Identification of the Bicyclic Sesquiterpenes Drimane and Eudesmane in Petroleum

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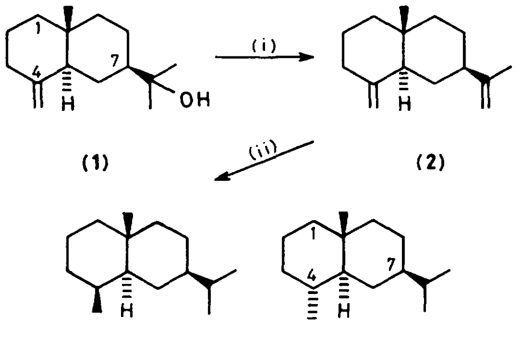
Drimane and eudesmane have been identified in petroleum; eudesmane is formed from higher plant precursors while drimane is probably derived from microbial sources.

The transformations of complex molecules of biological origin, biological marker compounds, are being used increasingly to provide information about the processes affecting organic matter in geological environments.[1-3] Studies of saturated steroid and triterpene hydrocarbons, both of which occur widely in petroleum extracts, have been particularly successful in providing information of use in petroleum exploration.[4,5] The presence of bicyclic sesquiterpenes in petroleum has been reported on a number of occasions;[6-10] however, with the exception of one report where two such compounds were identified,[10] rigorous proof of structure was not attempted. In this paper we describe the synthesis of sesquiterpene standards and their use in the identification of petroleum bicyclanes.

Two isomers of eudesmane (3a) and (3b) were synthesized from β-eudesmol (1) by the sequence outlined in Scheme 1. Capillary g.l.c. analysis of the product (OV-101 column, HP 5880 chromatograph) showed that the compounds were present in a 6:1 ratio. The major component (Kovats index



Scheme 1. Synthesis of $4\alpha(H)$-eudesmane (3a) and $4\beta(H)$-eudesmane (3b). (i) $POCl_3$; (ii) H_2–Adam's catalyst, MeOH.

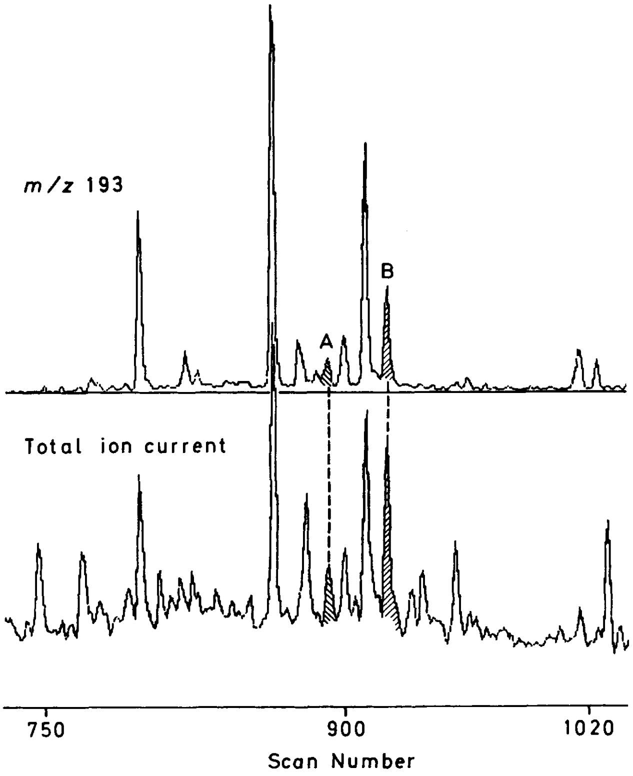


Figure 1. Expanded section of the computer-reconstructed total ion current and m/z 193 fragmentogram for Cormorant saturates (Gippsland, Australia). Analysed on an HP 5895B capillary g.l.c.–mass spectrometry computer data system, fitted with a 50 m × 0.02 mm ID WCOT OV-101 column. Operating conditions: 250 °C source temperature; 2600 V EM voltage; 70 eV electron energy.

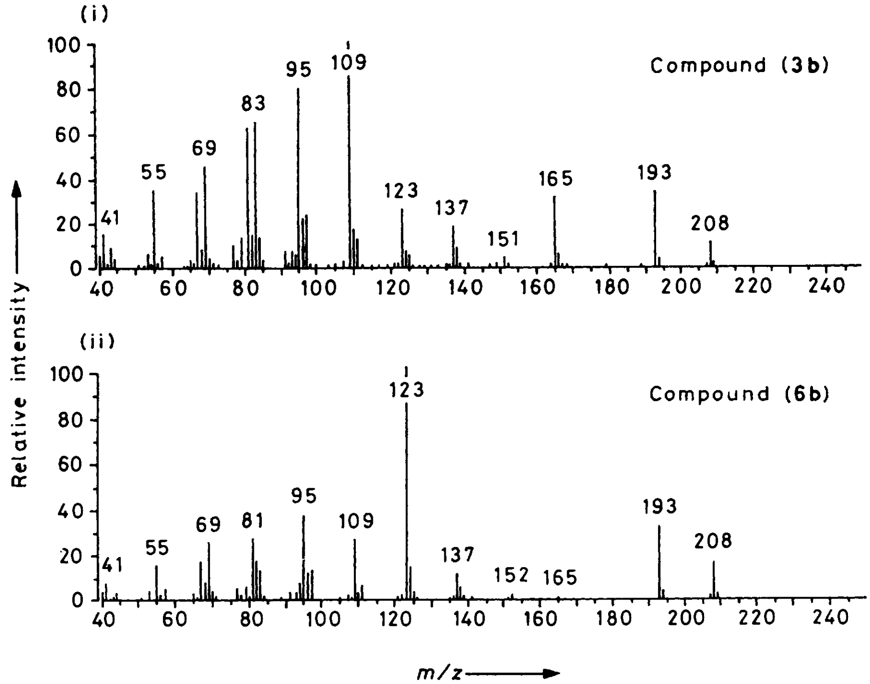
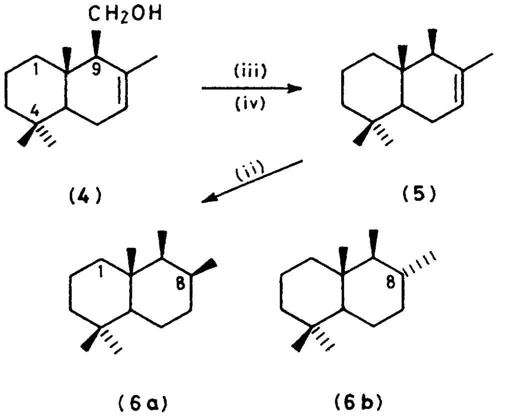


