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Normal and Isoprenoid Hydrocarbons Isolated from Oil-Shale Bitumen

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Normal and isoprenoid paraffins were identified in a bitumen obtained from Colorado oil shale. The identified *n*-paraffins represented 1.0 percent of the total bitumen and ranged from C₁₃ to C₃₃ compounds. Odd carbon numbered *n*-paraffins were present in greater quantity than even carbon numbered *n*-paraffins by a ratio of 3.6 to 1 in the range of C₂₅ to C₃₃ compounds. Five isoprenoid compounds represented 3.4 percent of the total bitumens and were identified as 2,6,10,14-tetramethylhexadecane, 2,6,10,14-tetramethylpentadecane, 2,6,10-trimethylpentadecane, 2,6,10-trimethyltridecane, and 2,6,10-trimethyldodecane. Identification of isoprenoid compounds in an oil-shale bitumen provides information for the presence of biological remains in oil shale and may serve as a means to the better understanding of the overall structure of kerogen.

VARIOUS COMPOUNDS of biological origin have been isolated and identified from petroleum, kerogen (insoluble carbonaceous material), and bitumen (soluble carbonaceous material). One of the first evidences of the presence of these compounds in petroleum was obtained when Treibs (14) discovered porphyrins in crude oils. Meinschein (9), working with sediment extracts and crude oils, isolated polycyclic hydrocarbons that appeared to be related to steroids. Phytane (2,6,10,14-tetramethylhexadecane) was isolated from petroleum by Dean (6). Seven isoprenoid compounds ranging from C₁₄ (2,6,10-trimethylundecane) to C₂₁ (2,6,10,14-tetramethylheptadecane) were isolated from petroleum by Bendoraitis (1, 2). Mair (7) recently identified 2,6,10-trimethylundecane and 2,6,10-trimethyldodecane in petroleum. Moore and Dunning (10) identified porphyrins in oil shale.

Meinschein (8) found that the soluble extracts from oil deposits contained more odd than even carbon numbered *n*-paraffins. Normal paraffin distributions in a wide variety of recent sediments, ancient sediments, and crude oils were determined by Bray (3). He described the relative abundance of odd over even carbon numbered *n*-paraffins in terms of carbon preference index (C.P.I.). C.P.I. values were approximately 1.0 for crude oils, 1.0 to 2.4 for ancient sediments, and 2.4 to 5.5 for recent sediments. More recently, Cooper and Bray (5) postulated that fatty acids were precursors of the *n*-paraffins in petroleum and proposed a mechanism to account for the differences in the C.P.I. values of the *n*-paraffins found in crude oil and those found in recent sediments. Normal paraffins were identified previously in this laboratory in room temperature tetralin extracts of kerogen (12) and from reduced kerogen oxidation products (13).

This report describes the identification and determination of the carbon preference index of C₁₃ to C₃₃ *n*-paraffins and the identification of a series of five isoprenoid compounds in a benzene-soluble extract from Colorado oil shale. This appears to be the first report of the identification of isoprenoid compounds from oil-shale extracts.

EXPERIMENTAL

Reagents. Alumina (Alcoa, F20, SO-200 mesh) was extracted with pentane, dried, and activated at 700° C. for two hours.

Silica gel (Davison Chemical Company, 200 mesh) was extracted with pentane and dried at 100° C.

Molecular sieves (Linde Air Products, 5A) were extracted with pentane, dried, and activated at 240° C. under vacuum overnight.

Benzene, ACS grade, was distilled prior to use.

Isooctane, knock engine grade, was passed through a column of 5A molecular sieves before use.

All other solvents were of ACS or equivalent grade and were shown to be of high purity by GLC prior to use.

Reference Standards. Phytane (2,6,10,14-tetramethylhexadecane) was prepared by hydrogenating phytyl alcohol (2,6,10,14-tetramethyl-2-hexadecane-1-OL) using chloroplatinic acid and sodium borohydride (4). The resulting dihydrophytol was converted to the *p*-toluenesulphonate, then was reduced to phytane using lithium aluminum hydride. The crude hydrocarbon was purified by GLC, and a trapped portion was used to obtain mass, infrared, and NMR spectra.

A C₁₈-isoprenoid hydrocarbon (2,6,10-trimethylpentadecane) was prepared from phytyl alcohol. Ozonization of

the double bond gave a C₁₈ketone which was reduced by the Clemmensen reduction to the C₁₈-hydrocarbon. This was subsequently fractionated by GLC.

