

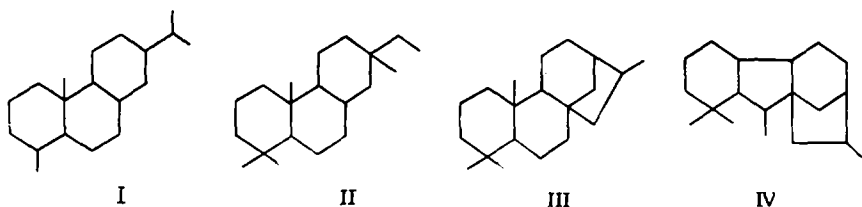
DITERPENOID TETRACYCLIC HYDROCARBONS OF PETROLEUM*

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DITERPENOID hydrocarbons are fairly widespread in various caustobioliths. However, if petroleum contains mainly acyclic diterpenoids (phytane, pristane and norpristane), cyclic diterpenes such as fichtelite (I), pimarane (II), iosene (kaurane) (III) and hibbane (IV) are often found in hydrocarbons isolated from coal and shale. Recent advances in the chemistry of diterpenoids isolated from caustobioliths, are described in a separate paper [1].



Much less is known about petroleum polycyclic diterpenoid hydrocarbons, particularly those with four saturated rings. A series of tetracyclic hydrocarbons $C_{19}H_{32}$ (molar mass 260), found in a number of light petroleum and gas condensates from the Jura deposits of Central Kara-Kum (Turkmen S.S.R.), [2] are examined here. These hydrocarbons are present in petroleum and condensates from the Davaly, Erden, Ortakak, Southern Beurdeshik deposits, they are always identical and occur in the same ratios. The composition of the tetracyclanes isolated from the Ortakak gas condensates (well 17) will be examined in detail.

EXPERIMENTAL

The saturated hydrocarbons b.p. 300°–350°C from the Ortakak condensate was chosen for study. A chromatogram of this mixture (Fig. 1a), shows nine principal peaks eluted in the range $n-C_{18}$ – $n-C_{20}$. These hydrocarbons are normally absent from other paraffinic petroleum or gas condensates. All of these peaks correspond to isomeric tetracyclanes $C_{19}H_{32}$. Their concentration at some 1.5–2% of the initial condensate — is significant. The hydrocarbon sample was concentrated further by thermal diffusion under conditions described previously [3]. Mass

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spectrometry indicated that the lower fraction (10 TD), isolated from a 10-section thermal diffusion column, had the following composition: tetracyclanes 75, tricyclanes 13, bicyclanes 12%. The gas-liquid chromatogram of this concentrate is shown

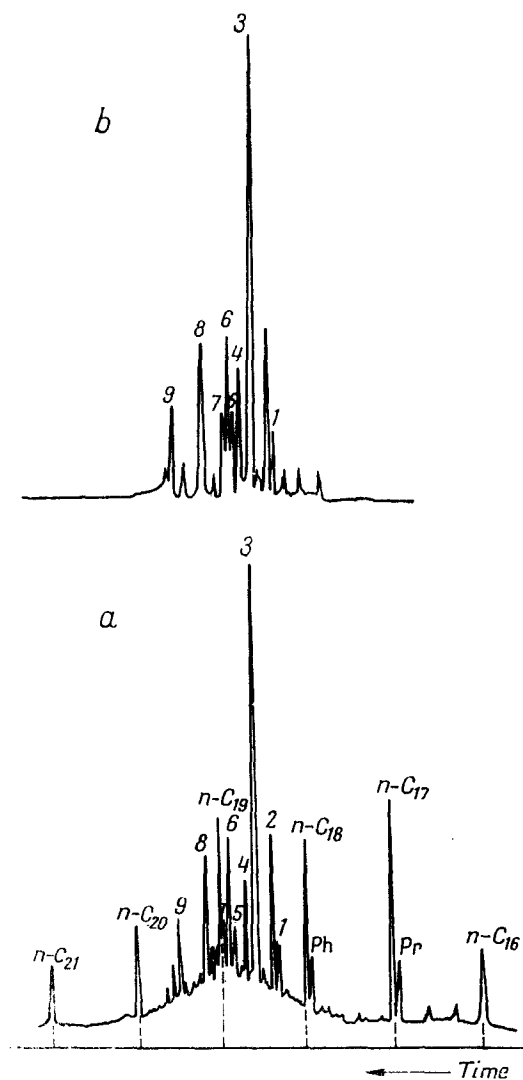


FIG. 1

FIG. 1. Chromatograms of saturated tetracyclic hydrocarbons: *a*—300°–350°C fraction of initial Ortakak condensate; *b*—tetracyclane concentrate isolated by thermal diffusion. Capillary column, 80 m, Apiezon L, carrier-gas—hydrogen. Temperature control 150°→2 deg/min. End of program 250°C.

