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DICADINANES AS PENTACYCLIC TRITERPANES OF CRUDE OIL*

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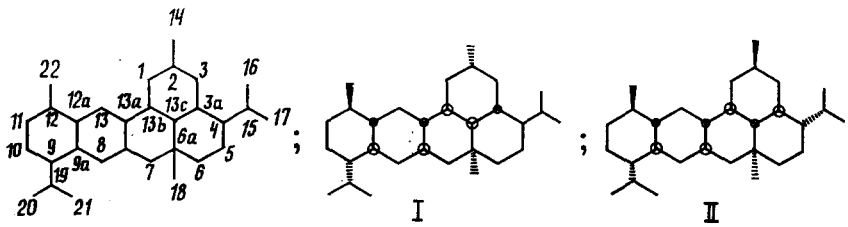
A new type of saturated pentacyclic triterpanoid of composition C_{30} was described for the first time in [1]. These hydrocarbons are characteristic of the continental crude oils of South East Asia that are produced in the South China Sea, Western Iran and in South Sumatra. The structure of one of the hydrocarbons was subsequently established in [2], where ^{13}C NMR was used to demonstrate that the main hydrocarbon of the given series is so-called dicadinane (II), i.e. a saturated cadinene dimer (III).

The full name of the hydrocarbon is 2,6*a*,12-trimethyl-4,9-diisopropylperhydrobenzo[*de*]naphthacene or 6,12,21-trimethyl-8,9-diisopropylpentacyclo[14,4.0.$0^{2,4}$1^{4,8}O^{7,12}]heneicosane. The structure of the compounds examined is given in scheme 1:



The present work is devoted to an investigation of the composition of dicadinanes in one of the Indian crude oils.

RESULTS AND DISCUSSION

We discovered dicadinanes in a study of crude oil of the South Assam basin.† The biodegraded crude oil lies in Cenozoic deposits at a depth of 350 mm. A chromatogram of the saturated hydrocarbons (b.p. >200°C) is given in Fig. 1*a*. Peaks *1–3*, belonging, as will be shown below, to cadinane and two epimeric dicadinanes present in a 40:60 ratio, stand out clearly in Fig 1*a*. As regards the distribution of dicadinanes, the specimen investigated is similar to crude oil *A* of the South China Sea, described in [1]. It is significant that, besides dicadinanes and a small amount of oleanane, the crude oil examined contains hardly any other pentacyclic triterpanes. The steranes, contained in small concentrations, comprise only C_{29}

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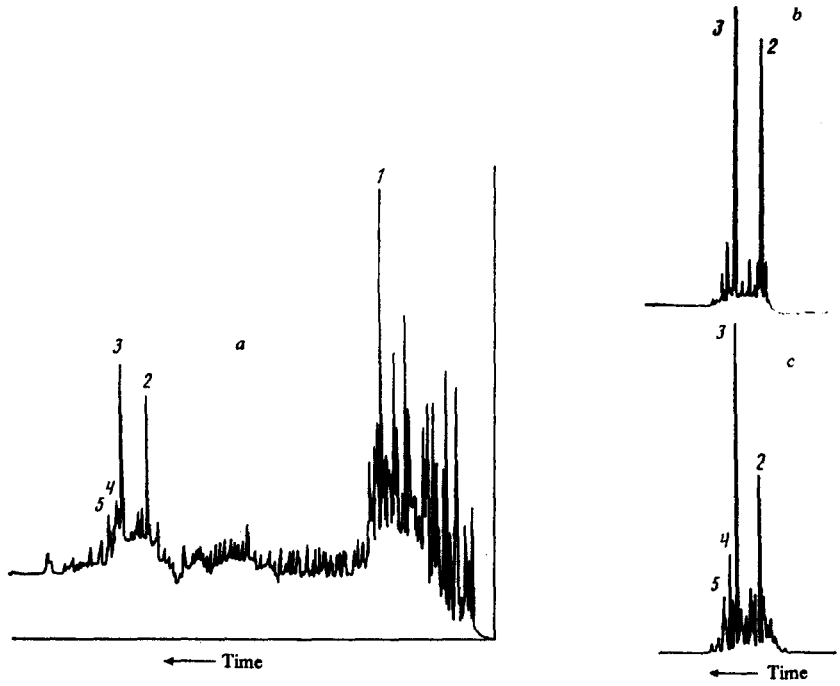


FIG. 1. Chromatograms of saturated hydrocarbons of crude oil of South Assam basin (*a*) and products of separation of saturated hydrocarbons of >350°C fraction on 10*X* zeolites (*b*, *c*) (different stages of separation).

