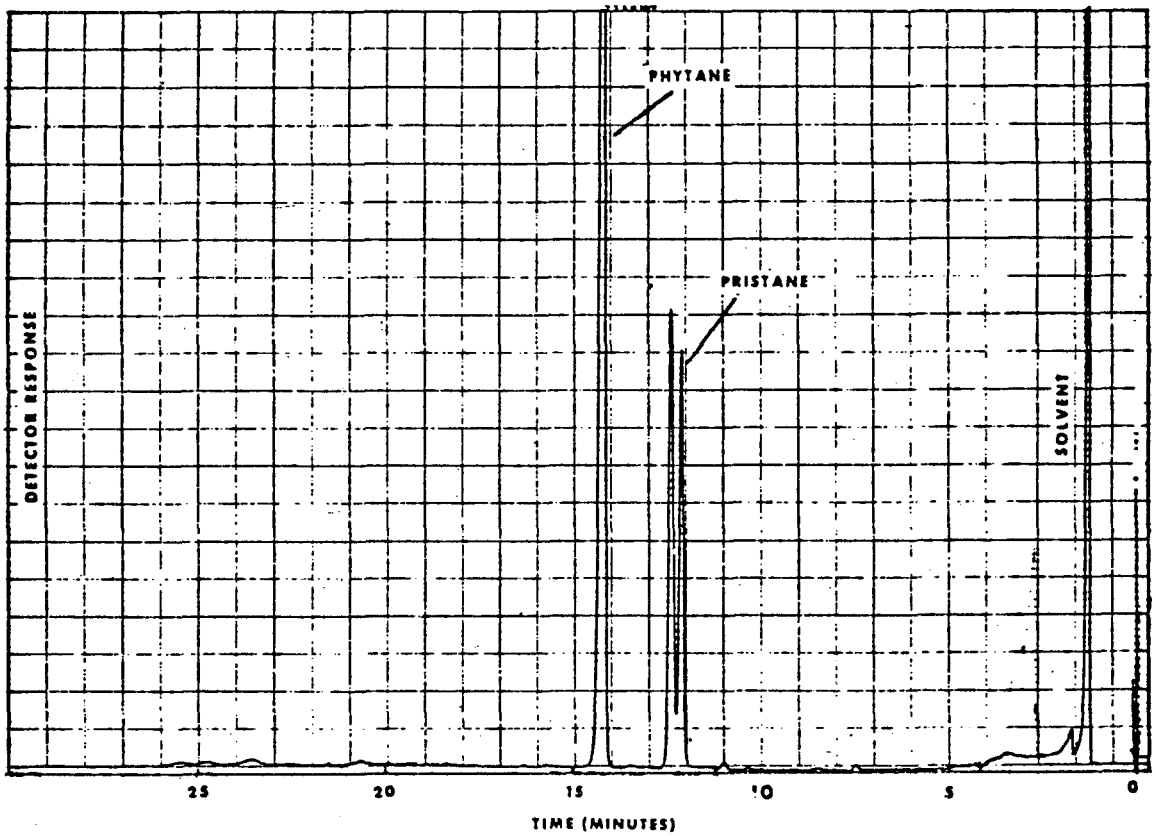


FIGURE 5

GAS CHROMATOGRAM OF OIL-SHALE HYDROGENOLYSIS PRODUCTS

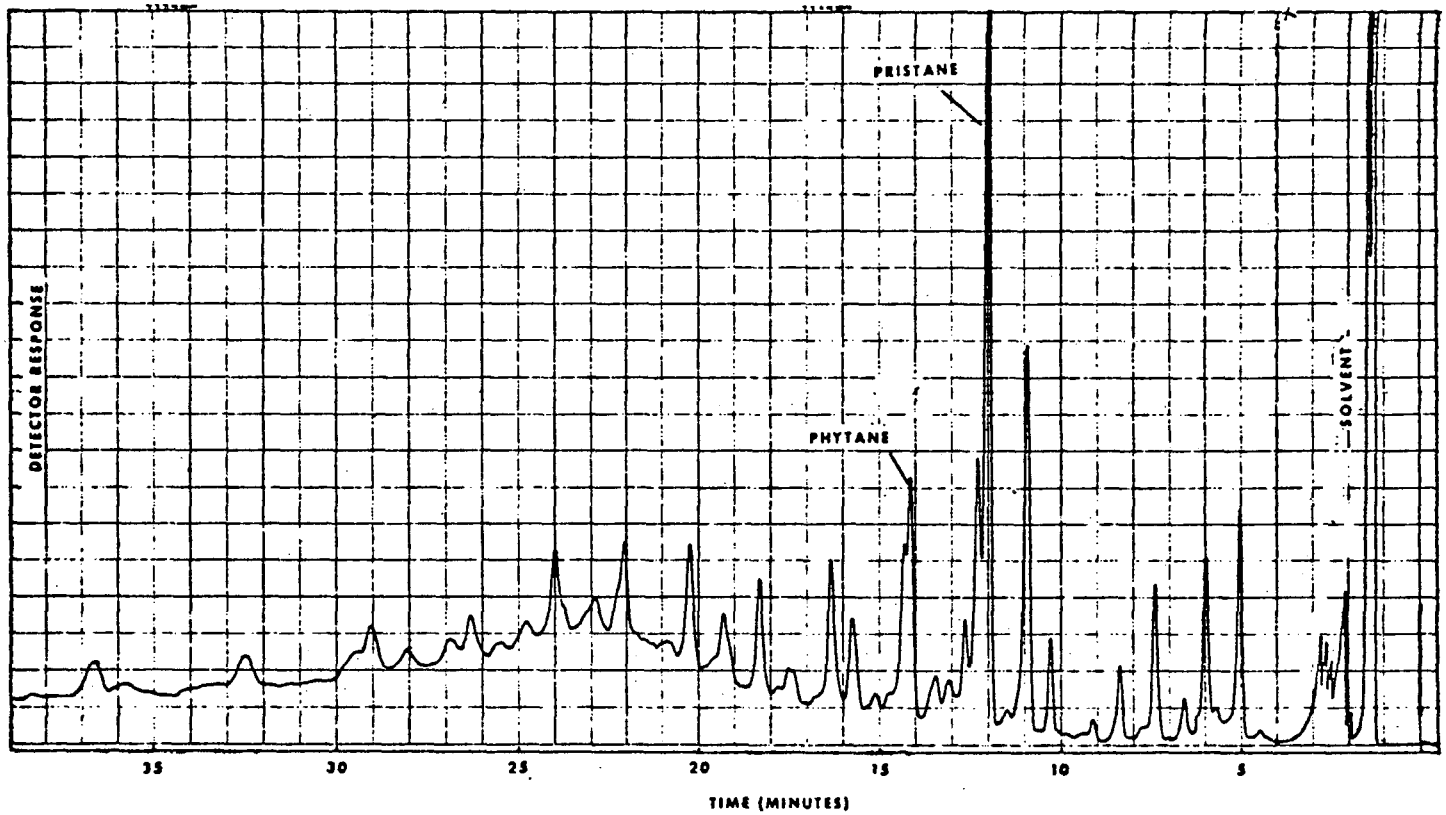


FIGURE 6

PARTIAL MASS SPECTRA OF OIL SHALE BITUMEN

