

OBTUSENYNE, A NEW ACETYLENIC NINE-MEMBERED CYCLIC ETHER FROM LAURENCIA OBTUSA

Trevor J. King

Department of Chemistry, The University, Nottingham NG7 2RD, England

Sedat Imre* and Aysel Öztunc,

Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey

and

Ronald H. Thomson

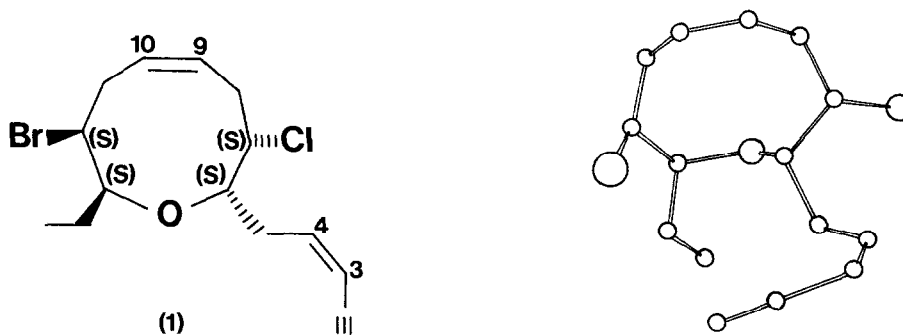
Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

Of the large number of metabolites isolated from algae of the Laurencia genus, most are halogenated sesquiterpenes but a smaller group consists of C₁₅ halogenated acetylenic cyclic ethers.¹ The latter appear to be restricted to Laurencia, related compounds found in Aplysia opisthobranch molluscs² probably having a dietary origin in Laurencia.

Several sesquiterpenes have been isolated³ from L. obtusa, a species of wide distribution, and we now report a new acetylenic cyclic ether obtained from this alga collected on Gökceada in the Aegean Sea. Extraction of the air-dried material (2 kg) with ether gave a brown-green oil which was chromatographed on silica gel. After elution of hydrocarbons with petrol (b.p. 60-80°C), the fraction obtained with petrol-benzene (10:1) was further purified by PLC in petrol-benzene (1:1) to give obtusenylene (365 mg).

Obtusenyne (1), C₁₅H₂₀BrClO⁴, m.p. 63-63.5°C (from methanol) $[\alpha]_D^{21.6} + 155^\circ$ (CHCl₃) showed λ_{\max} . (MeOH) 223 nm (ϵ 13,244), $[\lambda_{\max}$. (CHCl₃) 247 nm], ν_{\max} . (KBr) 3245 and 2087 cm⁻¹, and δ 3.1' (1H, d, J 2Hz), with the base peak in the mass spectrum at m/e 265 (M⁺-65) (followed by losses of HCl and HBr). There was no evidence for hydroxyl or carbonyl functions. These data are typical for cyclic ethers having a C₅ terminal enyne side chain attached to an α carbon atom. ¹H and ¹³C n.m.r. signals for four =CH- groups⁵ established the existence of another carbon-carbon double bond in addition to that in the side chain, and hence of one ring in the molecule. The remaining structural features and the stereochemistry were determined by X-ray crystallography which defined obtusenylene as (1).

Crystal Data: Orthorhombic, a = 13.740(3), b = 8.151(2), c = 13.698(3) Å, U = 1534.1 Å³, $D_c = 1.39$, $D_m = 1.38$ g cm⁻³, Z = 4, F(000) = 680, space group P2₁2₁2₁ from systematic absences, Mo-K α radiation (graphite monochromator) $\lambda = 0.71069$ Å, $\mu = 30.0$ cm⁻¹. Reflections were scanned ($\omega - 2\theta$ mode) for $\theta \leq 27.5^\circ$, and of the 2047 which were observable in this region 1293 had a net count $\geq 3\sigma$ and were deemed observed and used in the refinement.



The structure was solved by heavy atom methods. The oxygen atom was identified by its low temperature factor when refined as carbon. When anisotropic refinement had converged structure factor calculations⁶ for the two enantiomers with anomalous dispersion corrections gave Hamilton weighted R values for the two structures of 7.73% and 6.42%, a significant difference which defines the absolute configuration of the compound.

Hydrogen atoms were first found from a difference map and were then included in the calculations in fixed, computed positions with $U = 0.05$. The weighting scheme used in the final stages of refinement was $w = 1/(1 + ((F_o - A)/B)^2)$ with $A = 30.0$ and $B = 20.0$.

At final convergence the maximum shift/standard deviation was 0.02 and the conventional R was 0.044. A perspective drawing (PLUTO⁷) is shown above.

The unusual feature of obtusenyne is the 9-membered ring which is the largest ring size so far encountered in this group. Dr. W. Fenical has sent us a sample of obtusenyne isolated (as an oil) in his laboratory⁸ from *L. obtusa* collected at Positano, Italy. It was identical with ours in solution.

S.I. and R.H.T. thank NATO for a grant in support of this work.

REFERENCES

- ¹ R.E. Moore in "Marine Natural Products" (ed. P.J. Scheuer), Vol. 1, p.43, Academic Press, New York, 1978.
- ² F.J. McDonald, D.C. Campbell, D.J. Vanderah, F.J. Schmitz, D.M. Washecheck, J.E. Burns, and D. Van der Helm, *J. Org. Chem.*, **40**, 665 (1975); D.J. Vanderah and F.J. Schmitz, *J. Org. Chem.* **41**, 3480 (1976); R. Kinnel, A.J. Duggan, T. Eisner, and J. Meinwald, *Tet. Lett.*, 3913 (1977).
- ³ B.M. Howard and W. Fenical, *Tet. Lett.*, **41** (1976); D.J. Faulkner, *Phytochemistry*, **15**, 1992 (1976); A.G. González, D. Darias, D. Díaz, J.D. Fourneron, J.D. Martín, and C. Pérez, *Tet. Lett.*, 3051 (1976); A.G. González, J.D. Martín, V.S. Martín, M. Norte, J. Fayos, and M. Martínez-Ripoll, *Tet. Lett.*, 2035 (1978).
- ⁴ M^+ , 330.0384, calc. for $C_{15}H_{20}BrClO$ M , 330.0385.
- ⁵ 1H $\delta(CDCl_3)$ 6.00 (dd, H-4), 5.52 (d, H-3), 5.65 (m, H-9 and H-10); ^{13}C , $\delta(CDCl_3)$ 140.6 (C-4), 110.9 (C-3), 130.7 and 128.5 (C-9 and C-10).
- ⁶ Computations were carried out with the Oxford 'CRYSTAL' package, W.R. Carruthers, private communication.
- ⁷ Cambridge Data Centre, W.D.S. Motherwell, private communication.
- ⁸ B.M. Howard, Ph.D. Thesis, University of California (San Diego) (1978).

(Received in UK 21 February 1979)