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X-Ray Crystal and Molecular Structure of Kodo-cytochalasin-1

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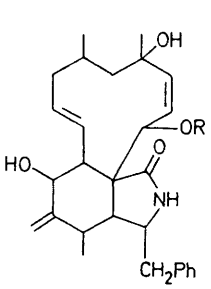
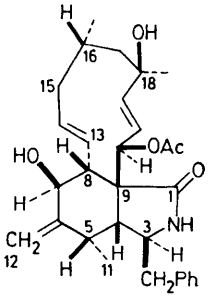
Summary Kodo-cytochalasin-1 and cytochalasin H have been shown to be identical in structure and stereochemistry by single-crystal *X*-ray diffraction analyses; an inadvertant error in the stereochemistry at C(18) reported previously for cytochalasin H is corrected.

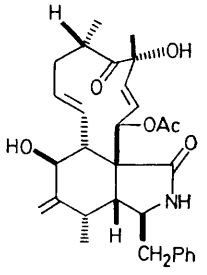
Phomopsis paspalli, Pendse and Kanitkar, a fungal pathogen of kodo millet (*Paspalum scrobiculatum* Linn. Syn. *P. commerionii* Lam), a minor food grain crop of India, elaborates two major toxins. These compounds, essentially on the basis of spectral data, have been assigned gross structures (**1**) and (**2**), and have been designated kodo-cytochalasin-1 and kodo-cytochalasin-2, respectively.[1] Kodo-cytochalasin-1 is obtained as white needles, m.p. 258—263 °C, from a $CHCl_3$–Et_2O solution. The present work confirms these gross structures and establishes the stereochemistry as depicted in (**3**) for kodo-cytochalasin-1. Further, we have



(1) R = Ac
(2) R = H



(3)



(4)

TABLE

Unit cell constants

Kodo-cytochalasin-1	Cytochalasin H (ref. 3)
a 15·348(4)	*c* 15·330(4)
b 13·089(3)	*b* 13·053(6)
c 7·347(3)	*a* 7·338(2)
β 97·23(3)°	*β* 97·02(2)°
λ(Cu-K_α) 1·54178 Å	λ(Mo-K_α) 0·71069 Å

demonstrated by independent crystal structure investigations that kodo-cytochalasin-1 and a fungal toxin recently

isolated from *Phomopsis sp.* infected pecans,[2] described as cytochalasin H,[3] are in fact identical. Some uncertainty on this point was caused by a clerical error in the formulation of the stereochemistry of cytochalasin H at C(18) in the structural formula (I) in ref. 3.

The full name of this toxin using the nomenclature proposed by Tamm *et al.*,[4a] is (7*S*,16*S*,18*S*,21*R*)-21-acetoxy-7,18-dihydroxy-16,18-dimethyl-10-phenyl[11]cytochalasa-6(12),13^t,19^t-triene-1-one.[4b] It is of interest that the relative stereochemistry at C(18) in this compound is different from that established for the same functionality in other closely related cytochalasins, *e.g.* zygosporin-A (**4**).[5]

The cell constants for kodo-cytochalasin-1, determined using a small, colourless, irregularly shaped crystal 0·3 mm in largest dimension, are compared with those for cytochalasin H in the Table. The space group in both investigations was found to be $P2_1$ with two molecules of $C_{30}H_{39}NO_5$ per unit cell. The structure of kodo-cytochalasin-1 was solved using *X*-ray crystallographic direct methods.[6] The co-ordinates of all atoms were refined by full-matrix least-squares methods, with all non-hydrogen atoms having anisotropic thermal parameters, to an *R*-factor of 0·043 for 1945 non-zero reflections collected on a Syntex $P2_1$ diffractometer. A drawing of a molecule of kodo-cytochalasin-1 is shown in the Figure. The structure determined from this *X*-ray work and of that reported in ref. 3 for cytochalasin H conform to that depicted in (**3**).

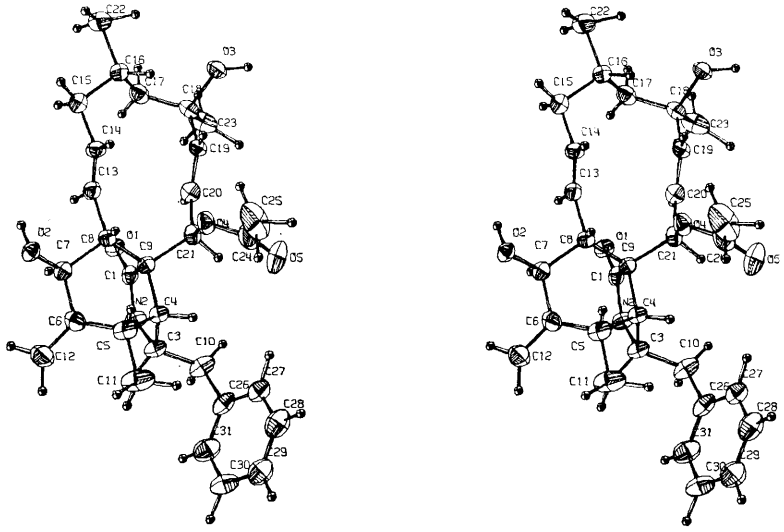


FIGURE. Stereoscopic view of the structure of a molecule of kodo-cytochalasin-1 (**3**).

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[1] S. A. Patwardhan, R. C. Pandey, S. Dev, and G. S. Pendse, *Phytochemistry*, 1974, **13**, 1985.
[2] J. M. Wells, H. G. Cutler, and R. J. Cole, *J. Canad. Microbiol.*, in the press.
[3] M. A. Beno and G. G. Christoph, *J.C.S. Chem. Comm.*, 1976, 344.
[4] (a) M. Binder, C. Tamm, W. B. Turner, and H. Minato, *J.C.S. Perkin I*, 1973, 1146; (b) note should be taken that the name in ref. 3 was incorrect, reflecting the improper labelling of the ORTEP figure in that report. Full details of that work will appear elsewhere: M. A. Beno, R. H. Cox, J. M. Wells, R. J. Cole, J. W. Kirksey and G. G. Christoph, *J. Amer. Chem. Soc.*, submitted for publication.
[5] Y. Tsukuda, M. Matsumoto, H. Minato, and H. Koyama, *Chem. Comm.*, 1969, 41; Y. Tsukuda and H. Koyama, *J.C.S. Perkin II*, 1972, 739.
[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.