Striatin A, B, and C: Novel Diterpenoid Antibiotics from *Cyathus striatus*; *X*-Ray Crystal Structure of Striatin A[1]

By HANS-JÜRGEN HECHT

(*Institut für Kristallographie, Fachbereich Chemie der Freien Universität Berlin, Takustrasse,* 6, *D*-1000 *Berlin* 33, *W. Germany*)

GERHARD HÖFLE and WOLFGANG STEGLICH

(*Institute für Organische Chemie der Technischen Universität Berlin, Strasse des* 17. *Juni* 135, D-1000 *Berlin* 12, *und der Universität Bonn, Gerhard-Domagk-Strasse* 1, D-5300 *Bonn, W. Germany*)

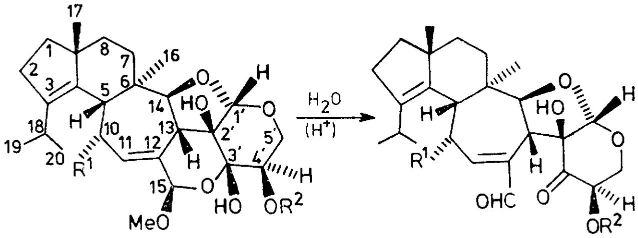
and TIMM ANKE and FRANZ OBERWINKLER

(*Lehrbereich Spezielle Botanik der Universität Tübingen, Auf der Morgenstelle* 1, D-7400 *Tübingen, W. Germany*)

Summary Striatin A has been shown by *X*-ray structure analysis to contain a cyathin skeleton triple linked to a pentose unit; this result allows the assignment of structures to the closely related striatins B and C by n.m.r. spectroscopy.

THE striatins are novel antibiotics with antibacterial and antifungal properties.[2] After submerged cultivation the mycelium of the producing strain of *Cyathus striatus* (Huds. ex Pers.) Willd. was extracted with methanol. The striatins A, B, and C were purified as described earlier.[2] In addition a new, closely related compound, $C_{25}H_{36}O_8$, has been isolated.

Striatin A (**1**) crystallizes from methanol in the monoclinic space group $P2_1$ with lattice constants $a = 13{\cdot}017(3)$, $b = 10{\cdot}133(3)$, $c = 10{\cdot}873(3)$ Å, $\beta = 90{\cdot}86(1)°$, $Z = 2$. The intensity data of 2792 unique reflexions with $\theta < 70°$ were measured with a Siemens diffractometer using the θ—2θ scan technique and Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). The structure was solved by direct methods[3] and refined by least squares techniques[4] to an R-value of 4·6% for the 2746 reflexions with intensity $I > 2\sigma$. Anisotropic temperature factors were used for carbon and oxygen atoms, and isotropic temperature factors for hydrogen atoms. The hydrogen atom at C(15)† was kept unrefined during the last cycles of refinement because of unreasonable parameter shifts.‡



(1) $R^1 = H$ $R^2 = Ac$
(2) $R^1 = OH$ $R^2 = Ac$
(3) $R^1 = OH$ $R^2 = H$

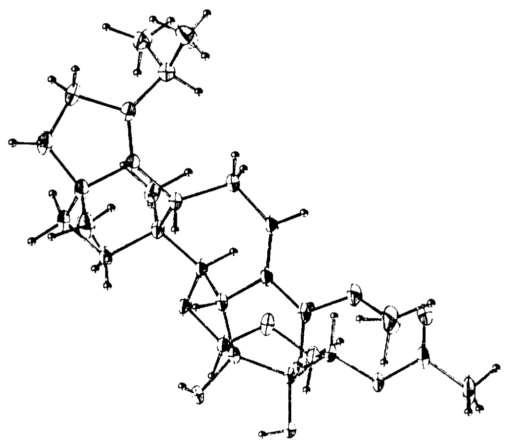
(4) $R^1 = H$ $R^2 = Ac$
(5) $R^1 = OH$ $R^2 = Ac$
(6) $R^1 = OH$ $R^2 = H$

Striatin A (**1**) crystallizes with one molecule of methanol, forming a system of hydrogen bonds with the angular OH groups at C(2′) and C(3′). A plot of the molecule is shown in the Figure.[5]

After completing the X-ray structure all 270 MHz ^1H n.m.r. signals ($CDCl_3$) of (**1**) could be assigned. Thus 5′-H_2 and 4′-H form an ABX-pattern (δ 3·49, 3·93, and 4·98; J 11, 9, and 5 Hz), 1′-H and 15-H singlets (δ 5·00 and 5·25), 14-H a doublet (δ 4·19, J 10 Hz), and 11-H, 13-H, and 10-H_2 multiplets (δ 6·04, 3·04, and 2·50).

