An Optically Active Triterpane, Gammacerane in Green River, Colorado, Oil Shale Bitumen

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IN an earlier Paper,[1] the isolation of three pentacyclic triterpanes from an optically active petroleum distillate from Nigerian crude oil was reported. It was suggested there that the optically active hydrocarbons isolated by Oakwood *et al.*[2] and the hydrocarbon, m.p. 292—297°, separated from a Green River Colorado oil shale bitumen by Cummins and Robinson,[3] might also be pentacyclic triterpanes.

Upon request, after the work[1] had been reported, the group at Laramie Petroleum Research Centre kindly made available a sample of their hydrocarbon,[3] m.p. 292—297°. As received, it bore the reference KR 62—148 and for convenience will be referred to by this code number.

The melting points of KR 62—148 (292—297°)[3] and gammacerane (290°)[4,5] indicated that KR 62—148 might be identical with gammacerane (I), since gammacerane is the only triterpane of known structure which melts above 250°.

Professor F. B. Mallory[4] kindly provided us with a few mg. of tetrahymane (gammacerane)[5] and we were able to compare this with the hydrocarbon KR 62—148.

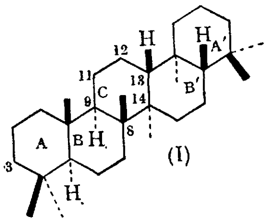
The nuclear magnetic resonance spectra (80 Mc./sec.) of tetrahymane and KR 62—148 which

TABLE

Relative retention volumes

0·01 in. i.d. glass capillary columns*		Relative retention volume n-C_{30} = 1·0		
Stationary phase	Length	Tetrahymane	KR 62–148	Mixture (1 : 1 wt)
SE 30 gum	58 ft.	1·49	1·49	1·47
SE 52 gum	148 ft.	1·69	1·68	1·70

* The approximate retention times from the methane peak to the $C_{30}H_{52}$ hydrocarbon on the SE 30 and SE 52 silicone gum columns, were respectively 1·75 and 2·5 hr.



(I)

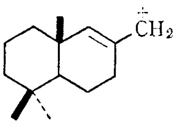
were virtually identical, showed that there were eight methyl groups in each molecule. These two spectra were different from, but showed certain similarities to the n.m.r. spectra of lupane and adiantane, a pentacyclic triterpane and nortriterpane respectively. All of these spectra also showed certain similarities to those of our triterpanes "E" and "F".[1]

Gas–liquid chromatograms were obtained from glass capillary columns coated with silicone gum. The carrier gas was hydrogen and the column was operated at 252° with a flame ionization detector. The relative retention volumes (R.R.V.) listed in Table 1 were determined on tetrahymane, KR 62—148 and on a 1 : 1 mixture of the two hydrocarbons. The mixed hydrocarbons showed a single symmetrical peak on each column and there was no evidence for any shoulder. The purity of tetrahymane on these columns appeared to be >99% whilst KR 62—148 was about 95%. Peak "O" in the gas–liquid chromatogram of the pentacyclic naphthene concentrate[1] has an R.R.V. of 1·49 (SE 30 gum 148 ft; n-C_{30} = 1·0) and may possibly be identical with tetrahymane and KR 62—148. Work in progress is directed towards the isolation from Nigerian crude oil of the hydrocarbon related to peak "O".

Tetrahymane had a specific optical rotation $[\alpha]_{546}^{21}$ + 29·4°±0·3° and the hydrocarbon KR 62—148 $[\alpha]_{546}^{21}$ + 31·9°±0·4°. These values were determined on as little as 1 mg. of sample using a new method developed by Mr. G. C. Speers for organic geochemical work at Sunbury. A full description of the method will appear in a future publication.

Uncorrected melting points determined in the laboratories at Sunbury were taken concurrently in open melting-point tubes in an oil bath. Tetrahymane, m.p. 301°; KR 62—148 m.p. 285—286°; a mixture (1 : 1) of tetrahymane with KR 62—148 melted at 288—292°. Each sample tended to sublime above 275° and showed signs of decomposition at the melting point. The slight differences in specific rotation and m.p. between these two hydrocarbons may be due to the presence in KR 62—148 of the impurities noted in its gas–liquid chromatogram.

