

## Identification of 1,2,2,5-Tetramethyltetralin and 1,2,2,5,6-Pentamethyltetralin as Racemates in Petroleum

Robert Alexander, Trevor P. Bastow, Robert I. Kagi and Raj K. Singh

*Petroleum and Environmental Organic Geochemistry Centre, Curtin University of Technology, Box U1987 GPO, Perth 6001, Western Australia*

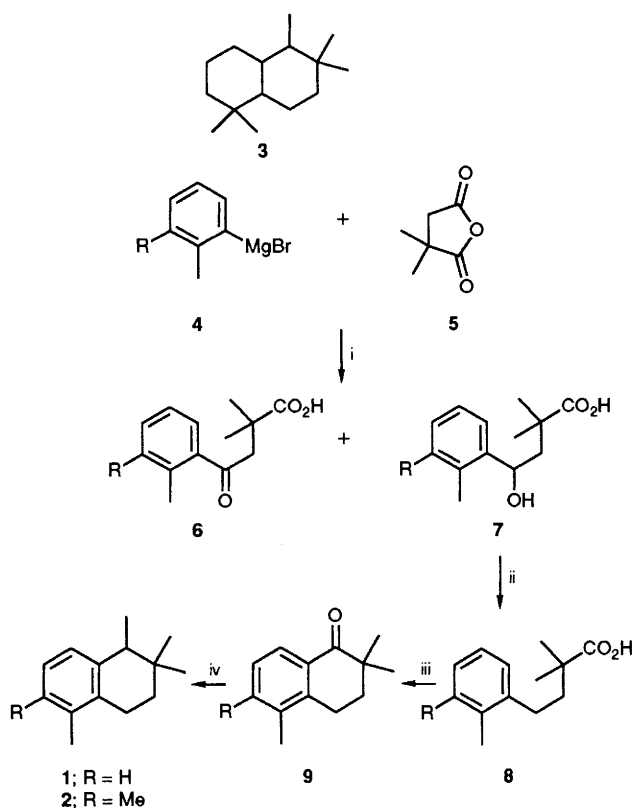
1,2,2,5-Tetramethyltetralin and 1,2,2,5,6-pentamethyltetralin have been synthesized and identified as racemates in crude oil and are proposed from dehydrogenation experiments as intermediates in the formation of alkylnaphthalenes in crude oil.

Alkylnaphthalenes are major components of the aromatic hydrocarbon fraction of most crude oils and solvent extracts from organic-rich sediments.<sup>1</sup> Although some of the trimethylnaphthalenes and one tetramethylnaphthalene have been shown to be formed from triterpenoid and other terpenoid precursor natural products *via* intermediate tetralins, the formation mechanisms of many of the alkylnaphthalenes remain obscure.<sup>2-4</sup> In order to elucidate further the origins and formation of alkylnaphthalenes in petroleum we have synthesised 1,2,2,5-tetramethyltetralin **1** and 1,2,2,5,6-pentamethyltetralin **2** and have identified them as racemic mixtures in crude oil using gas chromatography techniques

