

Fig. 2. A view along **b** of the unit-cell contents, showing hydrogen bonding and stacking.

**Discussion.** The atomic parameters are given in Table 1.\* Interatomic distances and angles are given in Table 2. These bonds and angles compare well with those of

\* Lists of structure factors, H-atom parameters and Fig. 3 [a view perpendicular to the (100) plane] have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38425 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

similar compounds, *e.g.* 3',5'-di-*O*-acetyluridine (de Graaff, Admiraal, Koen & Romers, 1977). The value of the phase angle of pseudorotation  $P = 166^\circ$  (Altona & Sundaralingam 1972), and  $\chi_{\text{CN}} = -113^\circ$  [C(2)—N(1)—C(1')—O(4')]. The C(4')—C(5') conformation is  $g^+$  (see Table 2). Figs. 2 and 3† illustrate the packing of the molecules in the cell. The only hydrogen bond present in the structure is that between O(2) and N(3) of bases related to one another by the twofold axis. The interatomic distance for these two atoms is 2.77 (2) Å.

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#### References

- ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.  
 GRAAFF, R. A. G. DE, ADMIRAAL, G., KOEN, E. H. & ROMERS, C. (1977). *Acta Cryst.* **B33**, 2459–2464.  
 LOW, J. N., TOLLIN, P. & WILSON, H. R. (1982). *Nucl. Acid. Res.* **10**, 5599–5604.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. A program for torsion-angle, mean-plane and libration-correction calculations. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

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## Structure of (*Z*)-1,3,4,5,6-Penta-*O*-acetyl-*keto*-D-fructose (2,4-Dinitrophenyl)hydrazone, $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_{14}$

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**Abstract.**  $M_r = 570.46$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.942$  (2),  $b = 12.737$  (3),  $c = 27.328$  (8) Å,  $Z = 4$ ,  $U = 2764.43$  Å<sup>3</sup>,  $D_x = 1.371$  Mg m<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 1.01$  mm<sup>-1</sup>,  $F(000) = 1192$ , room temperature; final  $R = 0.057$  for 1664 observed reflexions [ $I \geq 3\sigma(I)$ ]. The sugar occurs in the open-chain form and the compound is a true hydrazone. The C atoms of the sugar backbone [from C(2) to C(6)] form a nearly planar zigzag chain. N(1)—N(2)—C(1)—C(2)—C(3) are roughly planar and coplanar with the benzene ring. The sugar conformation is stabilized by an intramolecular

hydrogen bond between the hydrazone moiety and the nitro group [N(1)—H...O(1') 2.613 (7) Å].

**Introduction.** Phenylhydrazones of the sugars may appear in cyclic or acyclic forms. The crystal structures of arabinose (4-bromophenyl)hydrazone (Furberg & Petersen, 1962), glucose (4-bromophenyl)hydrazone (Dukefos & Mostad, 1965), ribose (4-bromophenyl)hydrazone (Bjåmer, Furberg & Petersen, 1964) and mannose (4-bromophenyl)hydrazone (Furberg & Solbakk, 1969) have been reported. The

compounds of arabinose and glucose were found to be hydrazides with the sugar in the pyranose chair form, whereas that of ribose and mannose are true hydrazones with the sugar in the open-chain form. The acyclic hydrazones may exist as *E* and *Z* isomers; the presence of the *E* and *Z* isomers of saccharide hydrazone in solution is proposed by Takeda (1979). The mixture of *E* and *Z* isomers of 1,3,4,5,6-penta-*O*-acetyl-*keto*-D-fructose (2,4-dinitrophenyl)hydrazone was obtained by reaction of 1,3,4,5,6-penta-*O*-acetyl-*keto*-D-fructose with (2,4-dinitrophenyl)hydrazine (Linek & Novotná, 1980). Separation of this mixture on the silica-gel column afforded pure *E* and *Z* isomers in the crystalline form. The *Z* isomer has m.p. 394–395 K and  $[\alpha]_D^{25^\circ\text{C}} + 47.2^\circ$  ( $c = 0.5 \text{ g dm}^{-3}$ ; ethyl acetate). Isomer *E* has m.p. 382–383 K and  $[\alpha]_D^{25^\circ\text{C}} - 54.7^\circ$  ( $c = 0.5 \text{ g dm}^{-3}$ ; ethyl acetate). The X-ray structure determination was undertaken in order to establish the correct isomer assignment. The crystal structure of the *Z* isomer is presented in this paper.

