Identification of 2,2,7,8-Tetramethyl-1,2,3,4-tetrahydronaphthalene in Petroleum

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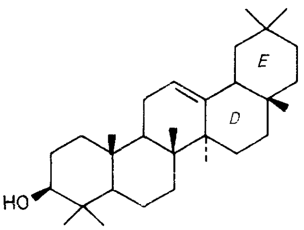
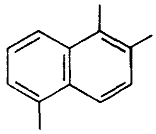
2,2,7,8-Tetramethyl-1,2,3,4-tetrahydronaphthalene, a proposed key intermediate in the degradation and aromatisation of triterpenoids of the oleanane skeletal-type, has been synthesized and identified in Cretaceous sediments and crude oils.

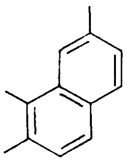
Natural products deposited in sediments can be converted into compounds known as biomarkers which provide information of use in the exploration for petroleum.[1] The transformations of compounds that can be related to specific organisms or plant families are particularly useful if the products of such transformations can be recognised in sediments and crude oils when other microscopic or macroscopic evidence has been destroyed.[2] One example of natural products with a restricted occurrence is the group of triterpenoids with the oleanane skeleton, *e.g.* β-amyrin (**1**). These triterpenoids are confined to the angiosperms (flowering plants)[3,4] and are therefore restricted to sediments of Cretaceous and younger age which post-date evolution of these plants.[5] Recently 1,2,5-trimethylnaphthalene (1,2,5-TMN) (**2**) and 1,2,7-trimethylnaphthalene (1,2,7-TMN) (**3**) have been reported to occur in high abundance in sediments and crude oils where the organic matter was derived from such plant material.[6] The presence of 1,2,7-TMN, presumably derived from the *D*,*E* ring moiety of



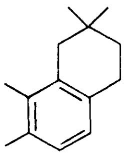
(**1**)



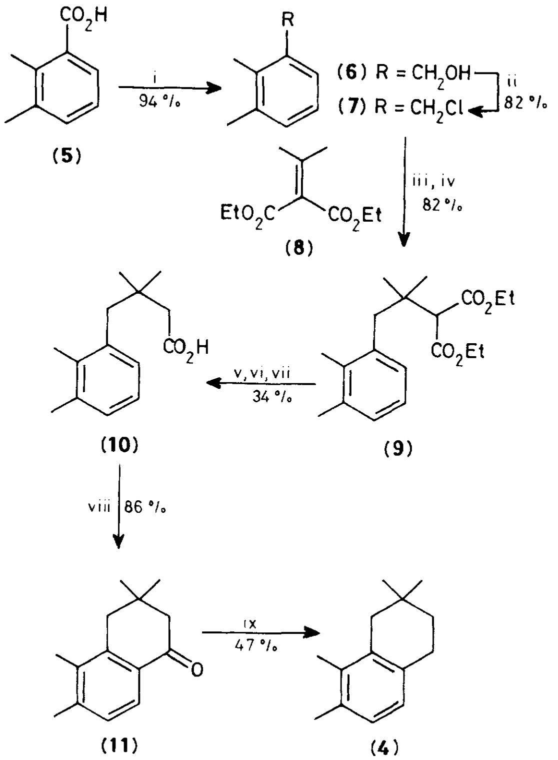
(**2**)



(**3**)



(**4**)



Scheme 1. *Reagents and conditions.* (i) $LiAlH_4$, ether, reflux; (ii) HCl, dry hexane, 0 °C; (iii) Mg, ether, $BrCH_2CH_2Br$; (iv) (**8**), ether, 20 °C, 2 h; (v) KOH, H_2O reflux, 3 h; (vi) H_2SO_4, H_2O; (vii) 120 °C, 1.5 h; (viii) PCl_5, $SnCl_2$; (ix) NH_2NH_2, KOH, diethylene glycol, reflux.