Figure 2. Mass spectra of synthetic standards, recorded at 70 eV (HP 5895B g.l.c.–mass spectrometry data system).



Scheme 2. Synthesis of 8α(*H*)-drimane (6a) and 8β(*H*)-drimane (6b). (ii) H_2–Adam's catalyst, MeOH; (iii) *p*-$MeC_6H_4SO_2Cl$, pyridine; (iv) $LiAlH_4$, ether.

1463) was assigned structure (**3a**) [4α(*H*)-eudesmane] because of the steric requirements for catalytic reduction (step ii).[11] The minor product (Kovats index 1425) was assigned structure (**3b**) [4β(*H*)-eudesmane].

Capillary g.l.c.–mass spectrometry was used to monitor the bicyclic sesquiterpene content of petroleum samples. The analyses were carried out on the branched and cyclic alkanes isolated from the total saturate fraction. Figure 1 shows a section of the computer-reconstructed total ion current and *m/z* 193 fragmentogram for Cormorant oil saturates (Gippsland Basin, Australia). By comparing g.l.c. retention times and mass spectra of the petroleum bicyclanes and the standards [Figure 2(i)], we have identified compound A (Figure 1) as 4β(*H*)-eudesmane (**3b**). The 4α(*H*)-epimer (**3a**), in which the 4-methyl group is axial, was not present in the geological sample.

In our experience, eudesmane is not a common constituent of crude oils. It is present in samples with a significant contribution of terrigenous source material but only occurs in low concentrations. Sesquiterpenes based on the eudesmane skeleton are widely distributed in higher plants,[13] and it is therefore reasonable to conclude that 4β(*H*)-eudesmane (**3b**) is an unambiguous marker for higher plant precursors.

Scheme 2 outlines the synthesis of two isomers of drimane (**6a**) and (**6b**) from naturally occurring drimenol (**4**).[14] Once again, capillary g.l.c. analysis showed that the two isomers (**6a**) and (**6b**) were produced in unequal quantities, with preferential formation of the 8α(*H*)-epimer (**6a**). This assignment was confirmed by reversing the order of reactions, using reagent (ii) first followed by reagents (iii) and (iv). In this case, two isomers of drimanol are formed from the hydrogenation (ii), of which the 8α(*H*)-epimer is the major product.[14] Reagents (iii) and (iv) then yielded isomeric drimanes, identical to those synthesized in Scheme 2 (**6a**) and (**6b**). Kovats indices for 8α(*H*)- and 8β(*H*)-drimane were 1470 and 1445 respectively, and the mass spectrum of 8β(*H*)-drimane (**6b**) recorded at 70 eV is shown in Figure 2(ii). Compound B in Cormorant saturates (Figure 1) was identified as 8β(*H*)-drimane (**6b**) by comparison of mass spectra and by coinjection of the standard with the geological sample. No significant concentration of 8α(*H*)-drimane (**6a**) was detected in this oil.

Sixteen other crude oils from worldwide sources were analysed for bicyclic sesquiterpenes by g.l.c.–mass spectrometry. These range in age from Cambrian to Tertiary and represent a wide variety of types. The samples contained similar, though not identical distributions of bicyclanes, and all contained 8β(*H*)-drimane (**6b**). In addition, bitumen extracts from drill-hole cuttings of wells in the Carnarvon and Canning basins, W. Australia, also contained 8β(*H*)-drimane as a component of their sesquiterpene content but the 8α(*H*)-drimane was not present in detectable amounts. These sediments varied in age from Ordovician to Early Cretaceous and spanned a wide range of maturity levels. The widespread geological and geographical occurrence of 8β(*H*)-drimane suggests that it is derived from a ubiquitous source. Furthermore, its appearance in Cambrian–Ordovician samples, where land plant input was not significant, rules out the possibility of its being derived from higher plant precursors. We therefore conclude that 8*β*(*H*)-drimane is most likely of microbial origin. It could arise either from microbial degradation of higher terpenes such as hopanes, or from direct formation of a compound or compounds containing the bicyclic ring system. This is in direct contrast with 4*β*(*H*)-eudesmane, which was found in a land plant-based crude, and undoubtedly reflects its higher plant origin.

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