Identification of Tetracyclic Diterpene Hydrocarbons in Australian Crude Oils and Sediments

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Tetracyclic diterpene hydrocarbons containing the kaurane, phyllocladane (13β-kaurane), and beyerane skeletons have been identified in some Australian petroleums and sediment extracts; these compounds are useful biological markers for higher plants.

Crude oils and sediments contain a variety of polycyclic alkanes, many of which have structures that closely resemble compounds of biological origin. In recent years, the widespread occurrence in petroleum of terpenes containing two, three, four, five, and six ring systems has been demonstrated. $^{1--7}$ Analysis of petroleum and sediment extracts from the Perth and Gippsland Basins of Australia has revealed, in addition to the commonly observed cyclic terpenes, several hitherto unidentified C_{20} tetracyclic diterpenes. In this paper we report the identification of these compounds based upon comparison with diterpenes prepared from natural product precursors.

Pure samples of beyerane (1) and $16\beta(H)$ -kaurane (3b) have been synthesized previously from *ent*-beyerol⁸ and 16α -(-)-kauran-17,19-dioic acid,⁹ respectively, and samples of $16\alpha(H)$ -phyllocladane (2a)† and $16\alpha(H)$ -kaurane (3a)† were prepared by catalytic hydrogenation of phyllocladene (4)¹⁰ and *ent*-kaurene (5),^{11,12} respectively. These hydrogenation reactions also produced minor amounts of the corresponding $16\beta(H)$ -isomers, (2b) and (3b), but in low yield.^{10,11} Consequently, $16\beta(H)$ -phyllocladane (2b) was synthesized in high yield from phyllocladene (4) by conversion into the α -epoxide, followed by Lewis acid rearrangement, base equilibration of the resulting aldehydes to the $16\beta(H)$ -configuration, and then reduction to the hydrocarbon.‡

The geological samples analysed in this study consisted of crude oils from the Gippsland Basin, Cretaceous sediments from the Perth and Gippsland Basins, and Yallourn lignite, a low-rank brown coal. The branched and cyclic alkanes were

isolated from each hydrocarbon extract, and analysed using combined gas chromatography–mass spectrometry (g.c.–m.s.).² The mass spectra of the diterpenes displayed base peaks at m/z 123 and molecular ions at m/z 274. Consequently, they were readily detected during g.c.–m.s. analysis as m/z 123 and 274 fragments.

Figure 1 shows an expanded section of the m/z 123 and 274

[†] Previous reports refer to these compounds as '\alpha dihydrophyllocladene' and '\alpha-dihydrokaurene' (ref. 10 and 11).

 $[\]ddagger$ Reaction scheme (i) $\emph{m}\text{-}ClC_6H_4CO_3H,~CH_2Cl_2;~(ii)}$ BF $_3 \cdot Et_2O,~C_6H_6;~(iii)$ KOH, MeOH; (iv) NaBH $_4,~MeOH;~(v)~\emph{p}\text{-}MeC_6H_4SO_2Cl,~C_5H_5N;~(vi)$ LiAlH $_4,~Et_2O.$ The product was shown to be identical to the minor component from the hydrogenation of phyllocladene, $16\beta(\emph{H})\text{-phyllocladane}~(ref.~10),~using~high~resolution~g.c.-m.s.$ Spectroscopic data were recorded for all intermediates, and these will be presented elsewhere.

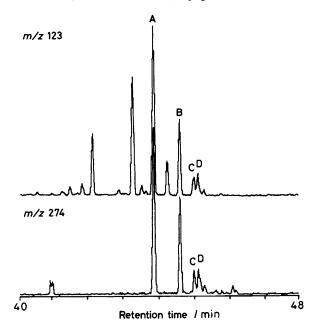


Figure 1. Expanded section of m/z 123 and 274 mass fragmentograms for a Cretaceous sediment (Gippsland Basin). Peaks A—D represent four tetracyclic alkanes, analysed using an HP 5985 B capillary GC-MS-data system fitted with a 50 m \times 0.2 mm internal diameter WCOT cross-linked methylsilicone column. Operating conditions: 250 °C source temperature, 2600 V electron multiplier voltage, 70 eV electron energy.

mass fragmentograms for a Cretaceous sediment from the Gippsland Basin. Peaks A—D represent four tetracyclic alkanes. By comparing the g.c. retention times, Kováts indices (I^{150}) , and mass spectra of these four cycloalkanes with those of the synthetically prepared diterpenes, we have assigned peaks A, B, C, and D as beyerane (1) $(I^{150} = 1929)$, $16\beta(H)$ -phyllocladane (2b) $(I^{150} = 1955)$, $16\beta(H)$ -kaurane (3b) $(I^{150} = 1967)$, and $16\alpha(H)$ -phyllocladane (2a) $(I^{150} = 1971)$, respectively. $16\alpha(H)$ -Kaurane (3a) $(I^{150} = 1991)$ could not be detected in this sample.

The relative abundance of these tetracyclic diterpene hydrocarbons in crude oils from the Gippsland Basin was similar to that of the sample shown in Figure 1. However, major differences were apparent in the extracts of Yallourn lignite. Whereas kaurane (3) was present as the $16\beta(H)$ epimer in crude oils and Cretaceous sediments, it occurred only as the $16\alpha(H)$ -compound in the lignite. Both the $16\alpha(H)$ and $16\beta(H)$ -phyllocladane epimers (2a) and (2b) were present in crude oils and Cretaceous sediments [(2a)/(2b) = 0.2], whereas only the $16\alpha(H)$ -compound (2a) was identified in the lignite. (This is consistent with previous reports of $16\alpha(H)$ phyllocladane as the mineral Bombiccite in lignites.)13 These differences suggest a maturity effect in which the thermodynamically preferred $16\beta(H)$ -configurations of phyllocladane and kaurane¶ predominate in ancient sediments and crude oils.

The occurrence of diterpenoids containing the beyerane (1), phyllocladane (2), and kaurane (3) skeletons in higher plants is well documented. 15,16 Compounds containing the phyllocladane (2) skeleton occur in many conifers, 15 but are limited to this group, and diterpenoids based on the beyerane (1) skeleton have been found only in a small number of higher plant species. On the other hand, diterpenoids based on the kaurane (3) skeleton are widely distributed in the higher plant kingdom, 15 and are particularly significant owing to their biosynthetic relationship to the gibberellin plant growth hormones.¹⁷ The occurrence of tetracyclic diterpenes in geological samples is therefore an indicator for higher plant contributions to crude oils and sedimentary organic matter. More specifically, the occurrence of phyllocladane strongly indicates that conifer resins were a significant component of the organic matter deposited during sedimentation.

We thank Professor P. R. Jefferies for several diterpenoid samples and helpful advice, and Professor R. C. Cambie for a generous sample of phyllocladene. Dr. A. G. Douglas is thanked for useful discussions, and one of us (R.N.) acknowledges the University of Western Australia for financial assistance. This project was partially supported by the National Energy Research Development Demonstration Program of Australia.

Received, 17th July 1984; Com. 1038

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 $[\]$ Kováts indices were measured at 150 °C using a 50 m \times 0.2 mm internal diameter fused silica cross-linked methylsilicone capillary column.

[¶] Preliminary calculations on relative stabilities of $16\alpha(H)$ - and $16\beta(H)$ -kauranes using the Allinger method (ref. 14) were done by Professor D. L. Kepert, Department of Physical and Inorganic Chemistry, University of Western Australia.