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Identification of some novel tetracyclic diterpene hydrocarbons in petroleum

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Abstract—A new group of tetracyclic diterpene hydrocarbons of molecular formula $C_{19}H_{32}$ has been found in the Jurassic oils and condensates of the Central Kara-Kum (Turkmenia, U.S.S.R.). The structure of the hydrocarbons has been determined by gas chromatography–mass spectrometry and ^{1}H and ^{13}C NMR. Of the compounds identified 4,8-dimethyl-13-isopropyltetracyclo[6.6.0.$0^{1,11}0^{3,7}$]- and 5,14-dimethyl-10-isopropyltetracyclo = [6.4.1.1.$^{1,9}0^{4,13}$]tetradecanes are present in the highest concentrations. Some ideas are put forward about the source and the reactions involved in the formation of the hydrocarbons under natural conditions by the enzymic C_5 cyclization of aliphatic isoprenoids.

Key words: tetracyclic diterpene, petroleum, mass-spectra, ^{13}C NMR

INTRODUCTION

Oils are known to contain a great number and variety of polycyclic alkanes of the terpenoid type. Although many studies have been performed on petroleum triterpenoid hydrocarbons, much less attention has been paid to polycyclic diterpenoids despite the fact that many oils are produced from continental deposits which are likely to contain these compounds.

Polycyclic diterpenoids are widely distributed in plant resins and due to their stability they are preserved in sediments and may be considered as good biological markers. Most of the studies on polycyclic diterpenoids have been carried out with oils (Philp *et al.*, 1981), coals (Philp *et al.*, 1983), and sediments (Simoneit, 1977; Barrick and Hedges, 1981; Livsey *et al.*, 1983).

Up to now the following polycyclic diterpenoid hydrocarbons were found in oils; beyerane, 16β(H)- and 16α(H)-phyllocladanes and 16β(H)-kaurane (Noble *et al.*, 1985).

The present paper deals with identifying a novel group of tetracyclic diterpenoid hydrocarbons of molecular formula $C_{19}H_{32}$ that were found in some oils and gas condensates deposited at a depth of 2300–3100 m at the south-east border of the Kara-Kum fault of Central Turkmenia (U.S.S.R.) (oil fields Ortokak, Davaly, Beurdeshik, Khalimergen) (Solodkov *et al.*, 1980). These oil reservoirs are located in fractured limestones of the Oxfordian-Tithonian stage of the Upper Jurassic.

These oils and condensates can be classified as the methane–naphthene–aromatic type by their chemical composition. At 350°C 95% of the condensate components and 60% of the oil components boil. Besides the tetracyclic diterpenoids of molecular formula $C_{19}H_{32}$ no other hydrocarbons with an unusual structure were found in the samples under study. The source organic matter of these oils appears to be of the marine type; the pristane/phytane ratio is 1:1, and the ratio of ethylbenzene to the sum of C_8-arenes is 1:5.

In the present work the tetracyclic diterpenoid hydrocarbons of molecular formula $C_{19}H_{32}$ isolated from the condensate of the Ortokak oil field have been investigated.

EXPERIMENTAL

A mixture of saturated hydrocarbons boiling between 300 and 350°C was used as the initial material. The gas chromatogram of the mixture is given in Fig. 1. It shows nine peaks eluting between n-C_{18} and n-C_{20}. All the peaks belong to isomeric tetracyclic alkanes of molecular formula $C_{19}H_{32}$. Their concentrations in the oil ranged between 1.5 and 2%. The cyclic components in this distillation fraction were then concentrated by thermal diffusion as described in Petrov (1971). The resultant concentrate had the following composition as determined by analysis using mass spectrometry; tetracyclics 75%; tricyclics 13%; bicyclics 12% (Fig. 1b). The structures of the hydrocarbons (numbered 1–9, Fig. 1b) were analyzed by GC–MS and ^{1}H and ^{13}C NMR. For the work we used a gas chromatograph–mass spectrometer (LKB-2091) with a dedicated computer system for data processing (LKB-2130) and a 50 m capillary column coated with Apiezon or SP-2100.

All the mass spectra were taken at the ionization energy of 70 eV and an ion source temperature of 250°C. The mass spectra of the tetracyclic hydrocarbons studied are given in Figs 2–4.

