Acta Cryst. (1982). B**38**, 1664–1666

Structure of a Mycotoxin Produced by *Fusarium nivale*: 4-Acetamido-2-buten-4-olide

BY ŽIVA RUŽIĆ-TOROŠ AND BISERKA KOJIĆ-PRODIĆ

Rudjer Bošković Institute, PO Box 1016, 41001 *Zagreb, Yugoslavia*

(*Received* 13 *October* 1981; *accepted* 4 *January* 1981)

Abstract. $C_6H_7NO_3$, $M_r = 141{\cdot}13$, monoclinic, $P2_1/c$, $a = 8{\cdot}790\ (4)$, $b = 5{\cdot}314\ (2)$, $c = 14{\cdot}264\ (3)$ Å, $\beta = 96{\cdot}47\ (3)°$, $Z = 4$, $U = 662{\cdot}03$ Å^3, $D_c = 1{\cdot}415$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}994$ mm^{-1}. Final $R = 0{\cdot}039$ for 963 observed reflexions [$I > 2\sigma(I)$]. Both D and L enantiomers appear in the structure. Bond lengths and angles are in agreement with expected values. The lactone ring is planar; mean value of the ring torsion angles is $0{\cdot}7\ (3)°$. The molecules are connected by hydrogen bonds N—H···O [3·000 (4) Å] forming infinite chains along **b**.

Introduction. Toxic metabolites produced by the mould *Fusarium nivale* on tall fescue (*Festuca arundinacea* Schreb.) cause various maladies in cattle (Tookey, Yates, Ellis, Grove & Nichols, 1972). Among the three isolated toxins (a butenolide, an unknown toxin, and a sesquiterpenoid), the butenolide is the most abundant (ratios 87:8:3) (Yates, Tookey, Ellis & Burkhardt, 1968). The structure of the butenolide, assigned as 4-acetamido-2-buten-4-olide on the basis of the IR, UV and NMR spectra, is in agreement with the X-ray structure determination. Although the butenolide possesses a chiral centre at the γ-carbon, the lack of optical rotation between 600 and 290 nm (Yates *et al.*, 1968) suggests isomerization or racemization during isolation and purification. An X-ray structure determination revealed the presence of both enantiomers in the crystalline state.

Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs recorded with Cu $K\alpha$ radiation. The cell dimensions given in the *Abstract* were refined from diffractometer measurements. The intensities were collected with a plate-like crystal, $0{\cdot}17 \times 0{\cdot}08 \times 0{\cdot}34$ mm, on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-scan mode [scan width = 2·10°, scan speed = $0{\cdot}07°$ s^{-1}] with graphite-monochromated Cu $K\alpha$ radiation. 963 independent reflexions [$I > 2\sigma(I)$] in the range $3 < \theta < 70°$ were recorded and used in the calculations. Three standard reflexions were measured every 2 h. The data were corrected for background, Lorentz and polarization effects. Overall temperature ($B = 2{\cdot}84$ Å^2) and scale factors were determined (Wilson, 1942) and used to compute normalized structure amplitudes by the *NORMAL* routine included in *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The E map based on 150 reflexions having $|E| \geq 1{\cdot}40$ and corresponding to the solution with the best figure of merit revealed the whole molecule. Refinement was by full-matrix least squares minimizing $\sum W(|F_o| - |F_c|)^2$. Weights were assigned as $W = W_1 . W_2$, where $W_1 = 1$ for $|F_o| \leq 35$ and $W_1 = 35/|F_o|$ for $|F_o| > 35$; $W_2 = 1$ for $\sin\theta \geq 0{\cdot}30$ and $W_2 = (\sin\theta)/0{\cdot}3$ for $\sin\theta < 0{\cdot}30$. Anisotropic refinement and a subsequent weighted difference synthesis located the H atoms. A scale factor, coordinates of all the atoms, anisotropic thermal parameters of the non-H atoms and isotropic thermal parameters for the H atoms (119 variables in all) were refined. Anisotropic thermal parameters are in the usual range: the maximum value is U_{22} for C(6) [0·069 (2) Å^2]. The final $R = 0{\cdot}039$ and $R_w = 0{\cdot}040$ for 963 reflexions.

Table 1. *Final fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (×10^2) *for non-*H *atoms*

$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$

	x	y	z	U_{eq} (Å^2)
O(0)	1422 (1)	−1960 (2)	1967 (1)	3·7 (3)
C(1)	452 (2)	−547 (4)	1374 (1)	3·7 (5)
O(1)	−666 (1)	−1480 (3)	936 (1)	5·1 (4)
C(2)	1024 (2)	2036 (4)	1384 (1)	3·8 (5)
C(3)	2290 (2)	2162 (4)	1971 (1)	3·8 (4)
C(4)	2678 (2)	−353 (4)	2388 (1)	3·4 (4)
N	2745 (2)	−400 (4)	3388 (1)	3·7 (4)
C(5)	3513 (2)	−2230 (4)	3906 (1)	3·8 (5)
O(2)	4250 (2)	−3838 (3)	3545 (1)	5·2 (4)
C(6)	3367 (3)	−2153 (7)	4944 (1)	5·4 (5)