hydrocarbons, which confirms the participation of higher plants in the genesis of this crude oil. The coefficient of maturation (the ratios of ββ/(ββ + α)-epimers), equal to 0·77, indicates considerable catagenic maturity. The crude oil is also characterized by relatively high concentrations of rearranged steranes. For a more detailed study of structures I and II, a fraction of saturated hydrocarbons (b.p. >350°C) was isolated. Further concentration of hydrocarbons I and II was carried out on 10*X* zeolites by the method described in [3]. Initially the desired hydrocarbons I and II are eluted (with eluate of structure I predominant in the first portions), and then the petroleum hump. Figure 1*b* shows chromatograms of mixtures at different stages of this separation. Thus tenfold enrichment of the initial mixture with hydrocarbons I and II made it possible to investigate their structure by means of ^{13}C NMR, and also to obtain reliable mass spectra. A study of ^{13}C NMR spectra using the procedure described in [3] showed that the spectrum of II is totally identical to the spectrum of standard *trans*-dicadinane [2]. Experimental data on the chemical shifts for compound I were in satisfactory agreement with calculated values (Table 1). Calculations were carried out with account taken of available published information on the chemical shifts of carbon in cadinane (IV), bicadinane (II), methyldecalins and also *trans,trans,trans*- and *trans,cis,cis*-perhydrophenalenes (V), which were synthesized to obtain more precise details on the stereochemistry of the perhydrophenalene ring in dicadinanes (Table 2). *Trans,trans,trans*-perhydrophenalene was produced by the isomerization of perhydrofluorene over aluminium bromide [4], while *trans,cis,cis*-epimer was produced by the hydrogenation of phenalene in an autoclave over Raney nickel at 180°C and 10 MPa. All substituents in hydrocarbons I and II (besides angular methyl) have an equatorial orientation. We should point out that, while we

TABLE 1. ^{13}C CHEMICAL SHIFTS OF 2,6*a*,12-TRIMETHYL-4,9-DIISOPROPYLPERHYDROBENZO[*de*]NAPHTHACENES (δ_{TMS})

C atom	$\delta^{13}C$			C atom	$\delta^{13}C$		
	I		II		I		II
	calculation	experiment	experiment		calculation	experiment	experiment
C-1	37,8	37,5	39,5	C-12	37,9	37,9	37,9
C-2	26,8	26,2	31,4	C-12*a*	49,7	49,8	49,7
C-3	40,2	39,8	39,5	C-13	34,0	34,0	34,0
C-3*a*	33,5	33,3	37,1	C-13*a*	41,0	39,6	49,5
C-4	49,5	49,0	49,5	C-13*e*	36,0	34,5	40,4
C-5	19,6	19,7	19,1	C-13*c*	50,0	51,7	54,2
C-6	41,3	41,8	42,2	C-14	23,0	23,3	23,3
C-6*a*	33,3	33,7	33,7	C-15	26,4	26,4	26,4
C-7	38,3	37,5	50,4	C-16	15,2	15,2	21,6
C-7*a*	37,3	37,3	37,3	C-17	21,6	21,6	15,2
C-8	37,9	37,9	37,9	C-18	28,2	28,0	18,7
C-9	48,0	48,1	48,0	C-19	26,4	26,4	26,4
C-9*a*	44,2	44,3	44,2	C-20	15,2	15,2	15,2
C-10	24,3	24,3	24,3	C-21	21,5	21,6	21,6
C-11	36,2	36,2	36,2	C-22	20,4	20,3	20,4

were carrying out this investigation, it was reported briefly [5] that the second epimer of dicadinane (I) has a *cis*-connection of rings in the perhydrophenalene fragment.

Besides ^{13}C NMR spectra we obtained mass spectra of the hydrocarbons investigated on an LKB-2091 mass spectrometer equipped with an LKB-2130 computer system. Chromatographic input was carried out using a glass capillary column with OV-101 (SP-2100) phase. The ionization energy was 70 eV. The mass spectra of hydrocarbons I and II are given in Fig. 2. They turned out to be similar to the mass spectra of compounds published in [1,2]. The mass spectra of I and II differ mainly in the intensity of fragmentary ion $(M-15)^+$, which in hydrocarbon I is 100%, but in hydrocarbon II only 10%. This difference can be easily explained, since, unlike the corresponding *trans*-decalin, ion $(M-15)^+$ is always maximum in angular-substituted *cis*-decalins [6]. The mass spectra of the compound (peak 4) (Fig. 1*c*) is identical to the spectrum of dicadinane II, whereas peak 5 consists of equal parts of dicadinane (probably having a different spatial arrangement of substituents) and homodicadinane (i.e. C_{31} hydrocarbon). In [1], hydrocarbons I and II were labelled with indices *W* and *T* respectively. The mass spectrum of cadinane (peak 1 in Fig. 1*a*) has the following values (intensity (%)):

TABLE 2. ^{13}C CHEMICAL SHIFTS OF PERHYDROPHENALENES (δ_{TMS})

C atom	Epimer		C atom	Epimer	
	trans,trans,trans-	*trans,cis,cis-*		*trans,trans,trans-*	*trans,cis,cis-*
C-1	34,4	32,7	C-6*a*	41,5	37,3
C-2	26,0	21,6	C-8	26,0	27,7
C-3	34,4	36,7	C-9*c*	53,7	45,8
C-3*a*	41,5	31,1			