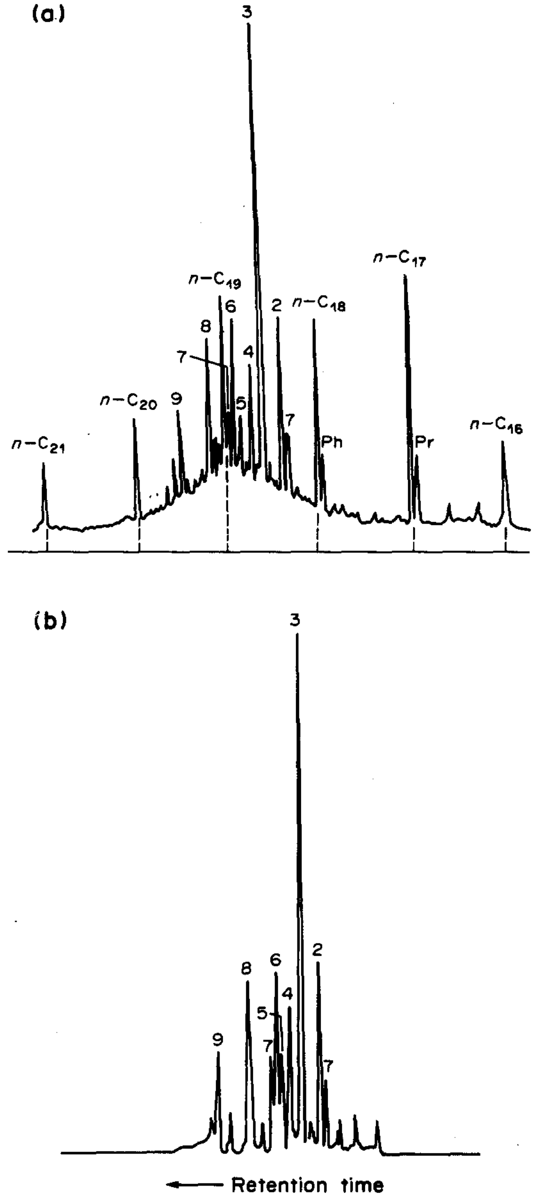

Fig. 1. Gas chromatograms of the saturated tetracyclic hydrocarbons. (a) 300–350°C distillation fraction from the initial condensate. (b) Concentrate of the tetracyclanes obtained by thermal diffusion. (Capillary column 50 m, diameter 0.35 mm, Apiezon L; carrier gas—hydrogen; linear temperature programming from 150 to 250°C at 2°C/min.).

^{1}H and ^{13}C NMR analyses were performed on three fractions (b–d) obtained by liquid adsorption chromatography using type 10X zeolites. Figure 5 shows gas chromatograms as histograms of the three fractions obtained and which were used for NMR analysis.

^{13}C and ^{1}H spectra were obtained at 125.7 and 500.13 MHz, respectively using a multinuclear Bruker AM500 spectrometer. The small amounts of hydrocarbons available did not permit the effective use of two-dimensional double quantum coherence correlation NMR spectroscopy (Mareci and Freeman, 1982) for elucidation of their structures. Therefore, the structures of the hydrocarbons were deduced by the following steps.

1. Determination of ^{13}C and ^{1}H chemical shifts from the heteronuclear (^{1}H–^{13}C) chemical shift correlation experiment with the decoupling in F_1 (Wong and Rutar, 1984).
2. Determination of carbon-carbon connectivities via the long range coupling constants $^2J_{CH}$ and $^3J_{CH}$ by the COLOC pulse sequence (Kessler *et al.*, 1984). The use for this purpose of ^{1}H–^{1}H coupling constants by the relayed coherence transfer (Bolton, 1982) is much less effective.
3. Building up the structure of the hydrocarbon with the aid of the obtained connectivities and available chemical shifts of various model compounds.
4. Checking the structure obtained with the COSY 2-D correlation diagram. Too crowded COSY diagram can be used at step 2 only for unambiguous determination of few carbon–carbon connectivities.

RESULTS AND DISCUSSION

The initial results of analysis by GC–MS revealed that the isomeric hydrocarbons obtained had different molecular frameworks. On the basis of fragmentation patterns one can divide the hydrocarbons into several groups. The first consists of compounds corresponding to peaks 1 and 2 (Fig. 2) that have a base peak fragment ion at m/z 189; the second has compounds corresponding to peaks 3 and 6 (Fig. 3) with characteristic intense fragment ions at m/z 164, 163 and 260; and the third is compounds corresponding to peaks 4, 7 and 8 (Fig. 4) with the strongest signal at m/z 217. At the same time, the mass spectra of the hydrocarbons within the same group are quite similar indicating that they may be mixtures of diastereomers. The hydrocarbons corresponding to peaks 5 and 9 have quite different structures with intense fragment ions at m/z 135 (100%) and 179.