Table 2. *Final positional* (×10^3) *and isotropic thermal parameters* (×10^2) *for* H *atoms*

	x	y	z	U (Å^2)
H(2)	48 (3)	333 (5)	101 (2)	5·2 (7)
H(3)	292 (3)	365 (5)	214 (2)	5·7 (8)
H(4)	369 (3)	−113 (5)	218 (2)	4·3 (7)
H(N)	218 (3)	65 (5)	364 (2)	4·8 (8)
H(6)1	305 (4)	−57 (8)	514 (3)	11 (2)
H(6)2	254 (5)	−324 (9)	506 (3)	13 (2)
H(6)3	419 (4)	−269 (8)	530 (3)	11 (1)

0567-7408/82/051664-03$01.00

Scattering factors given by Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965) were used.

The calculations were performed on a Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atom coordinates are listed in Tables 1 and 2.*

Discussion. The structural formula with the atom numbering and interatomic distances is shown in Fig. 1. Bond angles are listed in Table 3. The conformation of the molecule is defined by the torsion angles listed in Table 4. The molecular packing is illustrated in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters and bond angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36636 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°)

C(1)–O(0)–C(4)	108·9 (2)	O(0)–C(4)–N	110·1 (2)
O(0)–C(1)–O(1)	120·8 (2)	C(3)–C(4)–N	113·5 (2)
O(0)–C(1)–C(2)	108·8 (2)	C(4)–N–C(5)	121·4 (2)
O(1)–C(1)–C(2)	130·4 (2)	N–C(5)–O(2)	121·9 (2)
C(1)–C(2)–C(3)	108·6 (2)	N–C(5)–C(6)	115·2 (2)
C(2)–C(3)–C(4)	110·4 (2)	O(2)–C(5)–C(6)	122·9 (2)
O(0)–C(4)–C(3)	103·3 (2)		

Table 4. *Torsion angles* (°)

O(1)–C(1)–C(2)–C(3)	−179·8 (2)	C(4)–O(0)–C(1)–C(2)	−0·2 (2)
O(0)–C(1)–C(2)–C(3)	−0·5 (3)	C(2)–C(3)–C(4)–N	−120·3 (3)
C(1)–C(2)–C(3)–C(4)	0·9 (3)	C(3)–C(4)–N–C(5)	−159·6 (2)
C(2)–C(3)–C(4)–O(0)	−1·0 (3)	C(4)–N–C(5)–O(2)	4·0 (3)
C(3)–C(4)–O(0)–C(1)	0·7 (2)	C(4)–N–C(5)–C(6)	−175·0 (2)

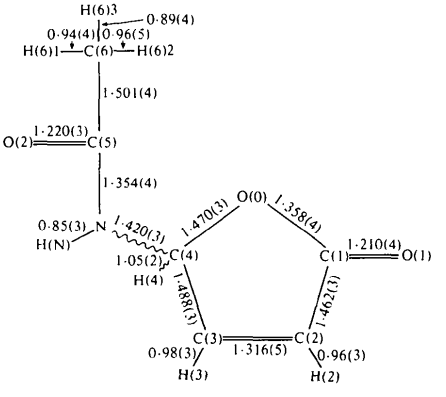

Fig. 1. The atom numbering and intramolecular distances (Å) with e.s.d.'s in parentheses.

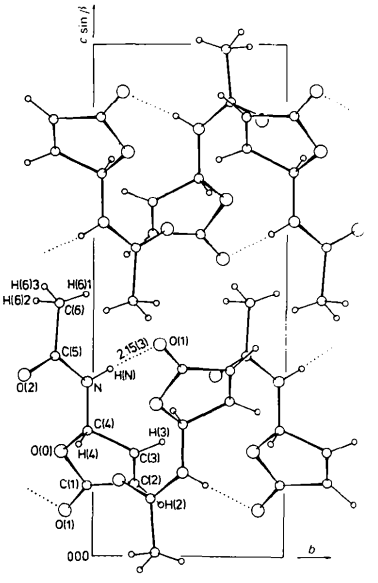

Fig. 2. View of the crystal structure along **a**. Hydrogen bonds are indicated by broken lines.

The single bonds C(1)–C(2) [1·462 (3) Å] and C(3)–C(4) [1·488 (3) Å] are shortened due to the presence of the adjacent C=O and C=C double bonds. The C(1)–O(0) [1·358 (4) Å] and C(4)–O(0) [1·470 (3) Å] bonds are asymmetric with well pronounced differences from the normal C–O single bond of 1·428 Å (Sundaralingam, 1968). The asymmetry of N–C(4) [1·420 (3) Å] and N–C(5) [1·354 (4) Å] is due to the C(5)–O(2) double bond. The mean value of the endocyclic bond angles is 108·0 (2)°, equal to the angle in an ideal pentagon. The internal bond angles at C(2) [108·6 (2)°] and C(3) [110·4 (2)°] are far from the value expected for C in sp^2 hybridization. Departure of these bond angles from the normal value is due to the requirement of the geometry of five-membered rings. The lactone ring is planar within the limits of experimental error. Displacements of the atoms from the least-squares mean plane are ≤0·006 (4) Å (Table 5). The mean value of the endocyclic torsion angles is 0·7 (3)°. The molecular geometry of the title compound is in accord with those found in 2,3-unsaturated γ-lactones, *e.g.* 2-acetamido-2,3-dideoxy-D-*threo*-hex-2-enono-1,4-lactone (Ružić-Toroš & Kojić-Prodić,

Table 5. *Displacements* (Å) *from the least-squares plane of the lactone ring*

Atoms included in the calculation of the plane are denoted by asterisks.

