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OBTUSALLENE I, A NEW HALOGENATED ALLENE FROM *LAURENCIA OBTUSA*

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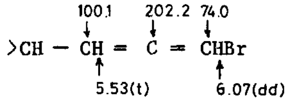
Abstract: Obtusallene, a new halogenated bicyclic ether with an allenic side chain, has been isolated from the red form of the alga *Laurencia obtusa*, and identified by spectroscopic methods and X-ray crystallography.

The numerous secondary metabolites elaborated by the red algal genus *Laurencia* include a group of C_{15} acetylenic cyclic ethers which show remarkable structural variation.[1] Usually they contain a terminal enyne system as in obtusenyne and *cis*-isodihydrorhodophytin which we found[2,3] in the yellowish green colour form of *L. obtusa*, and in laurenyne which occurs in the red form. In continuing our work on the red colour form, collected at Gökceada in the Aegean Sea, we have isolated two further members of the group in which the terminal enyne function is replaced by an allenic side chain. They were obtained by further chromatography of the ether extract[4] on silica gel in benzene.

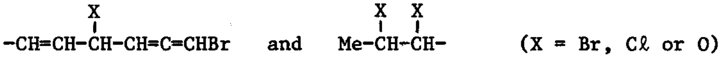
<u>Obtusallene I</u>, m.p. 165-167° (from ether-petrol), $[\alpha]_D^{17}$-257.6° (c 0.53, $CHC\ell_3$), $C_{15}H_{17}Br_2C\ell O_2$ (Found: M^+-$C\ell$, 386.9593, $C_{15}H_{17}{}^{79}Br_2O_2$ requires 386.9594; M^+-Br, 343.0100, $C_{15}H_{17}{}^{79}Br{}^{35}C\ell O_2$ requires 343.0099; M^+ too weak to measure). In the IR spectrum[5] a band at 1953 cm^{-1} first suggested the presence of an allene function, which was supported by a ^{13}C NMR peak[6] at 202.2 ppm attributable to the central carbon atom, and allenic proton coupling in the ^1H NMR spectrum[7] corresponding to the part structure below.



$$>CH-\underset{\uparrow \atop 5.53(t)}{\overset{100.1 \atop \downarrow}{CH}}=\overset{202.2 \atop \downarrow}{C}=\underset{\uparrow \atop 6.07(dd)}{\overset{74.0 \atop \downarrow}{CHBr}}$$

These data are in good agreement with those for the bromoallenes panacene[8] and laurallene.[9]

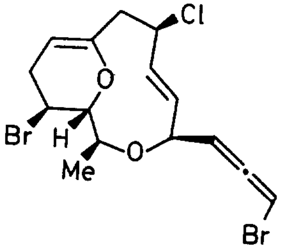
The IR and NMR spectra also provide evidence for a *trans* double bond and a trisubstituted double bond, the latter showing a vinyl proton signal at δ 4.60 and a ^{13}C singlet at δ 147.8 corresponding to an enol ether function. (It follows that the strong IR band at 1681 cm^{-1} arises from the enol ether and not from a carbonyl group as first supposed). The two remaining double bond equivalents and the two oxygen atoms can be accounted for by two ether rings. Extensive decoupling of the 360 MHz ^{1}H NMR spectrum established the existence of the part structures shown below



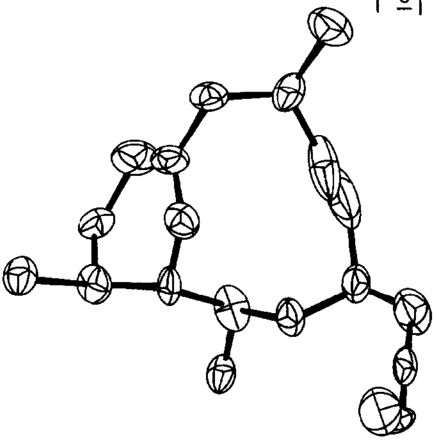
$$\text{-CH=CH-}\overset{X}{\overset{|}{\text{CH}}}\text{-CH=C=CHBr} \quad \text{and} \quad \text{Me-}\overset{X}{\overset{|}{\text{CH}}}\text{-}\overset{X}{\overset{|}{\text{CH}}}\text{-} \qquad (X = Br, C\ell \text{ or } O)$$

but further interpretation involving the -CHHal- and methylene protons was ambiguous. The remaining structural features and the relative stereochemistry were therefore determined by X-ray crystallography which defined obtusallene I as <u>1</u>. A perspective drawing is shown below.

The $C_{15}H_{17}Br_2C\ell O_2$ molecules crystallise in the orthorhombic space group $\underline{P}2_12_12_1$ with cell dimensions $\underline{a}$ = 5.545(9), $\underline{b}$ = 10.082(13), $\underline{c}$ = 28.589(14) Å and $\underline{Z}$ = 4. The crystal structure was elucidated by direct methods and the atomic parameters were subsequently adjusted by least-squares calculations that converged at $\underline{R}$ 8.2% over 1218 diffractometer $|\underline{F}_o|$ values.



<u>1</u>



Obtusallene I has the same bromoallenic side chain as laurallene,[9] isolated from *L. nipponica*, but the bridged 12-membered ring is a new structural type in *Laurencia*.

Obtusallene II, $C_{15}H_{19}Br_2C\ell O_2$, m.p. 142-145°, $[\alpha]_D^{17}$-258.9 ($CHC\ell_3$), $\nu_{max.}$ 1955 cm^{-1}, ^{13}C δ 200.5(s) is under investigation.

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[5] $\nu_{max.}$ (KBr) 3040, 2987, 2838, 1953, 1681, 1368, 1200, 1167, 1130, 1074, 1045, 973, 958, 919, 863, 840, 726, 657, 650 cm^{-1}; $\lambda_{max.}$ $CHC\ell_3$) 243 nm (ε 1,310).

[6] ^{13}C δ (25.2 MHz, $CDC\ell_3$), 202.2(s), 147.8(s), 139.8(d), 128.9(d), 100.1(d), 95.0(d), 81.9(d), 74.0(d), 69.9(d), 68.4(d), 59.4(d), 43.4(t), 41.5(d), 27.1(t), 16.4(q).

[7] ^{1}H δ (360 MHz, $CDC\ell_3$), 6.21(1H, dd, *J* 15.6, 10.5, -CH=), 6.07 (1H, dd, *J* 5.3, 2.0 Hz, =CHBr), 5.93 (1H, dd, *J* 15.8, 5.9 Hz, -CH=), 5.56 (1H, t, *J* 6.1, 5.8 Hz, -CH=C=), 4.60 (1H, bd, *J* 5.1 Hz, -CH=C$<^{O}$), 4.47 (1H, dt, *J* 6.1, 6.1, 1.7, -CHO-), 4.23 (2H, m, -CHX-), 3.97 (1H, dt, *J* 9.3, 1.7, 1.7 Hz, -CHX-), 3.62 (1H, dq, *J* 6.6, 2.7, MeCHO-), 2.81 (1H, dd, *J* 13.3, 6.1 Hz, 1H of CH_2), 2.52-2.30 (3H, m, 3H or $2xCH_2$), 1.10 (3H, d, *J* 6.9 Hz, CH_3CH).

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