Carbon-13 NMR spectra of three hydrocarbons corresponding to peaks 2, 3 and 7 indicate that they all have four methyl groups, two of which belong to an isopropyl moiety. Hence, their tetracyclic skeletons have only 14 carbon atoms, indicating crowded molecular structures for these hydrocarbons.

In the main hydrocarbon corresponding to peak 3, one of the methyl groups is angular. The chemical shifts of the isopropyl group (Table 1, C-17, 18, 19) show that it has no vicinal substituents. One of the two quaternary carbon atoms has an extraordinary low field shift at 67.3 ppm. According to the literature data, this shift can be attributed only to the derivatives of tricyclo[6.3.0.0^{1,5}]undecane (I, cf. Appendix) with the additional β-substituent to the quaternary carbon atom (Bohlmann *et al.*, 1977, 1979). Consideration of the chemical shifts from tricyclo[6.3.0.0^{1,5}]undecane (Vorobieva *et al.*, 1975) and from various alkyl substituted bicyclo [3.3.0]octanes, the additional vicinal effects between the rings and substituent effects of the methyl and isopropyl groups confirm the structure derived from the 2D NMR experiments as 4,8-dimethyl-13-isopropyltetracyclo[6.6.0.0^{1,11}0^{3,7}]tetradecane (II).

In the other isomer (peak 2) there is no angular methyl group and the only quaternary carbon atom has a more regular chemical shift (51.1 ppm). The unusual low field chemical shift (66.1 ppm) in this hydrocarbon corresponds to a tertiary carbon atom. Such a shift can be observed in the CH-group connected to the tertiary and quaternary carbon atoms due to numerous low field β-effects. Consideration of various NMR data leads to the structure of 5,14-dimethyl-10-isopropyltetracyclo[6.4.1.1^{1,9}0^{4,13}] tetradecane (III) consisting of fragments of trans- and cis-bicyclo[4.3.0]nonanes, bicyclo[3.2.1]octane and tricyclo[4.3.1.0^{1,5}]undecane (norcedrane) (IV).

The third hydrocarbon corresponding to peak 7 was analyzed in a fraction where it occurred as a minor component (Fig. 2d). Its carbon chemical

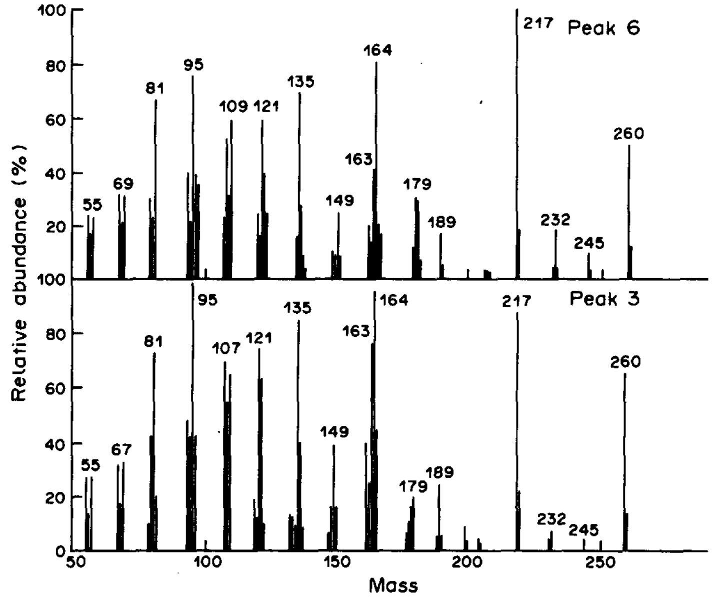

Fig. 2. Mass spectra of tetracyclic diterpene hydrocarbons. First group.