The hydrazones of saccharides are also of interest owing to their biological activities; they inhibit nucleoside and proteosynthesis in tumorous cells (Fuska, Linek & Buzinkay, 1974), growth of bacteria (Zemek & Linek, 1977) and *Trichomonas vaginalis* (Kettner, Mačičková & Linek, 1983).

**Experimental.** Preliminary cell dimensions and the space group determined from oscillation and Weissenberg photographs recorded with Cu *K* $\alpha$  radiation; final cell dimensions refined from diffractometer measurements; intensities collected on a Philips PW 1100 computer-controlled four-circle diffractometer in the  $\omega$ -scan mode [scan width  $1.50^\circ$  ( $\theta$ ), scan speed  $0.050^\circ$  ( $\theta$ ) $s^{-1}$ ] with graphite-monochromated Cu *K* $\alpha$  radiation; crystal  $0.91 \times 0.91 \times 4.55 \text{ mm}$ ; 1664 independent reflexions [ $I \geq 3\sigma(I)$ ] in the range  $3 < \theta < 70^\circ$  used in the calculations; three standard reflexions measured every 2h. Structure solved with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); a subsequent difference synthesis located the H atoms; refinement by full-matrix least squares minimizing  $\sum w_i |F_o| - |F_c|^2$  with unit weights; a scale factor, atomic coordinates, and anisotropic thermal parameters for the non-hydrogen atoms refined (361 variables in all); H atoms included in the structure factor calculations only; ratio of maximum least-squares shift to error in the final refinement cycle 1.449 [for C(7)] and average ratio of shift to error 0.203; anisotropic thermal parameters in the usual range, the maximum value being  $U_{22}$  for O(8) [ $0.172$  (7)  $\text{\AA}^2$ ]; final  $R = 0.057$ ; scattering factors from Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965); calculations carried out on the Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

**Discussion.** Atomic coordinates with the  $U_{eq}$  for the non-hydrogen atoms are listed in Table 1.\* The structural formula with the atom numbering are shown in Fig. 1. Bond lengths and angles for non-hydrogen atoms are in Table 2. The molecular packing is illustrated in Fig. 2.

Bond lengths and angles are in agreement with the given atom type and hybridization with the exception of the hydrazone part where a delocalization effect occurs (Table 2). The carbonyl bonds are in the range  $1.189\text{--}1.200$  (10)  $\text{\AA}$ . There are two more categories of C–O bonds: single C–O ranging from  $1.433$  (8) to  $1.447$  (7)  $\text{\AA}$  and those adjacent to a carbonyl group which are in the range  $1.343$  (9) to  $1.369$  (8)  $\text{\AA}$ . Bond distances in nitro groups are from  $1.219$  (11) to  $1.242$  (12)  $\text{\AA}$ . The C–C distances in the acetyl groups, involving terminal methyl groups, range from  $1.461$