Extraction of Bitumen. The raw oil-shale sample was obtained from the Mahogany-zone bed of the Green River formation near Rifle, Colo. The shale, crushed to pass a 100-mesh screen, contained approximately 34 percent organic material and assayed 66 gallons of oil per ton of shale.

Bitumen was extracted from 50 pounds of oil shale by benzene. Five-pound batches of the oil shale were extracted three times with 3.5 liters of fresh benzene at room temperature with continuous stirring for 24 hours. After the third extraction, the shale residue was Soxhlet extracted with fresh benzene overnight. Benzene was removed from the combined extracts by distillation.

Separation of Bitumen. Batches of bitumen were mixed in a 40 to 1 volume ratio of pentane to bitumen, allowed to stand overnight at 0° C. and filtered. The pentane-soluble material was freed of pentane, dried, and weighed. Five-gram batches of pentane-soluble material were placed on prewetted columns containing 125 grams of alumina and eluted with 500 ml. of pentane. The pentane-eluted material was freed of solvent, dried, and weighed. Five-gram batches of pentane-eluted material were placed on prewetted columns containing 125 grams of silica gel and eluted with 300 ml. of isooctane. The isooctane-eluted material, designated as paraffin concentrate, was freed of isooctane, dried, and weighed. Two-gram batches of the paraffin concentrate were placed on 5A molecular sieves to separate the *n*-paraffins from iso-plus-cycloparaffins using a method described by O'Connor and others (11).

The *n*-paraffin concentrate was fractionated by gas-liquid chromatography using a F and M, Model 500, programmed GLC having a four-foot, 1/4-inch diameter column of SE 30 silicone gum rubber supported on Gas Chrom A. Peak area measurements were made from the chromatogram and individual peaks were trapped for mass spectra analyses.

The iso-plus-cycloparaffin concentrate was fractionated by thermal diffusion in a 30-ml. column for six-weeks. The resulting fractions were combined on the basis of similar refractive indices into three broad fractions; top, middle, and bottom. The top and middle fractions were separated further by thermal diffusion in a 10-ml. column for 3 additional weeks. By this fractionation, the top and middle fractions were each separated into 9 fractions making a total of 19 thermal diffusion fractions including the bottoms.

Chromatograms were made for each of the 19 thermal diffusion fractions by programming at a rate of 11° C. per minute over the temperature range of 75° to 350° C. After completion of each chromatogram, peak area measurements were made. Chromatograms of fractions 1 through 6 have 10 predominant peaks, all of which emerged at temperatures less than 225° C. Only small amounts of material emerged above 225° C. In chromatograms of fractions 7 through 19 individual peaks were poorly resolved and most of the material emerged above 225° C. Because fraction 3 appeared to represent the lower-boiling portion of the iso-plus-cycloparaffin fraction, it was used for trapping the 10 peaks that emerged below 225° C.

RESULTS AND DISCUSSION

The *n*-paraffins represented a minimum of 1.0 per cent of the total bitumen, while the iso-plus-cyclic concentrate represent 14.0 per cent. Mass spectral and GLC data showed the iso-plus-cycloparaffin concentrate to contain about one-fourth isoparaffins and three-fourths cycloparaffins.

***n*-Paraffins.** Normal paraffins isolated from the paraffin concentrate ranged from C₁₃ to C₃₃ compounds. Identifica-

tions were made by comparing the GLC emergence time of individual peaks with those of standard samples and by mass spectral analysis of trapped GLC peaks.

The distribution of the *n*-paraffins was determined from GLC peak areas (Table I) and mass spectral data. The most prevalent *n*-paraffin was C₁₇ compound.

The ratio of odd over even carbon numbered *n*-paraffins (C.P.I.) calculated from GLC data by the method of Bray (3) was 3.6 in the C₂₅ to C₃₃ range. It is of interest that the C.P.I. value of 3.6 is higher than might be expected for this material. Comparable results were obtained from similar calculations using mass spectral data. With the exception of the C₂₂ *n*-paraffin, the even carbon numbered compounds are present in smaller amounts than the adjacent odd numbered carbon compounds.

Isoparaffins. The 10 trapped GLC peaks from thermal diffusion fraction 3 were shown by mass spectrometry to be predominantly isoparaffins. The carbon numbers for each of the trapped peaks were determined from parent *m/e* mass spectral peaks and ranged from C₁₃ to C₂₁ compounds. The percent distribution of the carbon numbers (Table II) was determined from the areas of the 10 peaks of the chromatograms obtained from the 19 thermal diffusion fractions. Comparable data were calculated from the mass spectrum of the unfractionated iso-plus-cycloparaffin concentrate.