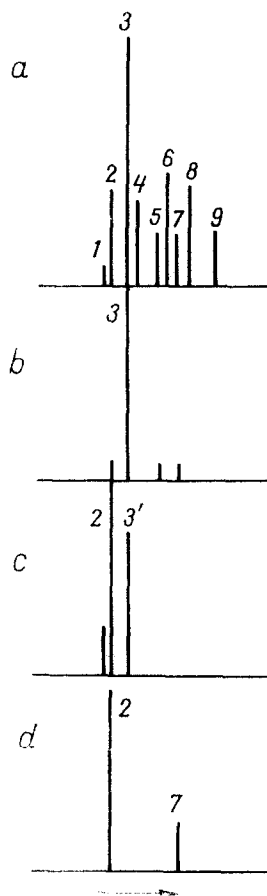


FIG. 2

FIG. 2. Standard chromatogram of separated products of the tenth thermal diffusion fraction on zeolites 10X: *a*—initial mixture; *b*–*d*—fractions 1–3; total solvent volume 35, 70, 120 ml, respectively. Identification of peaks is given in Table 1 and in the text.

in Fig. 1b. The structure of hydrocarbons (Nos. 1-9) was studied by GC/MS (Table 1) and supported by ^1H and ^{13}C NMR. GC/MS data came from a LKB-2091 "chromass" fitted with a capillary column (50 m) coated with Apiezon L or silicone phase SP-2100. Mass spectra were taken at 70 eV with the ionizing source at 250°C. These data were correlated using a LKB-2130 computerized data processing system.

Prior to NMR spectrometry the hydrocarbons were purified by liquid-adsorption chromatography from 10X zeolites calcined at 320°C, 5 hr. A concentrate sample (500 mg) was eluted with $n\text{-C}_5$ from zeolite (particle size <0.45 mm; column 1 m $\times$ 1 cm) previously wetted with n -pentane and retained for 40 min. Samples were taken every 5 ml. Separation of a tetracyclic hydrocarbon mixture into fractions 1-3 is shown in Fig. 2 to contain increased amounts of hydrocarbons (peaks 2, 3 and 7) which were used for further investigation.

TABLE 1. MS DATA OF TETRACYCLIC HYDROCARBONS

Peak number (Fig. 1)	Main molecular fragment ions and their relative intensity (% of the maximum peak)
1	260(10), 232(39.3), 217(34.9), 189(100), 190(21), 109(20), 95(18), 91(23), 81(40.8), 79(21)
2	260(24), 232(38), 217(38), 189(100), 190(20), 135(24), 121(20), 109(36), 107(27), 95(32), 91(93), 81(60), 79(27)
3	260(68), 232(7), 217(88), 189(25), 164(95), 163(77), 135(84), 121(77), 109(60), 107(70), 95(100), 81(91)
4	260(25), 232(25), 217(91), 189(46), 135(32), 123(20), 109(36.7), 108(30.4), 95(41), 81(100)
5	260(15), 217(8), 179(36.5), 178(26.6), 135(100), 121(18), 109(25.6), 107(27.8), 95(25.9), 93(28.2), 79(29), 67(26)
6	260(51.3), 245(5), 232(10), 217(100), 189(18), 177(32), 164(81), 163(44), 135(70.6), 121(55), 109(59.7), 95(78), 81(81.7)
7	260(37), 245(2), 232(10), 217(100), 189(32), 177(45), 161(10), 149(10), 135(37.8), 121(36.2), 107(29), 95(37)
8	260(60), 217(100), 189(15.5), 177(96.7), 178(39), 135(46), 121(45.3), 109(30), 107(32), 95(32), 93(34.6), 91(34.4), 81(67)
9	260(5), 217(6), 179(79), 135(93.8), 123(100), 109(79), 95(67), 81(67), 67(41)

NMR spectra were recorded from an AM-500 Brooker pulse spectrometer at frequencies 500.13 (^1H) and 125.7 Mc/sec (^{13}C). Structures of the hydrocarbons measured were established using the following mechanisms:

1. Chemical shifts were determined for ^{13}C nuclei and directly linked protons using a 2D correlation curve of chemical shifts for ^{13}C F_2 and ^1H F_1 nuclei with a by-pass in F_1 [4].