\* List of structure factors, anisotropic thermal parameters, atomic and isotropic thermal parameters of the H atoms, bond lengths and angles involving H, and atom displacements from the best least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38415 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for the non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ ( $\text{\AA}^2$ )
C(1')	367 (8)	5308 (5)	4676 (2)	3.6 (3)
C(2')	1771 (8)	5746 (4)	4917 (4)	3.7 (3)
C(3')	1572 (9)	6425 (5)	5311 (2)	4.7 (4)
C(4')	-22 (9)	6675 (5)	5460 (2)	4.5 (4)
C(5')	-1448 (9)	6297 (5)	5219 (2)	4.9 (4)
C(6')	-1263 (8)	5625 (5)	4838 (2)	4.6 (4)
N(1')	3490 (7)	5517 (5)	4759 (2)	4.8 (3)
N(2')	-216 (11)	7400 (5)	5871 (2)	6.6 (4)
O(1')	3750 (6)	4857 (4)	4442 (1)	5.9 (3)
O(2')	4620 (6)	6017 (4)	4959 (2)	6.7 (3)
O(3')	1036 (9)	7704 (5)	6087 (2)	9.5 (4)
O(4')	-1666 (9)	7672 (5)	5985 (2)	8.1 (4)
C(1)	-2540 (9)	3253 (5)	3527 (2)	5.1 (4)
O(1)	-2700 (5)	3583 (3)	3024 (1)	4.4 (2)
C(7)	-2404 (9)	2862 (6)	2673 (2)	5.4 (4)
O(2)	-1964 (8)	1988 (4)	2758 (1)	8.4 (4)
C(8)	-2636 (13)	3336 (6)	2179 (2)	8.0 (5)
C(2)	-858 (8)	3609 (5)	3723 (2)	3.8 (3)
N(1)	526 (6)	4642 (4)	4280 (1)	4.1 (3)
N(2)	-948 (6)	4282 (4)	4070 (1)	4.1 (3)
C(3)	711 (8)	3086 (4)	3498 (2)	4.0 (4)
O(3)	2107 (5)	3799 (3)	3486 (1)	4.1 (2)
C(9)	2221 (9)	4417 (5)	3078 (2)	5.1 (4)
O(4)	1182 (7)	4353 (5)	2760 (2)	9.1 (3)
C(10)	3658 (10)	5133 (5)	3095 (2)	6.3 (7)
C(4)	1198 (8)	2094 (5)	3767 (2)	4.0 (3)
O(5)	1669 (5)	2366 (3)	4262 (1)	4.6 (2)
C(11)	881 (10)	1839 (6)	4627 (2)	5.3 (4)
O(6)	14 (8)	1095 (5)	4551 (2)	9.2 (4)
C(12)	1365 (11)	2266 (7)	5113 (2)	7.2 (5)
C(5)	2677 (9)	1527 (5)	3525 (2)	4.6 (3)
O(7)	2111 (6)	1242 (3)	3042 (1)	4.8 (3)
C(13)	2850 (10)	1688 (5)	2652 (2)	5.3 (4)
O(8)	3985 (9)	2297 (6)	2690 (2)	12.4 (5)
C(14)	2059 (10)	1335 (6)	2186 (2)	6.7 (4)
C(6)	3147 (10)	526 (5)	3792 (2)	5.5 (5)
O(9)	4541 (6)	13 (3)	3550 (1)	5.6 (3)
C(15)	6092 (12)	315 (6)	3698 (2)	6.4 (5)
O(10)	6325 (8)	958 (4)	4008 (2)	7.8 (4)
C(16)	7434 (12)	266 (6)	3430 (3)	8.1 (6)

Table 2. Bond distances (Å) and angles (°) involving non-hydrogen atoms

C(1')-C(2')	1.409 (9)	N(2)-N(1)	1.383 (8)
C(1')-C(6')	1.427 (10)	C(3)-O(3)	1.433 (8)
C(1')-N(1)	1.380 (8)	C(3)-C(4)	1.512 (9)
C(2')-C(3')	1.391 (9)	O(3)-C(9)	1.369 (8)
C(2')-N(1')	1.461 (9)	O(4)-C(9)	1.200 (10)
C(3')-C(4')	1.368 (11)	C(9)-C(10)	1.461 (11)
C(4')-C(5')	1.395 (11)	C(4)-O(5)	1.447 (7)
C(4')-N(2')	1.462 (9)	C(4)-C(5)	1.529 (10)
C(5')-C(6')	1.356 (10)	O(5)-C(11)	1.356 (9)
N(1')-O(1')	1.225 (8)	O(6)-C(11)	1.189 (11)
N(1')-O(2')	1.228 (8)	C(11)-C(12)	1.485 (10)
N(2')-O(3')	1.219 (11)	C(5)-O(7)	1.442 (8)
N(2')-O(4')	1.242 (12)	C(5)-C(6)	1.515 (10)
C(1)-O(1)	1.443 (8)	O(7)-C(13)	1.343 (9)
C(1)-C(2)	1.509 (10)	O(8)-C(13)	1.193 (11)
O(1)-C(7)	1.349 (8)	C(13)-C(14)	1.489 (10)
O(2)-C(7)	1.190 (9)	C(6)-O(9)	1.445 (9)
C(7)-C(8)	1.489 (11)	O(9)-C(15)	1.353 (11)
C(2)-N(2)	1.281 (8)	O(10)-C(15)	1.191 (10)
C(2)-C(3)	1.541 (9)	C(15)-C(16)	1.491 (13)