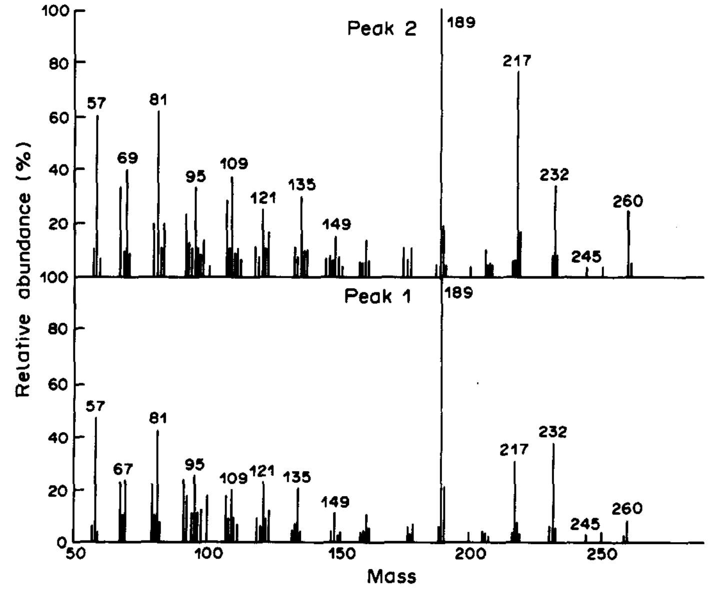

Fig. 3. Mass spectra of tetracyclic diterpene hydrocarbons. Second group.

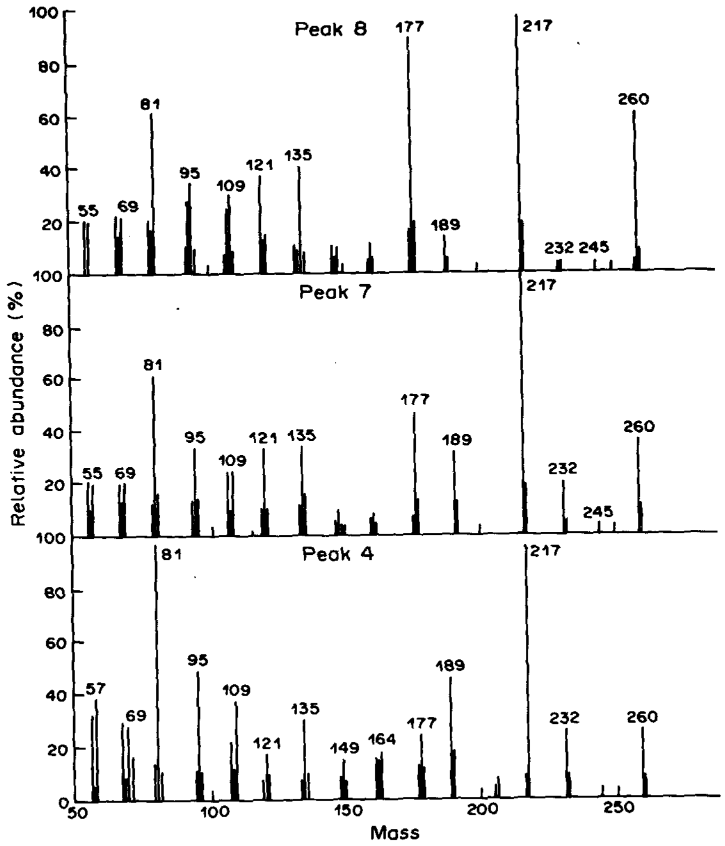

Fig. 4. Mass spectra of tetracyclic diterpene hydrocarbons. Third group.

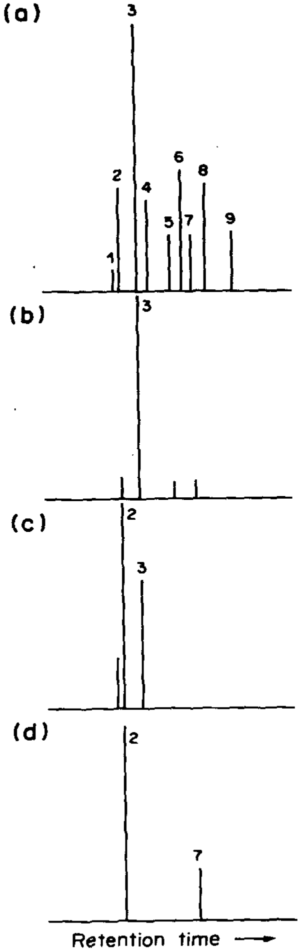

Fig. 5. Chromatograms (histograms) of the products obtained by the concentrate separation on zeolite 10X. (a) Initial mixture; (b, c, d) fractions 1–3; total volume of solvent (ml) 35, 70, 120, respectively. Identification of the peaks is given in the text and the Appendix.