O(0)*	0·003 (1)	C(4)*	−0·005 (2)
C(1)*	0·000 (3)	O(1)	−0·008 (2)
C(2)*	−0·004 (4)	C(5)	1·099 (3)
C(3)*	0·006 (4)		

1976) and its D-*erythro* isomer (Ružić-Toroš & Lazarini, 1978), 2-acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-D-*threo*-hex-2-enono-1,4-lactone (Ružić-Toroš & Leban, 1978), and L-ascorbic acid (Hvoslef, 1968).

Molecules are connected by hydrogen bonds between acetamido and carbonyl groups, N—H(N)···O(1), 3·000 (4) Å, forming infinite chains along **b**. The angle N—H(N)···O(1) is 171 (2)°.

The authors thank MSc M. Bruvo for collecting the intensities at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, and Dr S. G. Yates, US Department of Agriculture, Northern Regional Research Center, Peoria, Illinois for the crystals used in this study.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HVOSLEF, J. (1968). *Acta Cryst.* B**24**, 23–35.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN* 80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

RUŽIC-TOROŠ, Ž. & KOJIĆ-PRODIĆ, B. (1976). *Acta Cryst.* B**32**, 2333–2336.

RUŽIĆ-TOROŠ, Ž. & LAZARINI, F. (1978). *Acta Cryst.* B**34**, 854–858.

RUŽIĆ-TOROŠ, Ž. & LEBAN, I. (1978). *Acta Cryst.* B**34**, 1226–1230.

STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.

TOOKEY, H. L., YATES, S. G., ELLIS, J. J., GROVE, M. D. & NICHOLS, R. E. (1972). *J. Am. Vet. Med. Assoc.* **160**(11), 1522–1526.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

YATES, S. G., TOOKEY, H. L., ELLIS, J. J. & BURKHARDT, H. J. (1968). *Phytochemistry*, **7**, 139–146.

Acta Cryst. (1982). B**38**, 1666–1669

Structure of (*E*)-2-Ethynyl-2-methoxy-5-phenyladamantane*†

BY S. Y. LIN, M. IONOV,‡ Y. OKAYA, D. M. CHIOU AND W. J. LE NOBLE

Chemsitry Department, State University of New York at Stony Brook, Stony Brook, New York 11794, *USA*

(*Received* 17 *April* 1979; *accepted* 5 *January* 1982)

Abstract. $C_{19}H_{22}O$, orthorhombic, $Pc2_1n$, a = 6·972 (2), b = 20·214 (7), c = 21·025 (6) Å, V = 2961 Å^3, Z = 8, ρ_o = 1·199 g cm^{-3}. R = 0·057 for 2065 observed reflections measured on a diffractometer using Cu $K\alpha$ radiation. The two chemically independent molecules in the asymmetric unit are arranged around a pseudo center of symmetry and the pairs thus generated pack in the structure using the symmetry of the space group. The OCH_3 group is in the *anti* configuration with respect to the phenyl group.

Introduction. This report is part of our systematic investigation into bridgehead phenyl-substituted adamantanes to determine their configurations and to study reaction mechanisms involving these compounds. Thus, in a methanolysis of (*E*)- and (*Z*)-2-chloro-2-ethynyl-5-phenyladamantanes,§ $C_{10}H_{13}.C_6H_5.(C{\equiv}CH).Cl$, these two isomers both produce the same mixture of 2-ethynyl-2-methoxy-5-phenyladamantanes. Regardless of the configuration of the starting isomer, it was observed that the product is a mixture of 3:1 in favor of one of the configurations, (*Z*) (le Noble, Chiou & Okaya, 1978). It was then postulated that the two reactions go through a common intermediate, and this is attacked preferentially from one side by CH_3OH because of a remote directing effect of the phenyl group in the 5-position. In view of this remarkable preference in the collapse of the intermediate, it seemed desirable to confirm the

* IUPAC name: (*E*)-2-ethynyl-2-methoxy-5-phenyltricyclo-[3.3.1.1^{3,7}]decane.

† Crystallographic Studies on Adamantanes. IV.

‡ A USSR–State University Exchange Program Scholar. Current address: Chemistry Department, Moscow State University, Moscow 117234, USSR.

§ The configurations of these isomers were unambiguously determined by crystallographic methods (Okaya, Lin, Chiou & le Noble, 1980).

0567-7408/82/051666-04$01.00