





**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 ( $I^{150}$ ),<sup>§</sup> 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 Yallowrn 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 Bombicite in lignites.)<sup>13</sup> These differences suggest a maturity effect in which the thermodynamically preferred 16 $\beta$ (*H*)-configurations of phyllocladane and kaurane<sup>¶</sup> predominate in ancient sediments and crude oils.

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

<sup>¶</sup> 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.

The occurrence of diterpenoids containing the beyerane (1), phyllocladane (2), and kaurane (3) skeletons in higher plants is well documented.<sup>15,16</sup> Compounds containing the phyllocladane (2) skeleton occur in many conifers,<sup>15</sup> 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,<sup>15</sup> and are particularly significant owing to their biosynthetic relationship to the gibberellin plant growth hormones.<sup>17</sup> 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.

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