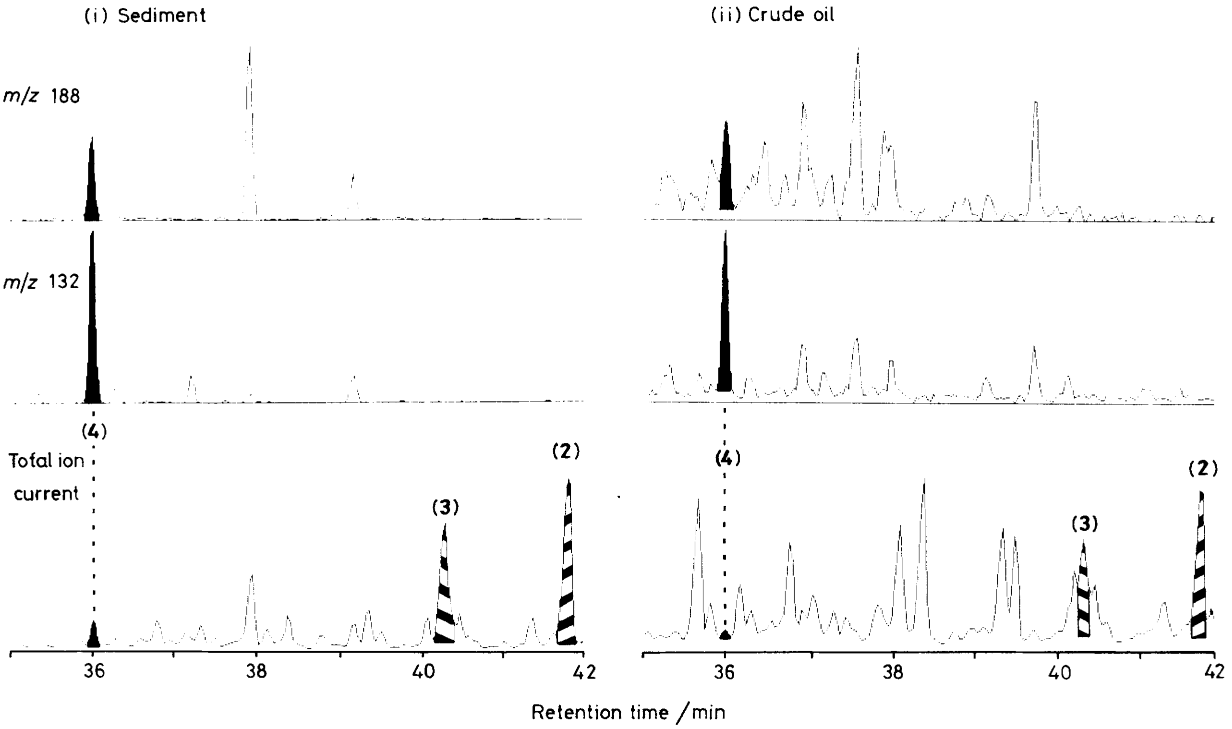


Figure 1. Partial computer-reconstructed total ion current, *m/z* 188 and *m/z* 132 mass chromatograms of the aromatic fractions from (i) sediment and (ii) crude oil samples from the Volador no. 1 (Gippsland Basin, Australia) exploration well. A Hewlett-Packard 5985B capillary GC/MS instrument fitted with a 50 m × 0.2 mm i.d. BP-5 fused silica column with hydrogen as the carrier gas at a linear velocity of 30 cm^{-1} was used for the analyses. Mass spectrometer operating conditions were: 250 °C source temperature; 2600 V EM voltage; 70 eV electron energy. GC was carried out with the oven temperature programmed from 70 to 300 °C at 2 °C min^{-1} and held at 300 °C for 10 min.

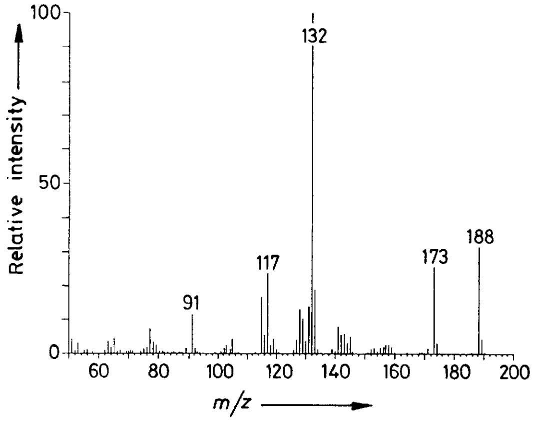


Figure 2. Mass spectrum of the tetralin (**4**).

the oleananes, has been proposed as a biomarker for angiosperms.[6] A key intermediate in the scheme proposed[7] for degradation and aromatisation of these triterpenoids is 2,2,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene (**4**). In this paper we report the synthesis of the tetralin (**4**) and its identification in sediments and crude oils which also contain enhanced levels of 1,2,7-TMN relative to the other TMN isomers.