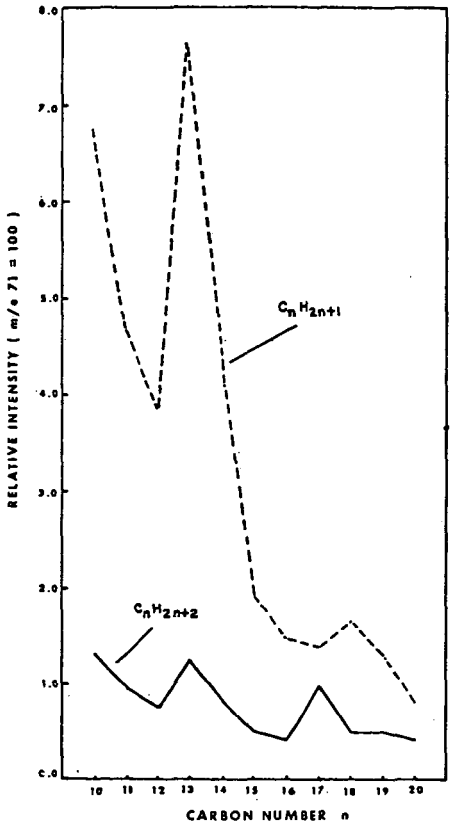


FIGURE 7

PARTIAL MASS SPECTRA OF OIL SHALE BITUMEN

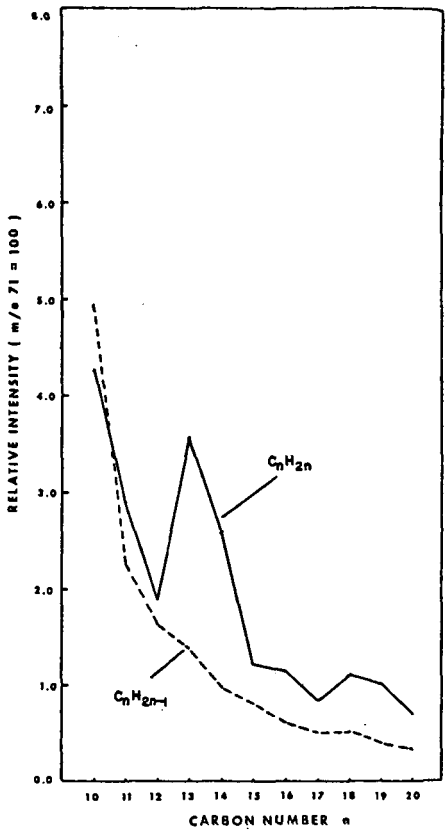


FIGURE 8

PARTIAL MASS SPECTRA OF OIL-SHALE HYDROGENOLYSIS PRODUCTS