The mass spectra of tetrahymane and KR 62—148 were recorded consecutively on an AEI MS-9 high-resolution mass spectrometer. These spectra were almost identical and relatively simple. The simplicity, no doubt, is due to the symmetry of the molecule which appears to favour fragmentation between C-8 and C-14, C-12 and C-13, C-9 and C-11, to yield identical fragments (II) at *m/e* 191 from rings A and B and from A' and B'.



(II)

This fragment (II), containing rings A and B, is classed by Djerassi and his co-workers[6] as one of the most characteristic fragmentation products of pentacyclic triterpanes. The molecular ion at *m/e* 412 and the fragment at *m/e* 397 ($M-15$, methyl) as well as the fragments at *m/e* 205, 191, 137, 123, and 109 are all prominent in the mass spectra of pentacyclic triterpanes.[1] The accurate mass of the molecular ion from KR 62—148 was 412·409 and confirmed its molecular formula as $C_{30}H_{52}$. The mass spectrum of KR 62—148 indicated the presence of approximately 2·5% of a C_{31} homologue.

These experimental results confirm the identity of the hydrocarbon KR 62—148 as gammacerane. Derivatives of gammacerane, and derivatives of hopane closely related to gammacerane, are fairly widely distributed in the plant kingdom but pentacyclic triterpenes appear to occur only rarely in the animal kingdom. In fact, tetrahymanol (gammaceran-3β-ol), is the first pentacyclic triterpenoid alcohol isolated from an animal.[5] The ciliated protozoan *Tetrahymena pyriformis*, from which tetrahymanol was isolated[4] is widely distributed in Europe and America, usually in ponds, streams, stagnant pools, and thermal springs. It also occurs in the soil and probably in brackish water.[7]

Thus gammacerane (KR 62—148), isolated from the Mahogany-zone bed of the Green River Formation near Rifle, Colorado (Eocene *ca.* 52×10^9 years),[3] may be derived either from relatively simple plant forms or perhaps from protozoa or both.

Other workers[8] have suggested the presence of triterpenoid types in fossil fuels and sediments, but few triterpenoids of known structure[9] have yet been identified amongst the compounds isolated from these sources. There appears to be less doubt now that the pentacyclic triterpenoids and related hydrocarbons had a biological origin, back in geological time.

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[1] I. R. Hills and E. V. Whitehead, *Nature*, 1966, **209**, 977.

[2] T. S. Oakwood, D. S. Shriver, H. H. Fall, W. J. McAleer, and P. R. Wunz, *Ind. Eng. Chem.*, 1952, **44**, 2568.

[3] J. J. Cummins and W. E. Robinson, *J. Chem. and Eng. Data*, 1964, **9**, 304.

[4] F. B. Mallory, J. T. Gordon, and R. L. Conner, *J. Amer. Chem. Soc.*, 1963, **85**, 1362.

[5] Y. Tsuda, A. Morimoto, T. Sano, Y. Inubushi, F. B. Mallory, and J. T. Gordon, *Tetrahedron Letters*, 1965, 1427.

[6] H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.

[7] "An Introduction to the Study of Protozoa", D. L. Mackinnon and R. S. J. Hawkes, Clarendon Press, 1961, 275.

[8] J. Marcusson, *Chem. Z.*, 1908, **32**, 377 and 391; W. G. Meinschein, *Bull. Amer. Assoc. Petrol. Geol.*, 1955, **43**, 925; *Geochim. Cosmochim. Acta*, 1961, **22**, 58; M. Louis, *Rev. Inst. franç. Pétrole*, 1964, **19**, 277; A. L. Burlingame, P. Haug, T. Belsky, and M. Calvin, *Proc. Nat. Acad. Sci., U.S.A.*, 1965, **54**, 1406.

[9] D. H. R. Barton, K. H. Overton, and W. Carruthers, *J. Chem. Soc.*, 1954, 2047; K. Hejno, M. Horák, V. Jarolim, M. Streibl, and F. Šorm, *Chem. and Ind*, 1958, 1142; *Coll. Czech. Chem. Comm.*, 1961, **26**, 459; 1963, **28**, 2318, 2443; 1965, **30**, 873.