Botryococcene—a Tetramethylated Acyclic Triterpenoid of Algal Origin

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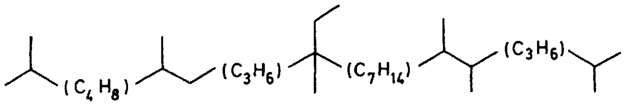
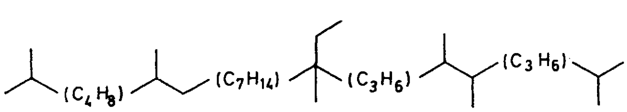
Summary Structure (**3**) is suggested on chemical and biosynthetic grounds for the major metabolite of the resting state of the alga *Botryococcus braunii.*

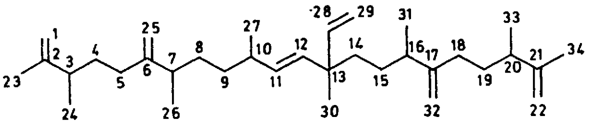
The green alga *Botryococcus braunii* (Kützing), implicated in the formation of certain geological deposits,[1–3] produces unusual isomeric $C_{34}H_{58}$ alkenes, botryococcene and isobotryococcene, during a particular physiological state.[3] On the basis of spectroscopic examination of botryococcene and the hydrogenated derivative botryococcane, partial structures (**1**) or (**2**) were suggested for the latter.[3] Structure (**3**) is now suggested for botryococcene from ^{13}C n.m.r. techniques, oxidative degradation, and established biosynthetic principles.



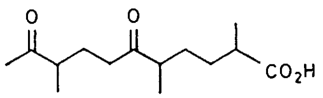
(1)



(2)



(3)



(4)

TABLE. ^{13}C *Chemical shifts* (*from* CS_2) *and assignments for the n.m.r. spectra of botryococcene and dihydrobotryococcene*

Carbon	Botryococcene	Dihydrobotryococcene
1,22	83·0	83·0
2,21	42·9	42·7
3,20	151·6	151·5
4,19	159·1	159·1
5,18	160·9	160·9
6,17	37·9,38·1	37·7
7	152·0	151·9
8	159·2	159·1
9	157·6	157·4
10	155·4	155·1
11	58·8	59·1
12	56·7	55·4
13	150·8	154·2
14	153·5	153·8
15	162·4	162·6
16	152·5	152·4
23,34	172·8	172·8
24,33	173·7	173·7
25,32	85·1,85·3	85·3
26,31	172·2,172·4	172·1,172·3
27	171·5	171·1
28	45·8	158·9
29	81·6	184·1
30	168·9	169·8

^{13}C N.m.r. spectra of botryococcene and dihydrobotryococcene ($CH{=}CH_2 \rightarrow CH_2CH_3$ using di-imide reduction[4]) were recorded on a Varian XL-100-15 spectrometer and decoupler modified for pulsed Fourier Transform operation.[5] Off-resonance decoupling techniques[5,6] were used to identify primary, secondary, tertiary, and quaternary carbon sites; pulsed decoupling[7] to avoid nuclear Overhauser effects was valuable in accounting for all carbons in spectra where overlap occurred. Eight methyl, 8 saturated and 5 unsaturated methylene, 5 saturated and 3 unsaturated methine, and 1 saturated and 4 unsaturated quaternary carbons were identified. Assignments of resonances were assisted by using the chemical shift parameters of Lindeman and Adams[8] and Dorman *et al.*[9] and by utilizing the spectrum of dihydrobotryococcene. The Table shows a comparison of the spectral data of botryococcene and dihydrobotryococcene. Not all resonances were attributed unequivocally. Thus, for example, the resonances attributed to methyl groups 23,34 and 24,33 respectively, may be the reverse of those indicated.

Permanganate–periodate oxidation[10] of botryococcene afforded, in low yield, (**4**) as the major (*ca.* 90%) isolable product, identified by i.r., ^{1}H n.m.r., and m.s. data on the methyl ester. Isolation of virtually one product suggested an origin from cleavage of the carbon–carbon double bonds in (**3**) affording (**4**) directly and a diketo-diacid which would readily decarboxylate to (**4**). The alkene has optical activity $[\alpha]_D^{22} - 3{\cdot}5°$ (c 6·1 in $CHCl_3$).

Botryococcene appears terpenoid in origin, assuming dimethylated C_{15} units linked tail-to-tail to give the saturated quaternary carbon in (**3**), a precedent for such a linkage existing in isodigeranyl.[11] The pattern of methylation is unusual for an acyclic isoprenoid but a similarity exists with the methylated side chain of cyclolaudenol.[12]

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