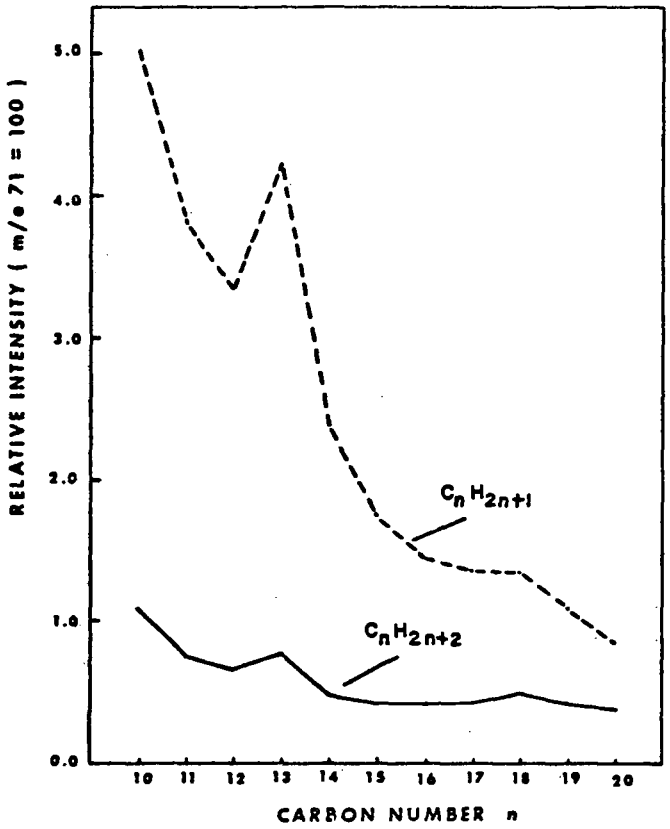


FIGURE 9

PARTIAL MASS SPECTRA OF OIL-SHALE HYDROGENOLYSIS PRODUCTS

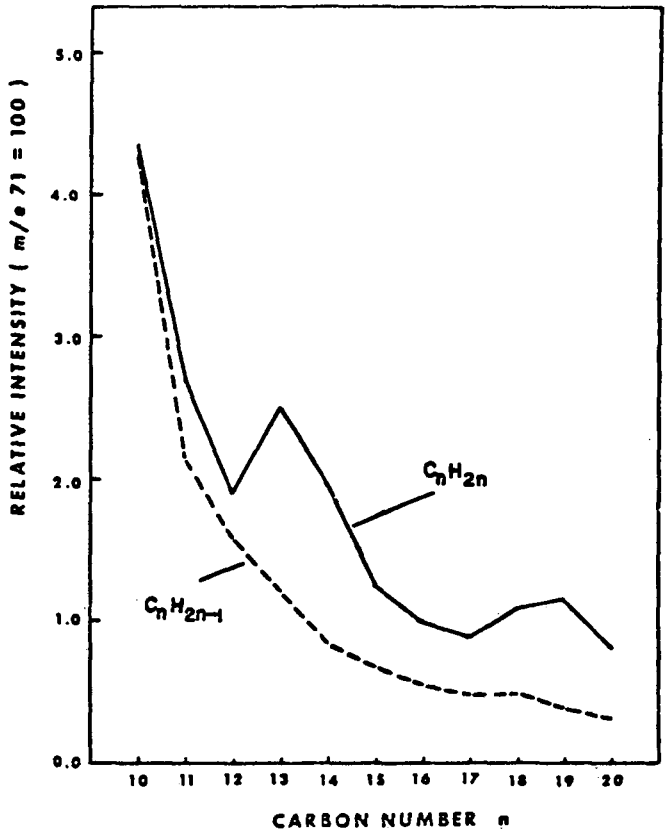


FIGURE 10

