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LAURENYNE, A NEW ACETYLENE FROM *LAURENCIA OBTUSA*: CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION

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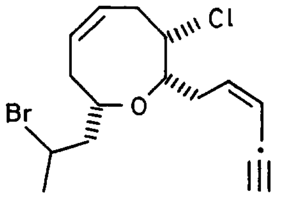
Summary: Laurenyne, a new chloroacetylene from the red form of the alga *Laurencia obtusa* has been identified and its crystal structure determined.

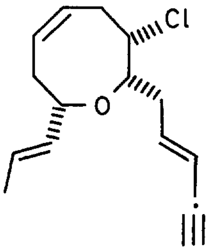
Numerous halogenated metabolites have been isolated from red algae of the *Laurencia* genus mostly terpenes but also a growing family of C_{15} acetylenic cyclic ethers. *L. obtusa* is widely distributed and in Turkish waters it varies in colour and to some extent in morphology. The yellowish green form, collected at Gökçeada, contains several sesquiterpenes and two acetylenes, obtusenyne[1] and *cis*-isodihydrorhodophytin[2,3] (1). We now report that the red form, also collected at Gökçeada (an island in the Aegean Sea), contains a new acetylenic cyclic ether, laurenyne.

Extraction of dried *L. obtusa* (red form) (1.7 kg) with ether gave a brown-green oil which was chromatographed on silica gel. The fractions obtained with petrol (b.p. 60-80°) and petrol-benzene (10:1) were further purified by PLC in petrol-benzene (1:1) to give laurenyne as needles, m.p. 78-80° (from petrol) (750 mg), $[\alpha]_D^{17}$ +22.64° (c 2.35, $CHC\ell_3$), $C_{15}H_{19}C\ell O$ (Found: 235.0890; $^{35}M^+$-Me requires 235.0889. M^+ was too weak to measure). It showed

$\lambda_{max.}$ (MeOH) 226 nm, and $\nu_{max.}$ (CCl_4) 3310, 2095(w) cm^{-1}, while in the mass spectrum there is an important doublet at m/e 185/187 (40%) corresponding to fragmentation of a characteristic C_5H_5 pentenyne side chain. This was confirmed by the n.m.r. spectra[4] which provided evidence for four additional vinyl protons, one of which (δ 5.65) was coupled to a methyl doublet at δ 1.69 (*J* 3 Hz) suggesting the presence of a C_3 side chain $CH_3CH{=}CH-$. Hydrogenation over palladium gave a decahydro derivative, $C_{15}H_{29}ClO$ ($^{35}M^+$, 260.1903; required 260.1906) whose mass spectrum showed significant peaks at m/e 225, 217, and 189 corresponding to losses of $Cl\cdot$, $C_3H_7\cdot$, and $C_5H_{11}\cdot$. As hydroxyl and carbonyl groups are absent the combined evidence suggests that laurenyne is an 8-membered cyclic ether either with α-propenyl and α'-pentenynyl side chains. The chlorine atom must be attached to the ring which includes a double bond. The location of these groups and the total stereochemistry was finally determined by X-ray crystallography which defined laurenyne as (2).



(1)



(2)

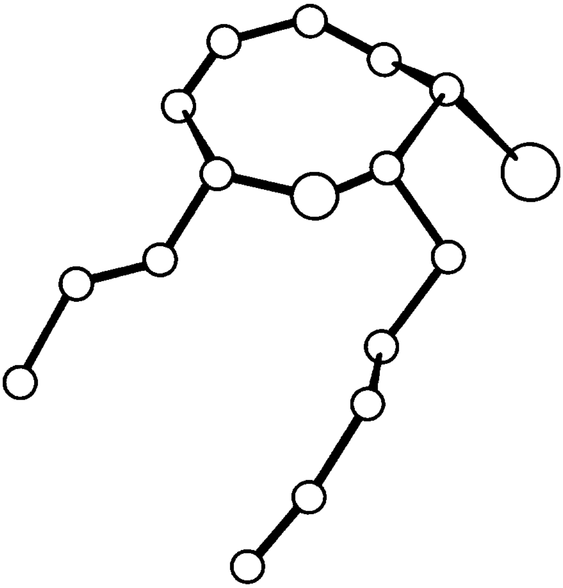
Crystal Structure Determination: The only crystals obtainable were very long (5 mm) laths which were not single but bunches of very fine needles. All attempts to cut the 'crystals' to a suitable length caused extreme 'fraying' of the ends. A sample of usable dimensions was eventually obtained by solvent treatment but not without appreciable damage to the remaining fragment which gave only broad diffuse reflections.

The 'crystal' was transferred to a Nonius CAD-4 diffractometer and the cell parameters were determined by least-squares from the setting angles of 25 reflections.

Crystal data: monoclinic, $a = 8.098(2)$, $b = 4.798(1)$, $c = 19.000(4)$ Å, $\beta = 99.37(2)°$, $U = 728.3$Å, $Z = 2$, $D_c = 1.19$ g cm^{-3}, space group $P2_1$. The structure was solved by heavy atom methods using 868 intensities ($I > 2.5\ \sigma I$) in the range $\Theta < 60°$ (CuK_α radiation, nickel filter). Refinement was by full matrix least-squares using anisotropic temperature factors. Hydrogen atoms could not be convincingly located on difference maps so were not included in the model structure. In view of the poor quality of the crystal the final conventional R-value of 8.6% was considered satisfactory.

The absolute configuration was determined in two ways. First using the statistical method when the Hamilton weighted R ratio was 1.016 (a ratio of about 1.006 would be significant at the .005 level). Secondly, by direct observation of the intensities of Friedel pairs with large calculated Bijvoet ratios (54 out of 55 such pairs confirmed the statistical result, one was inconclusive). A perspective drawing is shown below.

Interestingly, comparison of conventional R values would have led to an incorrect assignment of configuration (9.75% for the correct enantiomer, 9.68% for the wrong one).



It can be seen that laurenyne is the trans isomer of the dehydrobromo derivative of (1) but the two compounds were never found in the same plant in several extractions of both yellowish-green and red *L. obtusa*. Another cyclic ether, laurencienyne, was recently reported[5] from *L. obtusa* collected in Sicily.

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[1] T.J. King, S. Imre, A. Öztunç, and R.H. Thomson, *Tet. Lett.,* 1979, 1453.

[2] S. Imre, S. Islimyeli, A. Öztunç, and R.H. Thomson, *Phytochemistry,* in the press.

[3] Personal communication from W. Fenical.

[4] ^{1}H δ (220MHz, $CDC\ell_3$), 6.22, 5.93, and 5.65 (6H, m, 6 -CH=), 4.04-3.72 (3H, m, 3 -CHX-), 2.83 (1H, s, ≡CH), 2.98, 2.52, and 2.21 (6H, m, 3 CH_2), 1.69 (3H, d, J 3Hz); ^{13}C δ (20MHz, $CDC\ell_3$) 142.0(d), 131.8(d), 131.2(d), 128.5(d), 126.7(d), 111.6(d), 82.2(d), 81.7(d), 79.1(d), 75.4(d), 65.0(s), 38.1(t), 34.8(t), 34.5(t), 17.7(q).

[5] S. Caccamese, R. Azzolina, E.N. Duesler, I.C. Paul, and K.L. Rinehart, *Tet. Lett.,* 1980, 2299; E.N. Duesler, K.L. Rinehart, I.C. Paul, S. Caccamese, and R. Azzolina, *Cryst. Struct. Comm.,*1980, *9,* 777.

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