C(2')-C(1')-C(6')	117.5 (6)	C(2)-N(2)-N(1)	118.8 (5)
C(2')-C(1')-N(1)	122.4 (6)	C(2)-C(3)-O(3)	111.2 (5)
C(6')-C(1')-N(1)	120.0 (6)	C(2)-C(3)-C(4)	112.0 (5)
C(1')-C(2')-C(3')	121.2 (6)	O(3)-C(3)-C(4)	110.1 (5)
C(1')-C(2')-N(1')	121.5 (6)	C(3)-O(3)-C(9)	115.8 (5)
C(3')-C(2')-N(1')	117.2 (6)	O(3)-C(9)-O(4)	120.3 (7)
C(2')-C(3')-C(4')	118.7 (6)	O(3)-C(9)-C(10)	112.6 (6)
C(3')-C(4')-C(5')	122.1 (6)	O(4)-C(9)-C(10)	127.1 (7)
C(3')-C(4')-N(2')	118.2 (7)	C(3)-C(4)-O(5)	108.6 (5)
C(5')-C(4')-N(2')	119.6 (7)	C(3)-C(4)-C(5)	112.4 (5)
C(4')-C(5')-C(6')	119.4 (7)	O(5)-C(4)-C(5)	108.6 (5)
C(1')-C(6')-C(5')	121.0 (6)	C(4)-O(5)-C(11)	116.8 (5)
C(2')-N(1')-O(1')	120.2 (6)	O(5)-C(11)-O(6)	122.2 (6)
C(2')-N(1')-O(2')	116.6 (6)	O(5)-C(11)-C(12)	110.9 (7)
O(1')-N(1')-O(2')	123.2 (6)	O(6)-C(11)-C(12)	126.7 (7)
C(4')-N(2')-O(3')	119.1 (8)	C(4)-C(5)-O(7)	106.0 (5)
C(4')-N(2')-O(4')	117.8 (7)	C(4)-C(5)-C(6)	112.3 (6)
O(3')-N(2')-O(4')	123.2 (7)	O(7)-C(5)-C(6)	107.8 (5)
O(1)-C(1)-C(2)	109.2 (5)	C(5)-O(7)-C(13)	118.9 (5)
C(1)-O(1)-C(7)	117.6 (5)	O(7)-C(13)-O(8)	122.3 (7)
O(1)-C(7)-O(2)	123.3 (6)	O(7)-C(13)-C(14)	111.5 (6)
O(1)-C(7)-C(8)	110.3 (6)	O(8)-C(13)-C(14)	126.2 (7)
O(2)-C(7)-C(8)	126.3 (7)	C(5)-C(6)-O(9)	110.4 (6)
C(1)-C(2)-N(2)	114.5 (6)	C(6)-O(9)-C(15)	115.6 (6)
C(1)-C(2)-C(3)	116.4 (5)	O(9)-C(15)-O(10)	123.3 (8)
N(2)-C(2)-C(3)	129.0 (6)	O(9)-C(15)-C(16)	111.2 (7)
C(1')-N(1)-N(2)	116.8 (5)	O(10)-C(15)-C(16)	125.5 (9)

Table 3. Torsion angles (°)

O(1)-C(1)-C(2)-C(3)	-67.2 (7)	N(1)-C(1')-C(2')-N(1')	-0.1 (8)
O(1)-C(1)-C(2)-N(2)	115.5 (6)	C(1')-C(2')-N(1')-O(1')	-7 (1)
C(1)-C(2)-C(3)-C(4)	-88.6 (7)	C(1')-C(2')-C(3')-C(4')	-1 (1)
N(2)-C(2)-C(3)-C(4)	88.2 (8)	C(2')-C(3')-C(4')-C(5')	-2 (1)
C(2)-C(3)-C(4)-C(5)	175.9 (5)	C(3')-C(4')-N(2')-O(3')	-5 (1)
C(2)-C(3)-C(4)-O(5)	-63.9 (7)	C(3')-C(4')-C(5')-C(6')	3 (1)
C(3)-C(4)-C(5)-C(6)	-179.3 (6)	C(4')-C(5')-C(6')-C(1')	-1 (1)
C(3)-C(4)-C(5)-O(7)	-61.9 (7)	C(5')-C(6')-C(1')-C(2')	-2 (1)
C(4)-C(5)-C(6)-O(9)	179.6 (5)	C(2)-C(3)-O(3)-C(9)	-88.0 (6)
O(7)-C(5)-C(6)-O(9)	63.3 (7)	C(3)-O(3)-C(9)-O(4)	1 (1)
C(1)-O(1)-C(7)-O(2)	-3 (1)	C(3)-C(4)-O(5)-C(11)	127.0 (6)
C(1)-O(1)-C(7)-C(8)	179.7 (5)	C(4)-O(5)-C(11)-O(6)	10 (1)
C(1)-C(2)-N(2)-N(1)	178.8 (5)	C(4)-C(5)-O(7)-C(13)	114.2 (6)
C(2)-N(2)-N(1)-C(1')	-175.5 (6)	C(5)-O(7)-C(13)-O(8)	2 (1)
N(2)-N(1)-C(1')-C(2')	-178.7 (6)	C(5)-C(6)-O(9)-C(15)	88.6 (7)
N(1)-C(1')-C(2')-C(3')	179.1 (6)	C(6)-O(9)-C(15)-O(10)	0.1 (9)