PARTIAL MASS SPECTRA OF ALFALFA CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

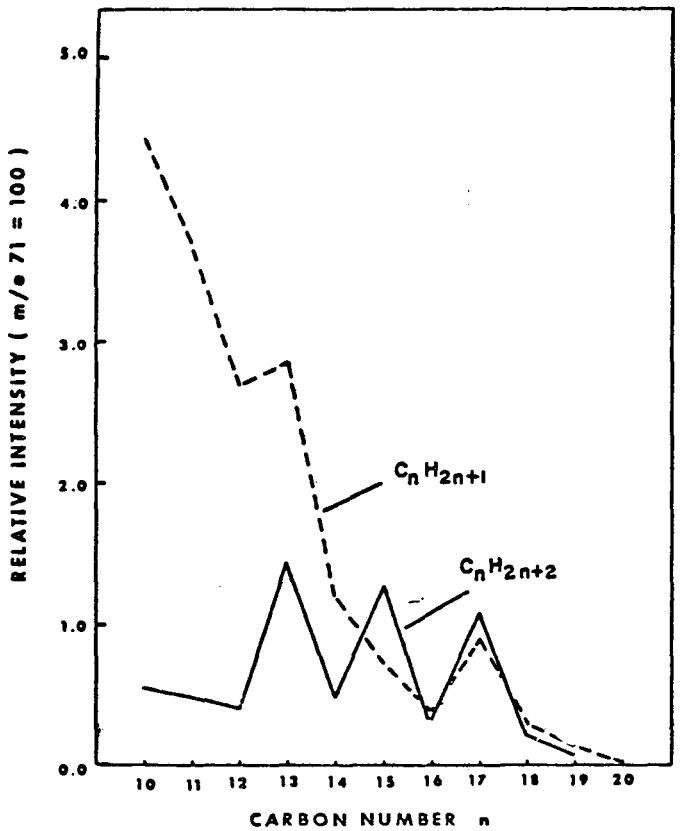


FIGURE 11

PARTIAL MASS SPECTRA OF ALFALFA CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