Five compounds (C₁₅, C₁₆, C₁₈, C₁₉ and C₂₀) represented more than 90 per cent of the compounds in the C₁₃ to C₂₁ range and were equivalent to 3.4 per cent of total bitumen.

Table I. Distribution of *n*-Paraffins

Carbon Number	Per cent of <i>n</i> -Paraffin ^a
13	0.2
14	0.3
15	1.3
16	10.7
17	12.3
18	3.6
19	5.7
20	4.0
21	6.8
22	9.0
23	6.4
24	3.5
25	6.0
26	2.7
27	7.4
28	2.6
29	10.7
30	1.4
31	3.6
32	0.1
33	0.8
Total	100.0

^a Based on GLC data.

Table II. Distribution of Isoparaffins

Peak Number	Carbon Number	Per cent of Iso-plus-Cycloparaffins ^a	Per cent of Bitumen
1	13	0.1	0.0
2	14	0.3	0.0
3	15	0.5	0.1
4	16	1.9	0.3
5	16,17	0.2	0.0
6	16,17	0.1	0.0
7	18	1.4	0.2
8	19	4.6	0.6
9	20	15.5	2.2
10	19,20,21	0.4	0.0
Total		25.0	3.4 ^b

^a Based on GLC data.

^b This value is equivalent to oil per cent of the total organic material in the oil shale.

The C₂₀ compound alone represents 2.2 per cent of the bitumen.

The five isoparaffin compounds having C₁₅, C₁₆, C₁₈, C₁₉, and C₂₀ carbon numbers were identified as isoprenoid compounds by mass, infrared, and NMR analyses of trapped GLC peaks. Partial mass spectra of the trapped compounds and those of available standards are shown in Table III. The patterns of the isolated C₂₀, C₁₉, C₁₈, and C₁₅ compounds are the same in all major respects to the patterns of phytane (2,6,10,14-tetramethylhexadecane), pristane (2,6,10,14-tetramethylpentadecane), 2,6,10-trimethylpentadecane, and 2,6,10-trimethyldodecane. The C₁₆ compound was not synthesized nor is an authentic spectrum available, however, the breakdown pattern is comparable to that expected from a C₁₆ compound having 3 isoprene units.

Infrared data support the isoprenoid structure for the compounds. A published spectrum (1) for pristane is nearly identical with the spectrum obtained for the pristane found. All five compounds (Table IV) show split absorption at 7.25 and 7.30 microns plus absorption at 8.55 and 8.67 microns characteristic of the isopropyl group. These bands are significant evidence for isoprenoid structure as the head of each isoprene unit contains an isopropyl group. Absorption at 13.61 microns, attributed to a chain of less than four methylene groups, also is typical of isoprenoid structure. This absorption results from the vibration of the three methylene groups situated between two methyl substituted carbon atoms. Each of the five compounds shows this absorption. In addition, the C₂₀ and C₁₅ compounds show absorption at 13.00 microns characteristic of

a terminal C₂H₅ group, and the C₁₈ compound shows absorption at 13.84 microns characteristic of four methylene groups in the terminal chain.

Confirmation of methyl branching characteristics of the isoprenoid compounds was obtained from NMR analysis. The spectrum obtained for pristane was very similar to that reported by Bendoraitis (1) and showed single resonance for methylene protons and methyl proton resonances, split into doublets. The chemical shifts were characteristic of alkane compounds. The number of methyl groups per molecule calculated from the area under resonance peaks was 6.10 for phytane and 6.04 for pristane. The theoretical value for these compounds is 6.00. Not enough sample was available to obtain NMR spectra for the other isoprenoid compounds.

It appears to be significant from biological considerations that the isoprenoid compounds identified represent 3.4 per cent of the total bitumen. The source of the isoprenoid compounds and the method by which they were altered appears to be very discreet and selective.

Cycloparaffins. Thermal diffusion fraction 10, which contained high percentages of cycloparaffins, was separated by GLC and trapped portions were analyzed by mass spectrometry. However, the fractions were too complex to permit identification of individual compounds. In general, the cycloparaffins range from 1- to 6-ring compounds with 2- to 3-ring compounds predominating. Fragmentation in the mass spectrometer suggested predominance of compounds having two ring systems connected by an aliphatic chain.