(11) to 1.491 (13) Å. In the sugar backbone, C—C distances are from 1.509 (10) to 1.541 (9) Å. Bond distances in the hydrazone moiety are affected by electron delocalization: C(1')—N(1) [1.380 (8) Å] and N(1)—N(2) [1.383 (8) Å] are shorter than normal single bonds and N(2)—C(2) [1.281 (8) Å] is longer than a normal double bond. These values are close to those found in mannose (*p*-bromophenyl)hydrazone [C(6')—N(1) 1.373 (19); N(1)—N(2) 1.370 (20);

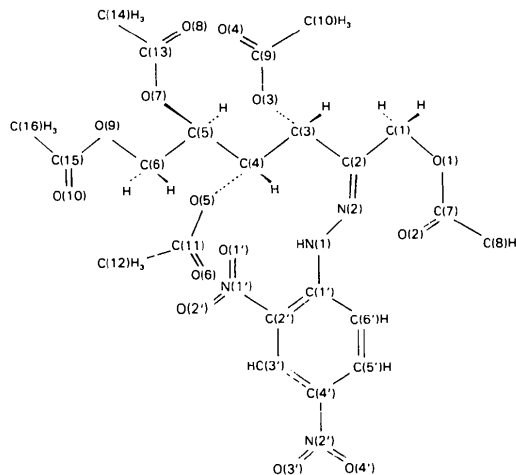
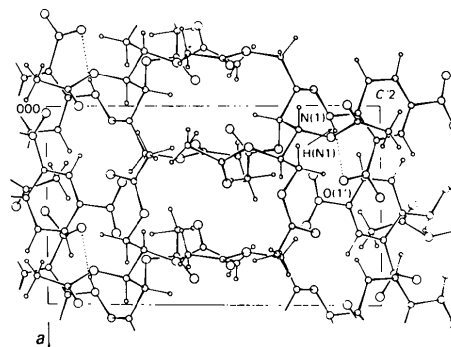


Fig. 1. Structural formula with the atom numbering.

Fig. 2. Molecular packing viewed along *b*. Hydrogen bonds are indicated by dotted lines.

N(2)—C(2) 1.254 (18) Å] (Furberg & Solbakk, 1969). Interatomic distances in the phenyl ring are somewhat scattered, 1.356 (10)—1.427 (10) Å. C(3')—C(4') [1.368 (11) Å] and C(5')—C(6') [1.356 (10) Å] are significantly shorter than in aromatic systems. C(4'), C(5') and C(6') are involved in van der Waals contacts: C(4')...O(9) 3.474 (8), O(2')...C(5') 3.222 (9) and C(6')...O(2) 3.323 (9) Å. Bond angles involving C(*sp*<sup>3</sup>) range from 106.0 (5)—112.4 (5)°. Bond angles at C(*sp*<sup>2</sup>) scatter over a wide range (Table 2). The values of bond angles in the hydrazone part are 116.8 (5) and 118.8 (5)°, giving evidence of *sp*<sup>2</sup>-hybridized N atoms.