The tetralin (**4**) was conveniently prepared in six steps from 2,3-dimethylbenzoic acid (**5**) (Scheme 1). Reduction of (**5**) gave the benzyl alcohol (**6**),[8] which was converted into the benzyl chloride (**7**).[9] 1,4-Addition of the Grignard reagent of (**7**) to diethyl isopropylidenemalonate (**8**)[10] gave the addduct (**9**), which was hydrolysed and decarboxylated to afford the substituted butanoic acid (**10**). The acid (**10**) was cyclised to the tetralone (**11**) and Wolff–Kishner reduction afforded the tetralin (**4**).†

Figure 1 shows the partial total ion current, *m/z* 188 and *m/z* 132 mass chromatograms of the aromatic fractions of (i) sediment and (ii) crude oil samples of Cretaceous age from the Volador no. 1 (Gippsland Basin, Australia) exploration well. The tetralin (**4**) was identified by comparison of mass spectra and by co-elution with the synthetic material on capillary GC. 1,2,7-TMN and 1,2,5-TMN have previously been identified in Volador no. 1 sediments.[1] The dominant ion at *m/z* 132 in the mass spectrum of (**4**) (Figure 2) can be attributed to the fragment resulting from a retro Diels–Alder reaction of (**4**).

It should be noted that the tetralin (**4**) is only a minor component relative to the trimethylnaphthalene isomers in the aromatic fractions from the above samples. Analysis of a series of sediment samples from Volador no. 1 also showed that the concentration of (**4**) relative to 1,2,7-TMN decreases as the depth and temperature of the sediments increase. These observations suggest that the tetralin (**4**) is an intermediate in the formation of 1,2,7-TMN from the degradation of oleanane triterpenoids in sediments. This is clearly demonstrated in the laboratory by selenium-catalysed dehydrogenation of β-amyrin (**1**). Previously 1,2,7-TMN had been reported as a product from dehydrogenation of (**1**).[11] We repeated this

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† *Spectral and physical data* for: (**4**) δ_H ($CDCl_3$) 0.99 (s, 6H), 1.51 (t, *J* 6.6 Hz, 2H), 2.21 (s, 3H), 2.26 (s, 3H), 2.41 (s, 2H), 2.78 (br t, 2H), 6.88 and 9.94 (AB q, *J* 7.8 Hz, 2H). (**9**) δ_H 1.05 (s, 6H), 1.29 (t, *J* 7.1 Hz, 6H), 2.22 (s, 3H), 2.27 (s, 3H), 2.95 (s, 2H), 3.38 (s, 1H), 4.22 (q, *J* 7.1 Hz, 4H), 7.00 (br s, 3H). (**10**), m.p. 75—76 °C δ_H 1.05 (s, 6H), 2.21 (s, 3H), 2.27 (s, 3H), 2.33 (s, 1H), 2.78 (s, 2H), 7.02 (br s, 3H). (**11**) δ_H 1.08 (s, 6H), 2.21 (s, 3H), 2.34 (s, 3H), 2.46 (s, 2H), 2.75 (s, 2H), 7.12 (d, *J* 8.0 Hz, 1H), 7.83 (d, *J* 8.0 Hz, 1H). M^+ 202(31), 187(4), 171(6), 159(8), 147(13), 146(100), 128(10), 118(22), 117(24), 115(16), 103(11), 91(12).

reaction and analysed the reaction products using GC/MS techniques. After reaction at 330 °C for 20 h the mixture contained 17% of the tetralin (**4**) and 31% of 1,2,7-TMN. Under the same reaction conditions the tetralin (**4**) gave 1,2,7-TMN.

No known natural products, other than the oleananes, possess a carbon skeleton which could lead to the tetralin (**4**). The co-occurrence of (**4**) with 1,2,7-TMN in sediments and their derived crude oils is consistent with an input of angiosperm-derived oleananes into the sediments. These compounds can therefore be regarded as biological marker compounds specific for angiosperms, which provide a means of dating sedimentary organic material as Cretaceous or more recent.

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