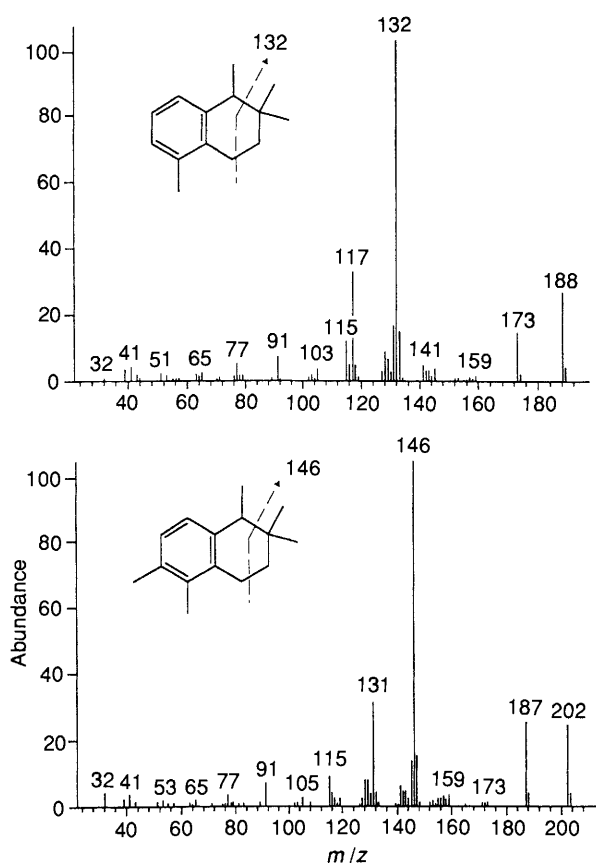
with a capillary column coated with a chiral stationary phase. These compounds have been further dehydrogenated and yield trimethylnaphthalenes and tetramethylnaphthalenes which also co-occur in the crude oil with the tetralins **1** and **2**.

The similarity in carbon skeletons of the tetralins and the rearranged drimane **3**, a common constituent of crude oil, suggests that there may well be a link between the naphthalenes on the one hand and the drimanes on the other in that these two groups of compounds may share common precursors, most probably of microbial origin.<sup>5</sup>

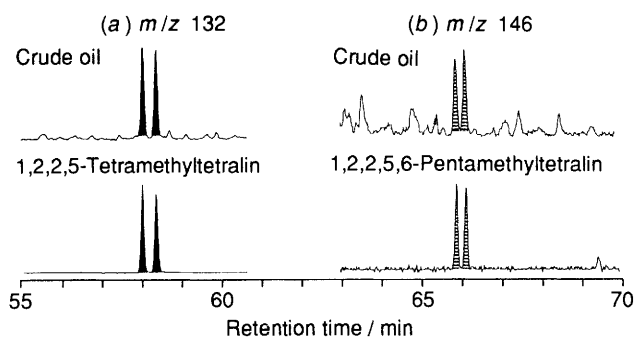
The tetralins **1** and **2** were conveniently prepared in good yield using the sequence of reactions shown in Scheme 1.



**Scheme 1** Reagents and conditions: i, dry diethyl ether,  $-20^{\circ}\text{C}$ ; ii,  $\text{H}_2$  (1 atm)/Pd-C, EtOH; Zn-Hg;HCl, reflux; iii, polyphosphoric acid,  $90^{\circ}\text{C}$ ; iv, MeMgI, dry diethyl ether;  $\text{H}_2$  (1 atm)/Pd-C, EtOH



**Fig. 1** Mass spectra of the tetralins 1 and 2



**Fig. 2** Partial  $m/z$  132 (a) and 146 (b) mass chromatograms of the monoaromatic fraction from a crude oil from the Eromanga Basin, Australia and the alkyltetralins. A Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a 5971 Series MSD was used. The chromatograph was fitted with a  $50\text{ m} \times 0.22\text{ mm}$  internal diameter fused silica capillary column with CYDEX-B (chiral) stationary phase (SGE, Australia). Helium was used as carrier gas at a flow velocity of  $26\text{ cm s}^{-1}$ . The oven was programmed from  $50$  to  $240^{\circ}\text{C}$  at  $2^{\circ}\text{C min}^{-1}$ . The MSD was operated with a  $70\text{ eV}$  electron beam energy, a source temperature of  $240^{\circ}\text{C}$  and  $1680\text{ V}$  EM voltage.

2,2-Dimethylsuccinic anhydride 5 was reacted with the appropriate Grignard reagent 4 to form a mixture of the keto and hydroxy carboxylic acids 6 and 7 in the proportion 4 : 1.<sup>6</sup> This mixture was subjected to hydrogenolysis<sup>7</sup> to afford a mixture of carboxylic acids 6 and 8 that was then reduced using zinc amalgam<sup>8</sup> to give the acid 8. The acid was cyclised to the ketone 9 on treatment with polyphosphoric acid.<sup>9</sup> The ketone was methylated using methylmagnesium iodide and the resultant tertiary alcohol function removed by hydrogenolysis. The NMR data for the tetralins are shown† and the mass spectrum for each compound is given in Fig. 1.