2. The correlation of carbon atoms was determined via distant constants of spin-spin bonds $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ by the method COLOC [5].

3. Proposed hydrocarbons structure.

TABLE 2. CHEMICAL SHIFTS OF ^{13}C AND ^1H NUCLEI OF HYDROCARBONS (VI) AND (VII) (δ_{TMS})

Carbon atom	(VI)		(VII)	
	$\delta^{13}\text{C}$	$\delta^1\text{H}$	$\delta^{13}\text{C}$	$\delta^1\text{H}$
C-1	67.3	—	56.5	—
C-2	46.9	1.15; 1.89	28.2	0.97; 1.37
C-3	50.4	1.90	24.1	1.43; 1.65
C-4	41.1	1.61	54.3	1.64
C-5	37.3	1.14; 1.84	41.6	1.72
C-6	28.1	1.43; 1.54	34.7	1.24; 1.72
C-7	54.7	2.22;	30.9	1.24; 1.79
C-8	51.5	—	42.1	2.19
C-9	42.4	1.46; 1.52	51.5	2.16
C-10	32.4	1.21; 1.84	50.5	0.92
C-11	57.1	1.65	25.1	0.98; 1.67
C-12	33.3	1.18; 1.76	37.1	1.10; 1.55
C-13	57.2	1.13	66.1	1.06
C-14	35.8	1.27; 1.45	50.0	1.32
C-15	21.5	0.95	20.7	0.90
C-16	20.5	0.86	14.7	0.85
C-17	34.4	1.39	31.2	1.31
C-18	21.4	0.90	21.4	0.87
C-19	22.4	0.88	22.4	0.87

4. The structure obtained was verified according to chemical shifts of ^1H and ^{13}C nuclei of model compounds.

Table 2 shows the chemical shifts of ^{13}C and ^1H nuclei of hydrocarbons (VI) and (VII) (δ_{TMS}); mass-spectra of these hydrocarbons are shown in Fig. 3.

RESULTS

The GC/MS data suggest that all hydrocarbons examined are isomers of different structures and are represented by various groups. Group I shows (peaks Nos. 1 and 2) with intense fragmented ions at m/z 232, 189; group II (peaks Nos. 1, 3 and 6) characterized by intense ions with m/z 164, 163 and 260 and group III (peaks Nos. 4, 7 and 8) with a prominent ion at m/z 217. Mass-spectra of hydrocarbons in the same group happen to be rather similar; they indicate that these hydrocarbons are probably epimers. Hydrocarbons (peaks Nos. 5 and 9) have a structure fundamentally different from those already examined.

^{13}C NMR spectra of the hydrocarbons (peaks Nos. 2, 3 and 7) are very typical. All hydrocarbons contain four methyl groups, two of which form an isopropyl group. The five carbon atoms accounted for leave the remaining 14 locked within a tetracyclic system, with consequent dense packing.

Detailed examination of the ^{13}C and proton NMR spectra from the main hydrocarbon (peak No. 3), (Table 2) indicates that it contains four methyl radicals, two of which form the isopropyl group and one is angular. Chemical shifts of ^{13}C nuclei of the isopropyl group show no vicinal steric interactions and the line of one

