First Discovery of Botryococcane in Petroleum[1]

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Summary The fossil biological marker botryococcane has been discovered in high concentration in a crude oil.

THERE are no previous reports of concentrations at the 1% level of a single complex fossil biological marker in a crude oil. We report here the discovery of botryococcane in the enormous abundance of 1·4 and 0·9% from Duri (500 ft depth) and Minas (2500 ft depth) crude oils, respectively, two giant oil fields which are the major known deposits in Sumatra.[2]

Figure 1 shows the capillary gas chromatograms (OV101 column) of the saturate portion[3] of Minas and Duri crude oils. The coinjection of authentic botryococcane[4] with Duri is indicated by the broken line and coincides, in retention time, with the major peak in that gas chromatogram. A similar coinjection experiment on a Dexsil 400 column using selective ion monitoring at *m/e* 183 on a Finnigan 4000 g.c.m.s. plus INCOS data system confirmed the coelution result. Previous reports of pristane[5] and phytane[6] at the 0·5 and 0·3% level in some crudes are also below the levels of Duri, which contains 1·0 and 0·7%, respectively (Figure 1). The isoprenoids are

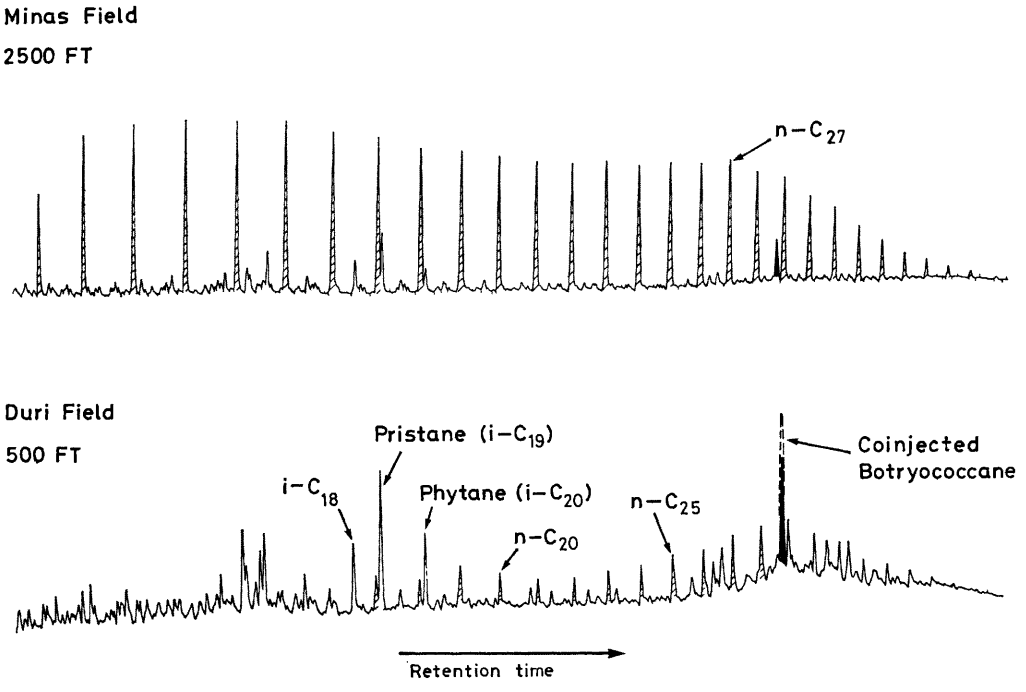


FIGURE 1. Capillary gas chromatography of Sumatra crudes, saturate fractions. 32 Ft OV 101 0·01-i.d. capillary column using He carrier gas in an HP 5834A chromatograph. Solid peaks: Botryococcane. Shaded peaks: n-paraffins.

