Structure of the Toxisterols$_2$: *X*-Ray Crystal Structure of Toxisterol$_2$-D Epoxide

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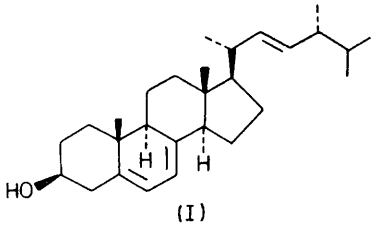
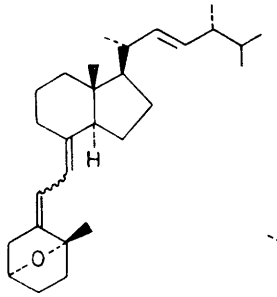
Summary The structures of toxisterols$_2$-D and -E, determined by spectroscopic evidence, have been confirmed by an *X*-ray crystallographic study of the derived toxisterol$_2$-D epoxide.

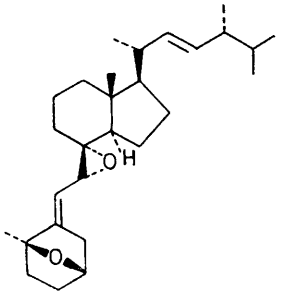
PHOTOLYSIS of ergosterol (I) (36 g) in ethanol (or cyclohexane) and chromatography[1] gave two toxisterol$_2$ ethers -D (155 mg) and -E (54 mg) (Table). Analyses and mass spectra indicated both compounds to be isomeric with ergosterol (I). Spectral data showed that both compounds had the dihydrotachysterol chromophore, an



(I)

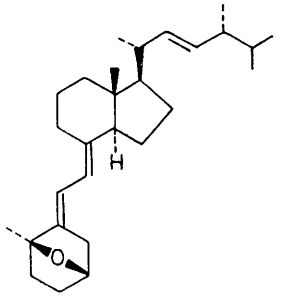


(II)

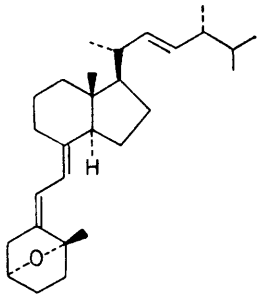


(III)

intact side chain, and an 18-methyl group. Formation of a cyclic ether between C-3 and C-10 was in accord with the polarity (absence of OH) and C-19 n.m.r. signals. Since the addition of ethanol during photolysis of ergosterol is known[2] then structure (II) is reasonable for toxisterols$_2$ -D and -E.



(IV)



(V)

Epoxidation of toxisterol$_2$-D (3-ClC$_6$H$_4$CO$_3$H, NaHCO$_3$, Et$_2$O, 0 °C, 4 days) gave a crystalline epoxide (34%). An *X*-ray crystallographic study showed the epoxide to have structure (III) and thus toxisterols$_2$-D and -E were assigned structures (IV) and (V) respectively.

TABLE

Toxisterols$_2$	M.p.	$[\alpha]_D$[a]	λ_{max}/nm (ϵ)[a]	τ[b]
D (IV)	Oil	+80°	243 (22,000)	8·49 (19-Me)
			252 (26,000)	9·44 (18-Me)
			262 (19,000)	
E (V)	Oil	+115°	243 (22,000)	8·58 (19-Me)
			252 (26,000)	9·34 (18-Me)
			262 (18,000)	
D-Epoxide (III)	141—142 °C	+69°	—	8·50 (19-Me)
				9·32 (18-Me)

[a] In cyclohexane. [b] In CCl_4.

Crystal data: toxisterol$_2$-D epoxide; $C_{28}H_{44}O_2$; M = 412·7; colourless prismatic monoclinic crystals; a = 14·967(6), b = 7·096(3), c = 12·652(5) Å, β = 99·35(2)°, D_m = 1·00 g cm^{-3}, Z = 2, D_c = 1·03 g cm^{-3}; space group $P2_1$ (C_2^2, No. 4); μ (Cu-$K\alpha$ radiation) = 4·8 cm^{-1}.

The structure analysis was based on 1427 unique reflections with $I/\sigma(I) \geqslant 3{\cdot}0$ measured over the range $0° \leqslant \theta \leqslant 60°$ using a Hilger–Watts Y290 automated four-circle diffractometer and Ni-filtered copper radiation. The intensity data were corrected for Lorentz and polarisation effects but not for absorption.

The structure was solved with some difficulty by direct methods and has been refined by full-matrix least-squares with all non-hydrogen atoms treated anisotropically to give a final R value of 0·067.

The structure of the molecule is shown in the Figure. Ring A adopts a boat conformation in which the atom defining the bow and the stern, C-3 and C-10, are bridged by an oxygen atom. The second oxygen atom forms an epoxide ring between the C-7 and C-8 positions. The geometry of the remainder of the molecule is similar to that found in other sterol structures.

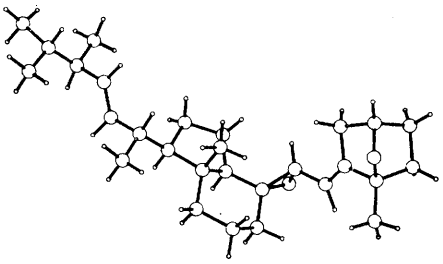


FIGURE. Structure of toxisterol$_2$-D epoxide (III).

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[1] A. G. M. Barrett, D. H. R. Barton, M. H. Pendlebury, L. Phillips, R. A. Russell, D. A. Widdowson, C. H. Carlisle, and P. F. Lindley, *J.C.S. Chem. Comm.*, 1975, 102.

[2] F. Boomsma, H. J. C. Jacobs, E. Havinga, and A. van der Gen, *Tetrahedron Letters*, 1975, 427.