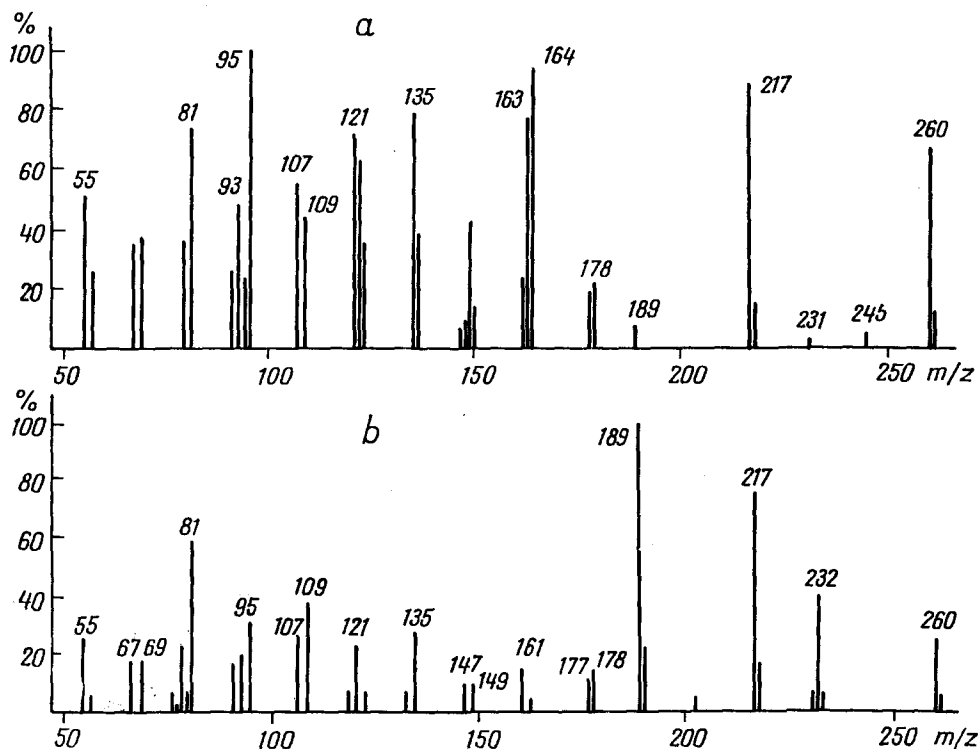
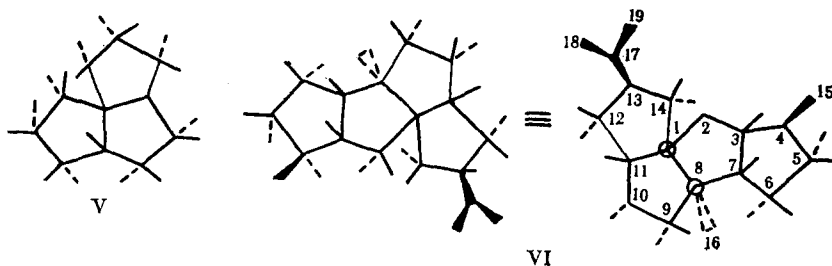
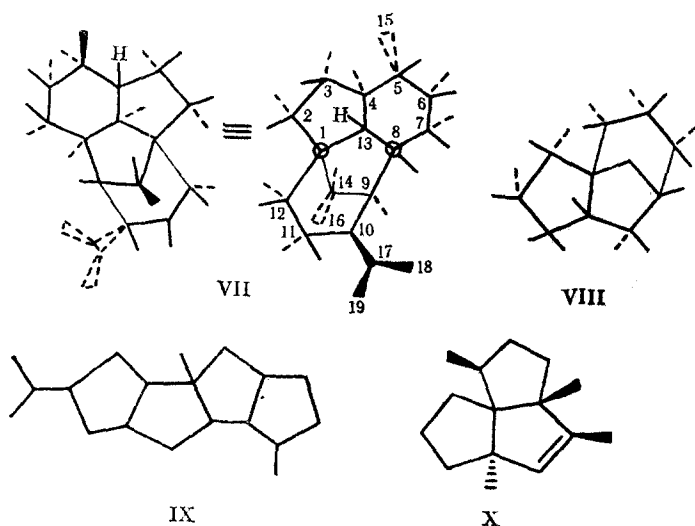


FIG. 3. Mass spectra of 4,8-dimethyl-13-isopropyltetracyclo[6.6.0.0^{1,11}.0^{3,7}]tetradecane (VI) (a) and 5,14-dimethyl-10-isopropyltetracyclo[6.4.1.1^{1,9}.0^{4,13}]tetradecane (VII) (b).

of the two quaternary carbon atoms is very strongly shifted into the weak field at 67.2 p.p.m. Judging by results in the literature, this chemical shift must correspond to a tricyclo[6.3.0.0]undecane system having further β -substituents at the quaternary carbon atom [6, 7]. The relationship between the chemical shifts of unsubstituted tricyclo[6.3.0.0^{1,5}]undecane [8], various alkyl-substituted bicyclo[3.3.0]octanes and vicinal interactions between rings and between substituents and rings, indicates that the structure obtained using 2D-techniques agrees with the hypothetical chemical shifts of 4,8-dimethyl-13-isopropyltetracyclo[6.6.0.0^{1,11}.0^{3,7}] tetradecane. Accordingly the hydrocarbon structure may be presented by the formula (VI):

