Organic Geochemistry of some Georgia–South Carolina Clays: C_{19}—C_{28} Isoprenoids and the Possible Presence of a Sesterterpene-derived Hydrocarbon

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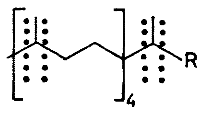
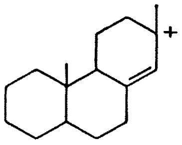
Summary The lipid extracts from several samples of Georgia–S. Carolina kaolins contained in abundance the regular C_{19}–C_{28} isoprenoid alkanes as well as a tetracyclic compound $C_{24}H_{42}$ which seems likely to have been derived diagenetically from sesterterpenes of hydrochrysene structure.

THE commercially important Georgia–South Carolina kaolins are judged to be secondary deposits of late Cretaceous–Paleocene times.[1] The crude matrix is well kaolinised; more than 90% is of particle size less than 300 mesh. The total (free + combined) carbon[2] amounts to 100—500 p.p.m. We have found that up to 70% of this is accounted for by the presence of (i) graphite, (ii) soluble humic material, and (iii) hydrocarbon oil.

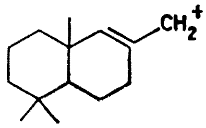
The graphite and humic material were thoroughly characterised.[3] The pale yellow oil contained free (dissolved) sulphur, but only little combined sulphur; moreover, it was free of the so-called asphaltenes (no precipitation of organic material by addition of n-pentane). The material of the sediment itself, the pale colour of the extracted oil, the presence in it of free but not combined sulphur, and the absence of asphaltenes, all point to relatively mild thermal history for the sediment.[4] The oil was chromatographed on silica gel and adducts were made with urea. Temperature-programmed gas chromatography–mass spectrometry† of the portion which formed adducts showed the presence of n-alkanes C_{16}—C_{38} with no discernible odd/even carbon number preference. The alkane portion which did not form adducts was of interest in that it contained in abundance the regular (head to tail) isoprenoid hydrocarbons from C_{16} through to C_{28}. The C_5—C_{26}, C_{28}—C_{31}, C_{33}—C_{36}, and C_{38}—C_{40} regular isoprenoids ($2,2 + 4n, \cdots$ methylalkanes) have been found in sediments and in petroleums.[5] Mass spectral fragmentation of such isoprenoids occurs preferentially at the site of branching. The C_{26} (**1a**) and C_{28} (**1c**) compounds each gave ions characteristic for the



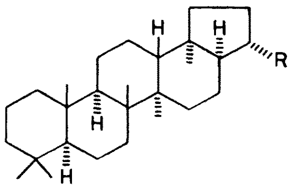
(1)
a; R = Pr^n
b; R = Bu^n
c; R = n-pentyl



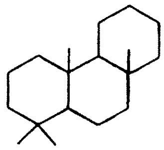
(2)



(3)



(4)
a; R = Pr^i
b; R = CHMeEt
c; R = CHMePr^n



(5)

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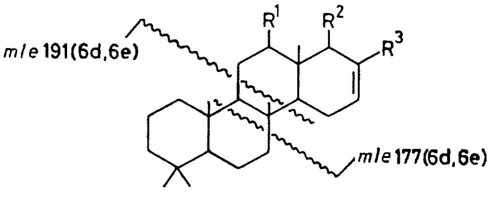
† G.c.–m.s. was carried out on several instruments. We thank Dr. P. W. Brooks and Mr. A. Aldridge of Masspec Analytical Speciality Services, Woodchester for allowing us to examine the mass spectrum of the $C_{24}H_{42}$ compound in reference 11(b) (25 m, 0·25 mm OV 1 coated glass capillary column; Finnigan 3200 quadrupole m.s. and 6110 data system). We also thank Mr. J. D. Robinson of V.G. Micromass, Altrincham (50 m × 0·30 mm OV 101 coated glass capillary column; VG 16 F m.s. and 2040 data system). G.c.–m.s. in Exeter was carried out on a 50 m × 0·40 mm OV 101 coated glass capillary column and VG Micromass 30 F m.s.; we thank Mr. Richard Bailey and Mr. David Whitmarsh for technical assistance.

fissions represented in (**1**) and their mass spectra agreed well with those published for these compounds.[6] The mass spectrum of the C_{27} compound fitted well into the series.[7]

The mass fragmentogram of the sterane-derived[8] ion (**2**), *m/e* 217, contained one prominent peak identified as that of 24-ethyl-5α-cholestane.[9] The mass fragmentogram for ion (**3**), *m/e* 191, had peaks corresponding to the 17α*H*-hopanes[10] (**4**), twin peaks being obtained for compounds (**4b**) and (**4c**) corresponding to *R*- and *S*-stereochemistry at C-22 in these compounds. Also present was a peak at *m/e* 330 which in spectra obtained from eight out of seventeen oils was the most prominent.

The compound with *m/e* 330 ($C_{24}H_{42}$) was clearly tetracyclic and its mass spectrum (ions *m/e* 315, 274, 251, 206, 192, 191, 177, 163, 150, 137, 136, 123, 121, 109, 97, 95, and 81) was different from those of previously reported $C_{24}H_{42}$ compounds.[11] These data were analysed by two different computer systems. In one,[12] (Probability Based Matching System, PBMS) the entire mass spectrum of the unknown with peaks suitably weighted with regard to mass and abundance is matched with mass spectra of known compounds. In the other[13] (Self Training Interpretive and Retrieval System, STIRS), the mass spectrum of the unknown is analysed for characteristic ions, loss of neutral fragments, and similar features and then compared with spectra of compounds of known structure; STIRS then provides probabilities of the existence of chemical substructures in the molecule of the unknown compound.

In the present application PBMS gave low *K* values and high ΔK values indicating poor matches with every one of the 32,000 spectra scanned; STIRS, however, established (i) the certain presence of two fused six-membered rings and the probable presence of a third fused six-membered ring and (ii) that the large *m/e* 191 and 192 peaks coupled with a neutral fragment loss of 56 a.m.u. agreed well with a 4,4,8,10-tetramethyldecalin system present in many terpenes. A most valuable feature of this computer-derived information is that it is positive and additive and leads, in the present instance, to a likely partial structure (**5**) which for completion requires the addition of one ring. The mass spectrum excludes a sterane structure.



(**6**)

a; R^1 = OAc, R^{2}R^3 = CH(OH)·O·CO
b; R^1 = OAc, R^{2}R^3 = CH(OH)·O·CH$_2$
c; R^1 = OAc, R^2 = R^3–CHO
d; R^1 = R^2 = H,R^3 = Me; 16,17-dihydro
e; R^1 = R^3 = H,R^2 = Me; 16,17-dihydro

Recently, sesterterpenes of hydrochrysene structure, *e.g.* scalarin (**6a**), deoxoscalarin (**6b**), and scalaradial (**6c**), have been identified in sponges growing in the Bay of Naples.[14,15] It is open to conjecture whether compound *m/e* 330 might have a similar structure, (**6d**) or (**6e**), derived by diagenesis of terpenes contained in sponges contemporaneous with the deposition of the clay sediments. The mass spectra of (**6d**) and (**6e**) would almost certainly contain all the ions[15] found in that of the compound with *m/e* 330.

We thank Dr. Dudley Williams for an introduction to, and Prof. F. W. McLafferty for access to, the Computer Services at Cornell; Dr. Barbara Atwater kindly carried out the data computation. Also we thank English China Clays for financial aid.

(*Received*, 17*th September* 1979; *Com.* 998.)

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