The molecular conformation is described by the torsion angles (Table 3) and for planar parts of the molecule by the deviations from the best least-squares plane. In acyclic sugars a C chain takes up a zigzag conformation. Such an arrangement occurs in the title compound; the C atoms [from C(2) to C(6)] of the sugar backbone form a nearly planar zigzag chain. The torsion angles along these bonds are 175.9 (5), -179.3 (6), 179.6 (5)°. The mean value of the atom displacement from the best least-squares plane [defined

by C(2), C(3), C(4), C(5), C(6)] is 0.004 (11) Å. N(1), N(2), C(1), C(2), C(3) are roughly planar and coplanar with the benzene ring. The torsion angles along bonds of the hydrazone part are very close to 180° (Table 3). The best least-squares plane defined by all these atoms gave displacements of the atoms from 0.005 (9) [for C(1')] to 0.078 (9) Å [for C(3')]. The dihedral angle between planes defined by N(1), N(2), C(2), C(3) and C(3), C(4), C(5), C(6) is 88.2 (8)°. The sugar conformation is stabilized by an intramolecular hydrogen bond between the hydrazone moiety and a nitro group [N(1)—H...O(1') 2.613 (7); N(1)—H(N1) 0.81; H(N1)...O(1') 2.10 Å;  $\angle 120^\circ$ ] (Fig. 2).

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### Structures of 3 $\beta$ -Hydroxy-5 $\beta$ -bufa-14,20,22-trienolide, C<sub>24</sub>H<sub>32</sub>O<sub>3</sub>, and 3 $\beta$ -Acetoxy-15 $\alpha$ -(*o*-nitrobenzoyloxy)-7-oxo-5 $\beta$ ,14 $\beta$ -bufa-8,20,22-trienolide, C<sub>33</sub>H<sub>35</sub>NO<sub>9</sub>\*

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**Abstract.** C<sub>24</sub>H<sub>32</sub>O<sub>3</sub> (I),  $M_r = 368.5$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.461$  (4),  $b = 12.725$  (6),  $c = 19.12$  (1) Å,  $V = 2058$  (2) Å<sup>3</sup>,  $D_x = 1.19$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo } K\alpha) = 0.042$  mm<sup>-1</sup>,  $F(000) = 800$ , final  $R = 0.073$  for 2160 reflections; C<sub>33</sub>H<sub>35</sub>NO<sub>9</sub> (II),  $M_r = 589.6$ , monoclinic,  $P2_1$ ,  $a = 11.301$  (6),  $b = 39.53$  (2),  $c = 7.650$  (4) Å,  $\beta = 103.92$  (2)°,  $V = 3317$  (3) Å<sup>3</sup>,  $D_x = 1.18$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo } K\alpha) = 0.052$  mm<sup>-1</sup>,

$F(000) = 1248$ , final  $R = 0.128$  for 3184 reflections; graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å) used in both determinations. A conformational analysis of the lactone ring with respect to the remainder of the molecule has been performed for both bufatrienolides. The crystallographically determined conformations correspond well with theoretically predicted energy minima.

\* Steroids and Related Natural Products 101 and Bufadienolides 34. For contributions 100 and 33 respectively refer to Nassimbeni, Niven, Pettit, Kamano, Inoue & Einck (1982).

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**Introduction.** Medicinal preparations derived from plants of the genus *Scilla* (Liliaceae family) and toads of the genus *Bufo* (Bufonidae family) have been used

#### References

- BJÄMER, K., FURBERG, S. & PETERSEN, C. S. (1964). *Acta Chem. Scand.* **18**, 587–595.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 DUKEFOS, T. & MOSTAD, A. (1965). *Acta Chem. Scand.* **19**, 685–696.  
 FURBERG, S. & PETERSEN, C. S. (1962). *Acta Chem. Scand.* **16**, 1539–1548.  
 FURBERG, S. & SOLBAKK, J. (1969). *Acta Chem. Scand.* **23**, 3248–3256.  
 FUSKA, J., LINEK, K. & BUZINKAY, Š. (1974). *Neoplasma*, **21**, 561–568.  
 KETTNER, M., MAČIČKOVÁ, T. & LINEK, K. (1983). *Experientia*. In the press.  
 LINEK, K. & NOVOTNÁ, Z. (1980). Czechoslovak Patent 208 807.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.  
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 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.  
 TAKEDA, Y. (1979). *Carbohydr. Res.* **77**, 9–23.  
 ZEMEK, J. & LINEK, K. (1977). *Folia Microbiol. (Prague)*, **22**, 237–238.