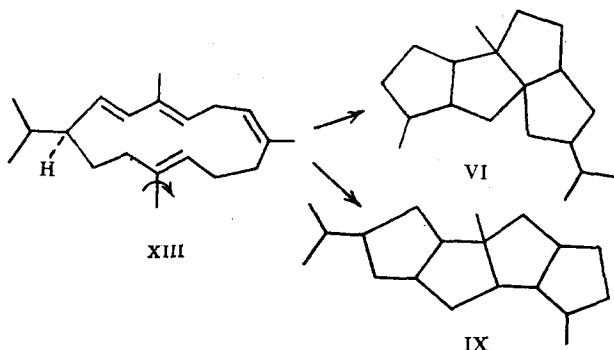
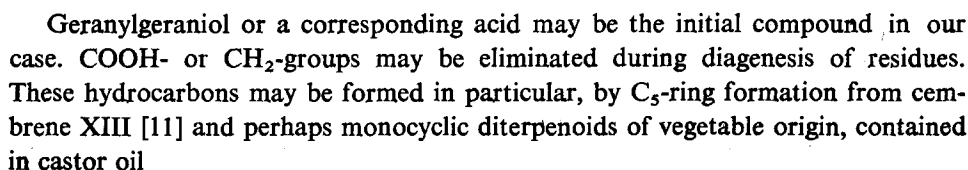


Isomers (peak No. 2, second in concentration terms) also contain four methyl groups, two corresponding to an isopropyl radical but unlike the principal isomer, the angular methyl group is absent from this isomer. A more regular chemical shift to (51.1 p.p.m.) corresponds to a quaternary carbon atom and an unusually high chemical shift (66.1 p.p.m.), to a lone tertiary carbon atom. Such chemical shifts are observed only for a CH-group combined with tertiary and quaternary carbon atoms, because of the existence of numerous β -effects. Consideration of 2D-experiments presupposes a 5,14-dimethyl-10-isopropyltetracyclo[6.4.1.1^{1,9}0^{4,13}]tetradecane (VII) structure, containing fragments of *trans*- and *cis*-bicyclo[4.3.0]nonanes, bicyclo[3.2.1]octane and substituted tricyclo[5.3.1.0^{1,5}]undecane (VIII) (norcedrane)



The third hydrocarbon (peak No. 7) has isopropyl and angular methyl groups (position of methyl group for 21.3 p.p.m.). However, it is free from quaternary spiro-carbon atoms, typical of hydrocarbons (VI) and (VII). This hydrocarbon appears to be based on a polycyclic system consisting of four condensed cyclopentane rings (IX). The ^{13}C spectrum of hydrocarbon (IX) is: *S*: 46.5; *d* 54.4; 53.2; 47.4; 42.2; 40.6; 37.8; 35.0; 30.7; *t*: 36.2; 34.0; 29.4; 27.2; 27.2; 23.0; 19.3; *q*: 19.6; 21.3; 20.0 and 20.7.

The structure of all the hydrocarbons examined is related to their supposed mechanism of formation. These compounds were apparently formed by fermentative C_5 -ring formation from unsaturated aliphatic polyisoprenoids, an example is the transformation of farnesol to isocomene (X) often found naturally [6, 9]. Similarly the formation of the pentacyclic sesterterpene (XII) from geranylfarnesylpyrophosphate (XI) [10] is also typical. Retigerenic acid, corresponding to hydrocarbon XII was found in a lichen.



The tetracyclic saturated hydrocarbon series reported here, based on condensed cyclopentane ring systems, is also of interest because these compounds may be regarded as a source of the pentalane hydrocarbon series, widely reported in petroleum [12], tricyclo[6.3.0.0^{1,5}]undecane and its methyl homologues [13].

The remainder of Ortakak condensate, apart from the hydrocarbons described, contained no new unusual structures. The evidence suggests that these hydrocarbons are formed apart from the condensate itself, thus the presence of these unusual hydrocarbons may be a consequence of the migration of the condensate or petroleum, followed by solution of the diterpenoids, which are presumed to have accumulated separately.

1. A new group of saturated diterpenoid tetracyclic hydrocarbons, ($C_{19}H_{32}$), of was found in Turkmen petroleum and condensates.

2. The structure of these hydrocarbons was confirmed by ^1H and ^{13}C NMR and GC/MS.

3. 4,8-Dimethyl-13-isopropyltetracyclo[6.6.0.0^{1.11}0^{3.7}]- and 5,14-dimethyl-13-isopropyltetracyclo[6.4.1.1^{1.9}0^{4.13}]tetradeccanes were found to be the main hydrocarbons of this series.

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PORPHYRINS OF SAKHALIN CRUDE OILS*

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PETROPORPHYRINS are structures, which retain the basic structural features of the carbon skeleton of their precursor biomolecules. Therefore, the study of the composition of these chemofossils from crude oils of different ages may provide information about the evolution of porphyrin group composition from mineral biomass, at particular stages of the earth's geological history and influence reconstruction of the geochemical conditions of formation of individual oil aggregates.

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