Table III. Partial Mass Spectra for Isoprenoid Compounds

m/e	Relative Peak Height ^a									
	C ₂₀ Synthetic	C ₂₀ Found	C ₁₉ Published ^b	C ₁₉ Found	C ₁₈ Synthetic	C ₁₈ Found	C ₁₆ Found	C ₁₅ Published ^c	C ₁₅ Found	
57	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
71	72.7	71.8	69.6	70.5	44.3	47.4	82.7	70.6	70.0	
85	37.0	38.2	26.1	27.3	18.5	22.1	38.8	30.6	31.3	
99	10.1	10.3	7.6	9.5	7.6	8.7	9.5	5.6	5.0	
113	11.8	11.6	16.2	15.8	4.9	6.2	12.2	9.7	9.4	
127	11.4	12.2	5.2	5.5	1.7	2.3	3.4	10.6	9.7	
141	3.8	3.7	2.2	2.4	1.0	1.3	11.6	1.6	1.6	
155	2.5	2.5	2.1	2.6	0.6	0.8	2.1	1.9	1.3	
169	1.8	1.9	0.5	0.7	2.7	3.5	0.7	0.9	1.6	
183	5.3	6.3	9.7	11.1	1.8	2.4	5.4	3.4	2.8	
197	5.1	5.6	0.5	0.6	0.1	0.2	0.9	1.1	0.9	
211	0.4	0.5	0.2	0.2	0.2	0.3	1.4	
225	0.3	0.4	0.3	0.4	0.3	0.3	
239	0.2	0.3	0.3	0.5	0.4	0.5	
253	1.0	1.1	0.7	0.8	
267	0.7	0.9	
281	

^a For series C_nH_{2n+1} peaks relative to m/e 57 peak. ^b Reported by Bendoraitis (2). ^c Report by Mair (7).

Table IV. Partial Infrared Data for Isoprenoid Compounds

Band Location, Microns	Absorption ^a					Structure Interpretation
	C ₂₀ C	C ₁₉ C	C ₁₈	C ₁₆ C	C ₁₅ C	
	R-CCCC ^b	R-CCC ^b	R-CCC ^b	R-CCCC ^c	R-CCCC ^c	
7.25	X	X	X	X	X	C(CH ₃) ₂
7.30	X	X	X	X	X	
8.55	X	X	X	X	X	
8.67	X	X	X	X	X	
13.00	X				X	C ₂ H ₅ less than (CH ₂) ₄ (CH ₂) ₄
13.61	X	X	X	X	X	
13.84			X			

^a Use of an X in the column indicates that absorption occurred.

^b R represents 3 (CCCC) isoprene units.
^c R represents 2 isoprene units.

Some evidence was found for the presence of cycloisoprenoid structures in the higher-boiling fractions. A white solid material crystallized from the cycloparaffin fraction. The white solid, which represents about 0.1 per cent of the bitumen, had a melting point of 292–297° C., had a molecular weight by mass spectra of 412 (C₃₀H₅₂), and was only slightly soluble in hot benzene. Mass spectral data showed large *m/e* peaks of 191 and 137 suggesting the presence of two ring systems connected by a carbon chain. The extremely high melting point of this material suggests the presence of bridge carbon atoms. A ring system similar to camphane would account for the *m/e* 137 peak and a camphane ring fused to a saturated ring would account for the *m/e* 191 peak.

CONCLUSIONS

Normal paraffins, ranging in carbon number from 13 to 33, have been identified in a bitumen from Colorado oil shale. These *n*-paraffins contain a predominance of odd over even carbon numbers similar to bitumens from recent and ancient sediments.

Five isoprenoid compounds, representing 3.4 per cent of the bitumen, were identified as phytane (2,6,10,14-tetramethylhexadecane), pristane (2,6,10,14-tetramethylpentadecane), 2,6,10-trimethylpentadecane, 2,6,10-trimethyltridecane, and 2,6,10-trimethyldodecane. It seems of particular importance to origin considerations that these isoprenoid structures represent such a high portion of the total bitumen.

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Vanadium and Nickel in Crude Petroleum of South American and Middle East Origin

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NUMEROUS surveys have been published concerning the inorganic constituents occurring in petroleum of United States origin (1, 4, 6), but only a limited number of analyses of petroleum from other producing areas have been reported (2, 3, 5). A more complete survey of the vanadium and nickel content of petroleum of South American and Middle East origin is reported in Table I.

A relationship of density to vanadium content in the crude petroleum of Western Venezuela has been found. The correlation is:

$$\log(\text{PPM Vanadium}) = 3.04 - 0.03 \text{ } ^\circ\text{API}$$

It must be emphasized that this relationship applies only to Western Venezuelan petroleum and even in those, occasional exceptions are noted.

The analytical methods used were essentially those of Wrightson (7) which were modified slightly to include an iron separation step when required. In analysis of crude petroleum, dry ashing was less troublesome and gave results equivalent to those obtained when sulfuric acid coking was used (3).

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