Fig. 2 shows  $m/z$  132 and 146 partial mass chromatograms of the crude oil and the alkyltetralins obtained using GC-MS techniques with a capillary column coated with a chiral stationary phase. Two peaks of the same area (shaded) were observed in each case representing the separate enantiomers. The compounds represented by the shaded peaks had similar mass spectra to the alkyltetralins with the same retention time. When analysed using capillary columns coated with the commonly used non-chiral phases BP-1 and BP-5 (SGE, Australia), both of the synthetic alkyltetralins gave a single peak in the chromatogram as did the corresponding components from the crude oil. These results show that 1,2,2,5-tetramethyltetralin 1 and 1,2,2,5,6-pentamethyltetralin 2 occur as racemic mixtures in the crude oil. To our knowledge this is the first reported demonstration of the occurrence of hydrocarbon racemates in crude oil using direct gas chromatography techniques, although it has been shown by less direct methods that certain isoprenoid alkanes are also racemic mixtures.<sup>10,11</sup>

A possible source of these sedimentary alkyltetralins is the bicyclic natural products that give rise to drimane and other bicyclic hydrocarbons with skeletons that appear to be derived by rearrangement of the drimanes.<sup>5,12</sup> We have observed that the abundances of these alkyltetralins decrease with increase in sample maturity, and suggest that they are intermediates in the formation of alkylnaphthalenes. Furthermore, treatment of 1,2,2,5-tetramethyltetralin with palladium on carbon at  $300^{\circ}\text{C}$  gave 1,2,3,5-tetramethylnaphthalene and 1,2,5-

†  $^1\text{H}$  NMR Spectral data for 1  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.92, 0.94 ( $2 \times \text{s}$ , 3H, *gem*-dimethyl), 1.16 (d,  $J$  7.1 Hz, 3H), 1.4 (m, 1H,  $\text{CH}_A\text{-CMe}_2$ ), 1.7 (m, 1H,  $\text{CH}_B\text{-CMe}_2$ ), 2.20 (s, 3H, Ar-Me), 2.49 (q,  $J$  7.1 Hz, 1H, Ar-CH-Me), 2.6 (m, 2H, Ar-CH<sub>2</sub>), 7.0 (m, 3H, Ar-H). For 2  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.91, 0.92 ( $2 \times \text{s}$ , 3H, *gem*-dimethyl), 1.16 (d,  $J$  7.1 Hz, 3H), 1.4 (m, 1H,  $\text{CH-CMe}_2$ ), 1.8 (m, 1H,  $\text{CH}_B\text{-CMe}_2$ ), 2.11 (s, 3H, Ar-Me), 2.25 (s, 3H, Ar-Me), 2.46 (q,  $J$  7.2 Hz, 1H, Ar-CH-Me), 2.6 (m, 2H, Ar-CH<sub>2</sub>), 6.93 (AB q,  $J$  7.3 Hz, 2H, Ar-H).

trimethylnaphthalene, two alkylnaphthalenes that are abundant in low maturity sediment samples.<sup>2,13</sup> Under the same conditions 1,2,2,5,6-pentamethyltetralin gave 1,2,5,7-tetramethylnaphthalene and 1,2,6-trimethylnaphthalene as major products. Again, all these alkylnaphthalenes have been reported to occur in crude oil.<sup>4,14</sup> Of special interest is the co-occurrence of 1,2,3,5-tetramethylnaphthalene and 1,2,2,5-tetramethyltetralin in the crude oil used in this study, suggesting that there may be a product-precursor relationship between these two compounds in the natural system, similar to that shown in our laboratory dehydrogenation experiments.

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