Table 1. ^{13}C and ^{1}H chemical shifts for 4,8-dimethyl-13-isopropyltetracyclo[6.6.0.0^{1,11}0^{3,7}]tetradecane (II) and 5,14-dimethyl-10-isopropyltetracyclo[6.4.1.1^{1,9}0^{4,13}]tetradecane (III)

	II		III	
Carbon atoms	^{13}C δ	^{1}H δ	^{13}C δ	^{1}H δ
C-1	67.3	—	56.5	—
C-2	46.9	1.15 and 1.89	28.2	0.97 and 1.37
C-3	50.4	1.90	24.1	1.43 and 1.65
C-4	41.1	1.61	54.3	1.64
C-5	37.3	1.14 and 1.84	41.6	1.72
C-6	28.1	1.43 and 1.54	34.7	1.24 and 1.72
C-7	54.7	2.22	30.9	1.24 and 1.79
C-8	51.5	—	42.1	2.19
C-9	42.4	1.46 and 1.52	51.5	2.16
C-10	32.4	1.21 and 1.84	50.5	0.92
C-11	57.1	1.65	24.1	0.98 and 1.67
C-12	33.3	1.18 and 1.76	37.1	1.10 and 1.55
C-13	57.2	1.13	66.1	1.06
C-14	35.8	1.27 and 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	21.4	0.87

shifts reveal the presence of an isopropyl and two methyl groups and a quaternary carbon atom: 46.5 (s); 54.4, 53.2, 47.2, 42.2, 40.6, 37.8, 31.1, 30.7 (all d): 36.2, 34.0, 29.4, 27.2, 23.0, 19.3 (all t); 21.3, 20.7, 20.0, 19.6 (all q). This hydrocarbon can be an isomer of structure V, consisting of four condensed five-membered rings, as shown in V.

The biochemical routes of formation of these highly condensed tetracyclic hydrocarbons consisting of five-membered rings can be viewed as one step further from the routes of formation of the well-known sesquiterpenes with various tricycloundecane skeletons (e.g. cedrene, isocomene, pentalene, hirsutene, modhepene); they both apparently originate by the enzymatic cyclization of unsaturated aliphatic polyisoprenoids. The formation of isocomene (VI) from farnesol as often found in nature (Bohlmann *et al.*, 1977; Zalcow *et al.*, 1977) can be taken as an example. The other characteristic example is the formation of pentacyclic sesterterpenes from geranylfarnesyl pyrophosphate proposed by Kaneda *et al.* (1972).

Some compounds of a microbiological origin with chemical structures very close to that of hydrocarbon II, have been found recently (Anke *et al.*, 1985).

This characterized series of tetracyclic saturated hydrocarbons with condensed cyclopentane rings is of great interest, as these compounds can be considered as a source of hydrocarbons of the pentalane series (Petrov, 1984), of tricyclo[6.3.0.0^{1,5}]undecane and its methyl homologues (Vorobieva *et al.*, 1979).

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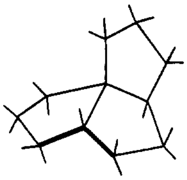
APPENDIX

Chemical Structures Cited in the Text



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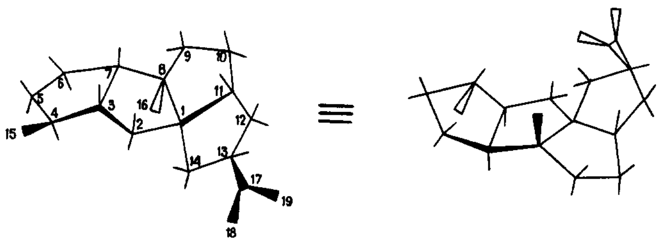

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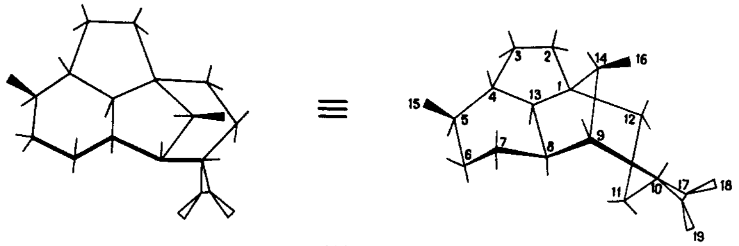

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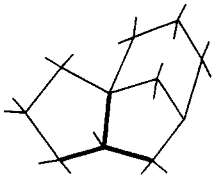

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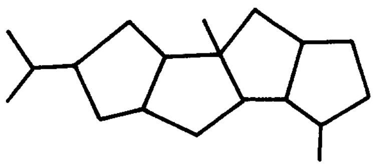

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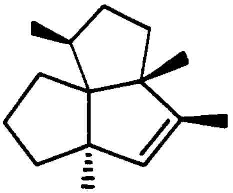

VI