P430-TH

OCCURRENCE OF MACROCYCLIC (C_{29+}) COMPOUNDS IN EXTANT ALGA *BOTRYOCOCCUS BRAUNII*

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Macrocyclic alkanes (ranging from C_{15} to C_{34}) and their methylated derivatives (ranging from C_{17} to C_{26}) were previously identified in some Torbanites and crude oils (Audino et al., 2001, 2002; Grice et al., 2001). Based on (i) their distribution, (ii) stable carbon isotopic data and (iii) the abundant presence of characteristic fossil remains in Torbanites, it was suggested that these macrocycles are formed during the diagenesis of *Botryococcus braunii* algaenan, i.e. the non-hydrolyzable and insoluble biomacromolecular material present in the cell walls. In order to determine if some macrocyclic compounds comprising no heteroatom in the cyclic skeleton are also present in the living organism, seven strains of this alga from different geographical origin were investigated.

The strains originated from lakes located in Australia, Bolivia, France, Ivory Coast and French West Indies; they were grown in a synthetic culture medium. The biomass was freeze dried when the algae entered the stationary phase of growth and the lipids, extracted with heptane, were purified using chromatographic techniques (column chromatography and thin layer chromatography). The purified fractions were examined by mass spectrometry and nuclear magnetic resonance (NMR). From these analytical investigations two families of macrocycle-containing compounds were isolated and their chemical structures determined using 1D and 2D (^{1}H-^{1}H and ^{1}H-^{13}C) NMR techniques. Both are series of acetal derivatives formed by the condensation of terpene diols specific of *B. braunii*, with triunsaturated macrocyclic aldehydes, ranging from C_{30} to C_{36} as established by GC-MS analysis of the products resulting from acid hydrolysis of the acetals. These novel and unusual aldehydes likely arise from the self-condensation of diunsaturated α,ω-dialdehydes. The resulting aldols would be dehydrated to give the triunsaturated macrocycles exhibiting a α-unsaturated, α-branched formyl pattern. Macrocyclic compounds have been isolated from races B and L of *B. braunii*, characterized by the production of botryococcenes (C_{30}-C_{37}) and lycopadiene (C_{40}), respectively (Metzger and Largeau, 1999). By contrast, no macrocycle has been identified so far in race A of *B. braunii*, a chemical race defined by the production of *n*-alkadienes and

trienes. Figure 1 shows the structure of typical macrocyclic acetals **1**, isolated from *B. braunii* race B.

We thus report for the first time the presence of macrocycles in extant alga *B. braunii*. The distribution observed in the series of acetals isolated in this study is, however, different from those observed in macrocyclic alkanes formed during the diagenesis of the fossil algae.

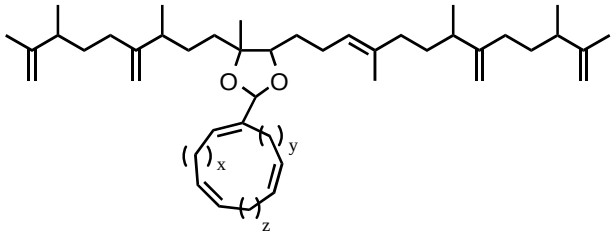

Figure 1. Structure of acetals **1** resulting from the condensation of a C_{32} or C_{34} macrocyclic aldehyde and a C_{34} triterpene diol (dihydroxy-tetramethylsqualene), isolated from *B. braunii* race B; (x + y + z = 25 or 27).

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