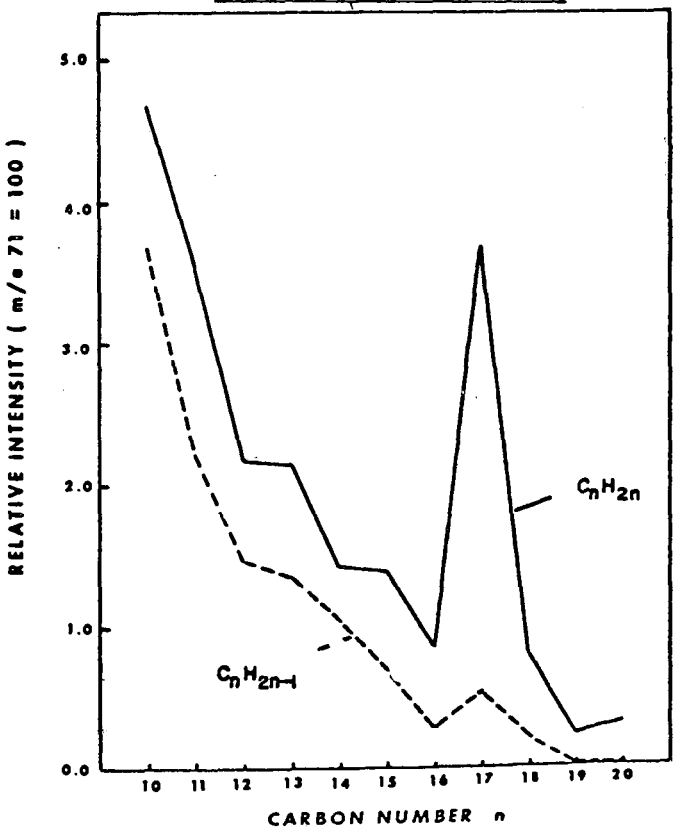


FIGURE 12

PARTIAL MASS SPECTRA OF ALGAL CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