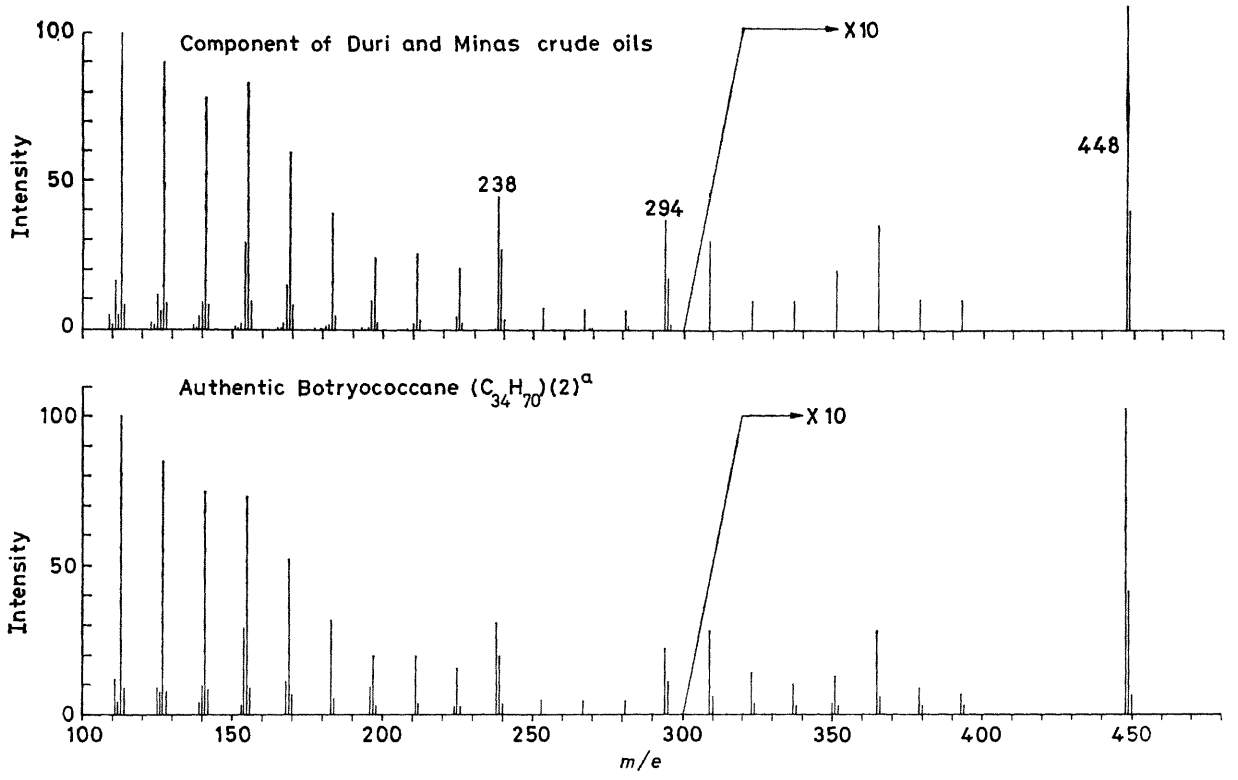
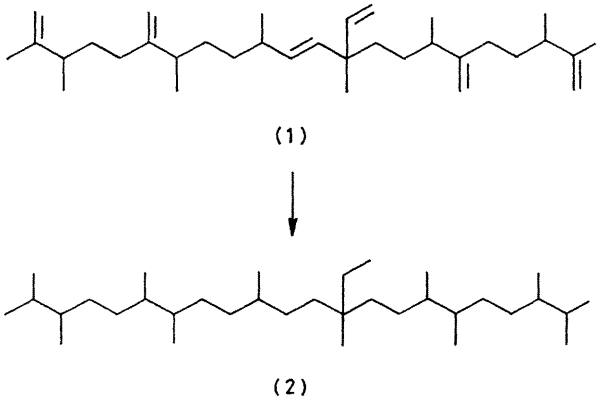


FIGURE 2. Identification of botrycococcane by g.c.– m.s. comparison. (Applied science, Dexsil 400 Quadrex capillary column, 75 m, Nuclide 12-90-g mass spectrometer, HP 7620A gas chromatograph). [a] Slight contamination from the mono-unsaturated impurity ($C_{34}H_{68}$). The difference in *m/e* 449/448 ratio between these spectra and that of ref. 4 is probably due to different instrumental conditions. We found *m/e* 449 > 448 in an AEI MS9 mass spectrum.

apparently unaffected by moderate biodegradation[7] in Duri oil as evidenced by n-paraffin depletion in Figure 1 (compare Minas to Duri).

A comparison of the background-subtracted g.c.–mass spectra of the authentic synthetic botryococcane with that found in Duri crude is shown in Figure 2. The most important spectral features are the ions, at *m/e* 238, 294, and 448, generated by cleavages around the quaternary carbon atom.

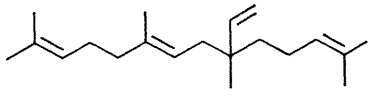


(1)

(2)

SCHEME. (**1**): Botryococcene ($C_{34}H_{58}$) from *Botryococcus braunii* alga. (**2**): Botryococcane ($C_{34}H_{70}$) from Sumatra, Indonesia Crude Oils.

The structure of the natural product botryococcene, the obvious biological precursor to botryoccane, was suggested by Cox *et al.*[8] to be the tetramethylated triterpene (**1**) on the basis of spectral evidence. At first glance, the methylation pattern in the molecule could lead to the conclusion that head-to-head linkages are present.[9] However, the original interpretation[8] that the structure is an analogue of that of isodigeranyl[10] (**3**) appears correct. The unconventional



(3)

Isodigeranyl

linkage of two C_{15} regular isoprenoids to give the saturated quaternary carbon has been called tail-to-tail,[8] but results in a very different structural arrangement than the common squalene-type tail-to-tail coupling.

Botryococcene has been observed in only one species, the fresh or brackish water alga, *Botryococcus braunii*. Concentrations in the 'senescent' phase of *B. braunii* are reported in the 70—90% range.[4,11] The implication is that the first example of a one-to-one correspondence between a single species and a crude oil has been shown on a molecular level (Scheme). The high crude oil concentrations of botryococcane can be used as evidence that the oil deposits

were generated principally from the organic material of prehistoric fresh or brackish waters

In other stages of its growth, *B braunii*, as well as other algae, have been found to contain odd carbon number, high molecular weight n-alkenes [12,13] This may account, at least in part, for the high molecular weight maximum in the n-paraffin distribution centred at C_{27} in the Minas oil (Figure 1), although the more common explanation of a contribution from the higher plant waxes[14] cannot be ruled out

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