In striatin B (**2**) an additional hydroxy group is attached to C(10). This follows from the n.m.r. spectrum in which 10-H appears at δ 4·84 as a doublet due to 8 Hz coupling to 11-H. The pseudoaxial orientation of this OH-group is deduced from the low field shift of 14-H ($\Delta\delta$ 0·42), 18-H ($\Delta\delta$ 0·49), and 16-Me ($\Delta\delta$ 0·23) induced by the nearby oxygen atom. As a consequence the dihedral angle between 5-H and 10-H becomes 90° and no vicinal coupling is observed.

Striatin C (**3**) differs from (**2**) in lacking the acetyl group (δ 2·15) which leads to increased shielding of 4′-H (δ 3·98).



FIGURE

All striatins are very sensitive to water in the presence of traces of acid. The n.m.r. spectra undergo typical changes which are in accord with the formation of ketoaldehydes (**4**), (**5**), and (**6**), respectively. With $CDCl_3$ as solvent partial transformation was observed during the n.m.r. measurements. The most characteristic changes are the low field shift of the olefinic proton in (**4**) to δ 6·98 and the conversion of 15-H into an aldehyde proton (δ 9·27). The presence of the $\alpha\beta$-unsaturated aldehyde and α-hydroxyketone functions follows also from the ^{13}C n.m.r. spectrum ($CDCl_3$) with signals at δ 196 and 201 p.p.m. and the i.r. spectrum of (**4**) in $CHCl_3$: ν_{max} 1750 (acetate), 1680 (ketone and aldehyde), and 1625 cm^{-1} (conj. double bond).

The reactivity of the acetal function is also demonstrated by the partial exchange of a methoxy by an ethoxy group during the recrystallization from ethanol. Therefore the possibility exists, that the methoxy group of the striatins is introduced during the isolation and purification procedure.¶ The position of the methoxy group also explains its easy ejection as methanol in the mass spectra leading to very intense M — MeOH peaks.§

Biogenetically the striatins are closely related to the cyathins, isolated by Ayer[6] from American *Cyathus* species. Condensation of a cyathin type precursor with a 3-oxopentose may lead to the unique D/E ring system of the striatins.

We thank the Deutsche Forschungsgemeinschaft for generous financial support.

(*Received*, 17*th April* 1978; *Com.* 388.)

---

† The numbering of the diterpene unit corresponds to that used in ref. 6 for cyathins. The absolute configuration shown in the formulae is arbitrary.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The elementary compositions given in ref. 2 therefore correspond to M — MeOH ions.

¶ *Added in Proof.* Extraction of the mycelium with CH_2Cl_2 followed by chromatography on silica (eluent, CH_2Cl_2) yielded compounds (**4**) and (**5**), striatals A and B, respectively.

[1] For previous paper in the series Antibiotics from Basidiomycetes see G. Schramm, W. Steglich, T. Anke, and F. Oberwinkler, *Chem. Ber.*, in the press.

[2] T. Anke, F. Oberwinkler, W. Steglich, and G. Höfle, *J. Antibiotics*, 1977, **30**, 221.

[3] P. Main, M. M. Woolfson, and G. Germain, MULTAN, University of York Printing Unit, York, Version 1975.

[4] XRAY 72, ed. J. M. Stewart, University of Maryland, Technical Report TR 442.

[5] C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[6] W. A. Ayer and H. Taube, *Tetrahedron Letters*, 1972, 1917; *Canad. J. Chem.*, 1973, **51**, 3842; W. A. Ayer and L. L. Carstens, *ibid.*, p. 3157.