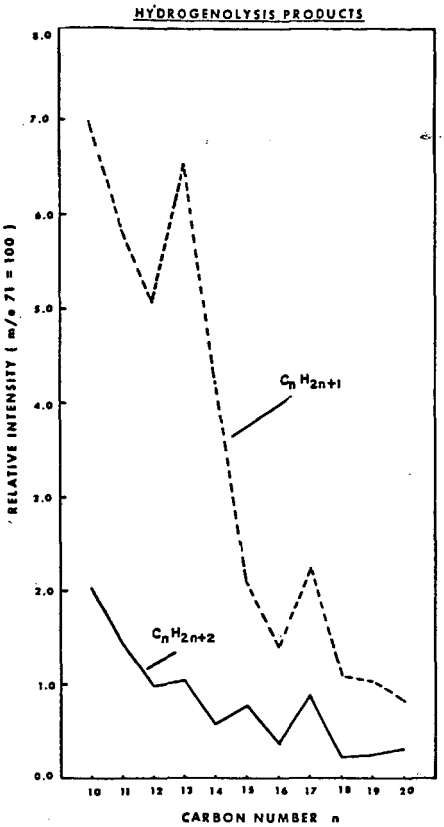


FIGURE 13

PARTIAL MASS SPECTRA OF ALGAL CHLOROPHYLL HYDROGENOLYSIS PRODUCTS

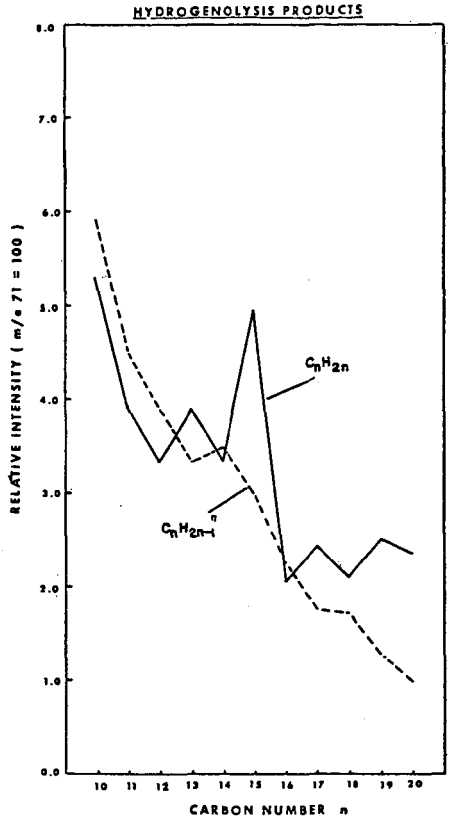
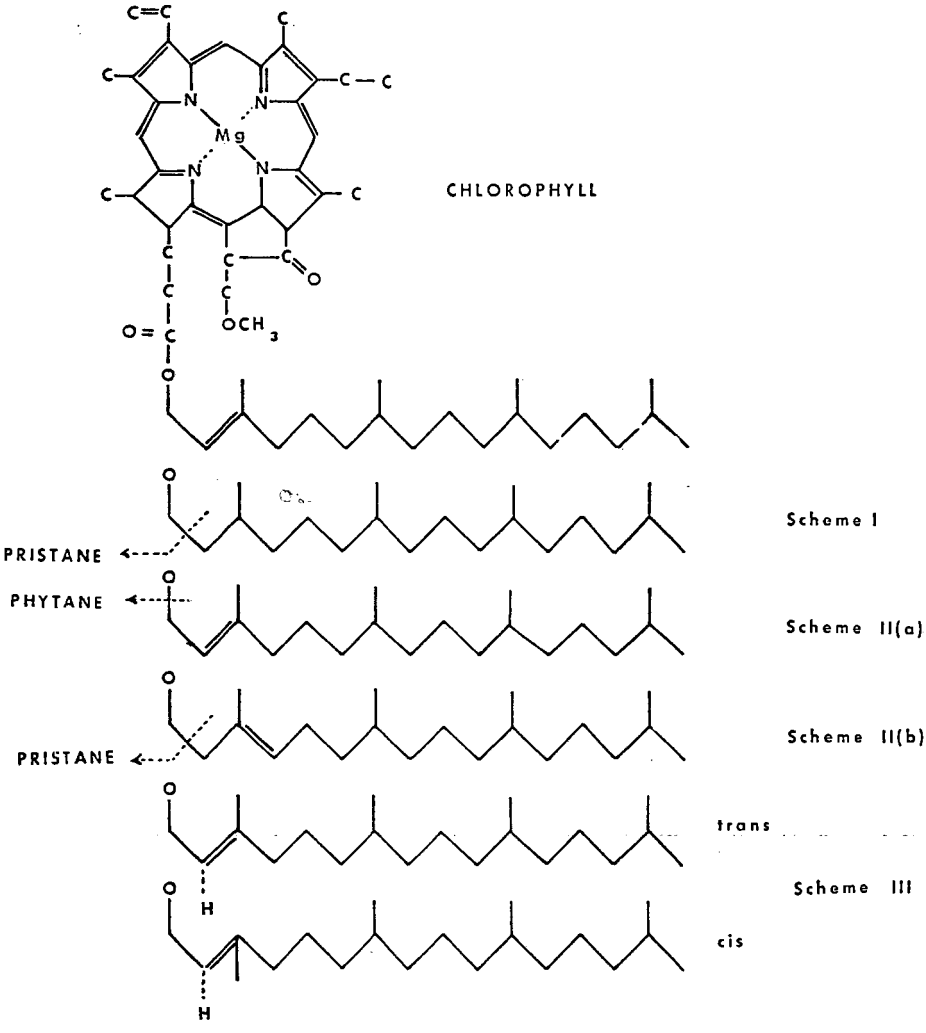


FIGURE 1 4


CHLOROPHYLL
PRISTANE
Scheme I
PHYTANE
Scheme II(a)
PRISTANE
Scheme II(b)
trans
Scheme III
cis

The cis and trans isomers shown in scheme III could account for such a difference since the relative rates of hydrogenation of these isomers under the hydrogenolysis conditions will be dependent upon the stereochemical hindrance from the rest of the molecule. Subsequent thermal cleavage would take place by scheme I. This would suggest that the olefinic bond in alfalfa chlorophyll is more susceptible to hydrogenation.

Clearly, the complex nature of the reaction sequences shown for the thermal degradation of these relatively simple molecules emphasizes the general lack of knowledge about the geochemical processes resulting in the formation of petroleum. It is hoped that continued research will result in a better understanding of some of these mechanisms.

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