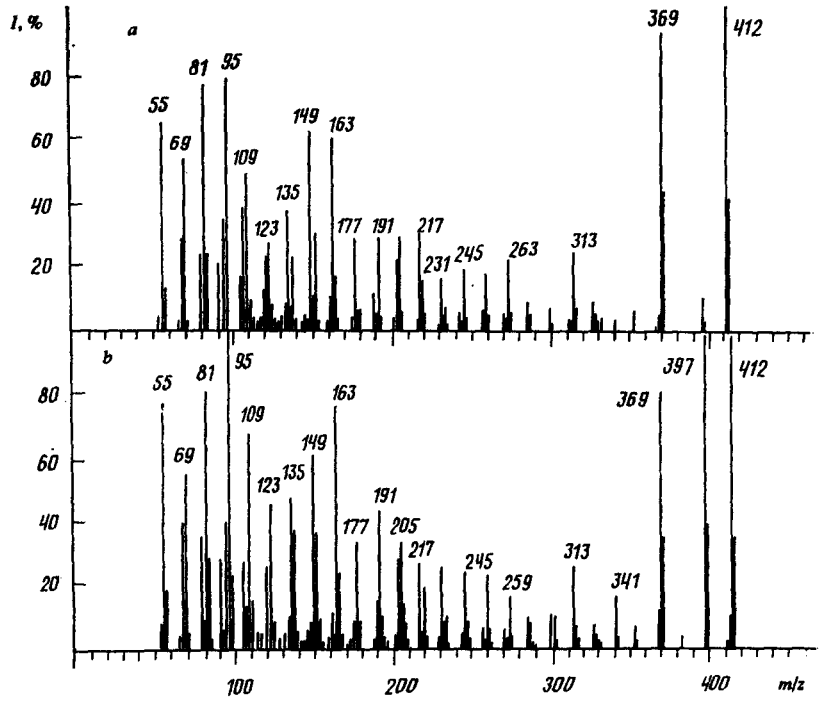
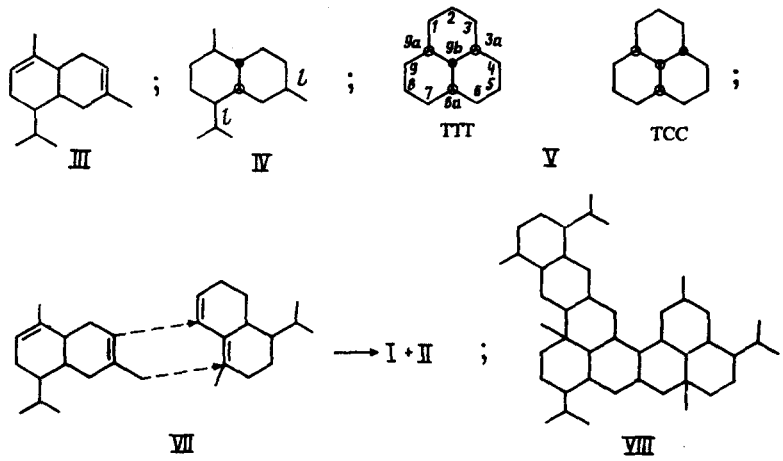


Fig. 2. Mass spectra of dicadinanes: *a* – II; *b* – I.

208 (32), 166 (52), 165 (100), 123 (23), 109 (81), 95 (76), 83 (72), 81 (71) and 67 (38). It corresponds to the spectrum of the standard hydrocarbon.

Besides dicadinanes, the octacyclic tricadinane (VIII) of composition C_{45} is also described in [4]; this is a saturated cadinane trimer. Its assumed structure is shown in scheme 2:



On the basis of mass spectra data, this hydrocarbon is absent in the crude oil investigated. Scheme 2 also presents a possible variant (VII) of formation of dicadinane (I and II) from cadinene (III).

In conclusion we shall point out the remarkably low apparent boiling point of the two

epimeric dicadinanes. Thus, hydrocarbons I and II are eluted in the region of C_{27} hopanes. Moreover, at 300°C hydrocarbon I is eluted jointly with C_{29} *n*-alkane. The relative retention times at this temperature (for 17-α-hopane) amount to 0·37 for I and 0·52 for II. The index of retention is 2900 for I and 3020 for II (temperature 300°C, capillary column with Apiezon L).

SUMMARY

Two epimers of saturated pentacyclic triterpane – dicadinane (C_{30}) – have been found in crude oil of the South Assam field (India). The hydrocarbon structure has been established by means of chromato-mass spectrometry and ^{13}C NMR spectrometry. The hydrocarbons are 2,6*a*,12-trimethyl-4,9-diisopropylperhydrobenzo[*de*]naphthacenes and can be regarded as saturated products of bicyclic sesquiterpene (cadinene) dimerization. Mass spectra and ^{13}C NMR spectra of the compounds investigated have been given.

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