

Fig. 2. A view of the unit-cell contents of structure (I) along [100].

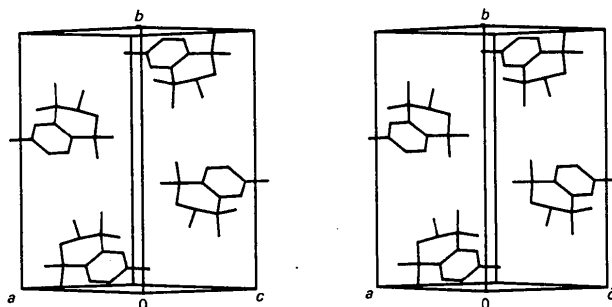


Fig. 3. A view of the unit-cell contents of structure (II) along [100].

The packing of the molecules is illustrated in Figs. 2 and 3 for musk tonalid and its precursor respectively. In both structures there are no intermolecular distances significantly shorter than the sum of the van der Waals radii.

The shortest intermolecular C—O distance in musk tonalid is 3.62 (2) Å [O(1)—C(17) through symmetry operation $1-x, 1-y, 1-z$].

Matching of the two molecules [leaving out the substituent on C(6) and the H atoms] resulted in an r.m.s. value of 0.09 Å, which means that the addition of the osmophoric group has little influence on the geometry of the molecule. The largest difference between the corresponding atoms occurs at C(11) and C(12).

The authors would like to express their thanks to Dr A. M. Cohen and Drs W. Lenselink of PFW-Nederland for providing the crystals and D. Heijdenrijk for technical assistance.

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 DE RIDDER, D. J. A., GOUBITZ, K. & SCHENK, H. (1990). *Acta Cryst.* C46, 468–470.
 DOMENICANO, A., VACIAGO, A. & COULSON, A. C. (1975). *Acta Cryst.* B31, 221–234.
 FOCES-FOCES, C., CANO, F. H. & GARCIA-BLANCO, S. (1976). *Acta Cryst.* B32, 3029–3033.
 LARSON, A. C. (1967). *Acta Cryst.* 23, 664–665.
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 SCHENK, H. & KIERS, C. T. (1983). *SIMPEL83. A Program System for Direct Methods*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD. Oxford: Clarendon Press.
 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, USA.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

Acta Cryst. (1990). C46, 2202–2205

Structure of Solanida-2,4,6-triene

BY SLOBODANKA STANKOVIĆ*

Institute of Physics, Faculty of Sciences, 21000 Novi Sad, Ilije Djuričića 4, Yugoslavia

AND DUŠAN MILJKOVIĆ, KATARINA GAŠI AND ZVONIMIR SAKAČ

Institute of Chemistry, Faculty of Sciences, Novi Sad, Yugoslavia

(Received 21 December 1989; accepted 8 February 1990)

Abstract. C₂₇H₃₉N, $M_r = 377.6$, orthorhombic, $P2_12_12_1$, $a = 16.066(2)$, $b = 13.575(2)$, $c = 10.332(2)$ Å, $V = 2253(1)$ Å³, $Z = 4$, $D_x =$

1.12 Mg m^{-3} , $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 0.44 \text{ mm}^{-1}$, $F(000) = 832$, $R = 0.042$ for 2253 unique observed reflections. The six-membered *A* ring has a half-chair conformation, the *B* ring exhibits a transitional form between sofa and half-chair conforma-

* Author to whom correspondence should be addressed.

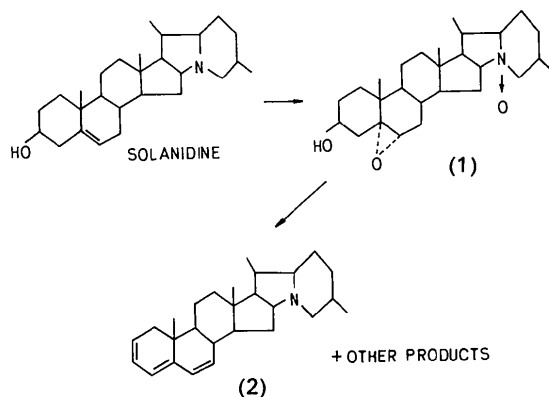
Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N	0.4033 (2)	0.4403 (2)	-0.0223 (3)	3.9 (1)
C(1)	0.9075 (2)	0.5947 (2)	0.0058 (4)	4.5 (1)
C(2)	0.9777 (2)	0.6648 (3)	-0.0189 (4)	5.5 (2)
C(3)	0.9685 (2)	0.7429 (3)	-0.0963 (4)	5.4 (2)
C(4)	0.8885 (2)	0.7651 (2)	-0.1531 (4)	4.7 (1)
C(5)	0.8186 (2)	0.7175 (2)	-0.1180 (3)	3.8 (1)
C(6)	0.7388 (2)	0.7383 (2)	-0.1764 (3)	4.2 (1)
C(7)	0.6688 (2)	0.6904 (2)	-0.1483 (3)	4.1 (1)
C(8)	0.6663 (2)	0.6079 (2)	-0.0522 (3)	3.7 (1)
C(9)	0.7540 (2)	0.5623 (2)	-0.0344 (3)	3.6 (1)
C(10)	0.8201 (2)	0.6425 (2)	-0.0064 (3)	3.8 (1)
C(11)	0.7534 (2)	0.4765 (2)	0.0632 (3)	4.1 (1)
C(12)	0.6888 (2)	0.3980 (2)	0.0278 (3)	4.2 (1)
C(13)	0.6019 (2)	0.4429 (2)	0.0126 (3)	3.6 (1)
C(14)	0.6063 (2)	0.5241 (2)	-0.0916 (3)	3.7 (1)
C(15)	0.5145 (2)	0.5473 (2)	-0.1229 (3)	4.3 (1)
C(16)	0.4725 (2)	0.4454 (2)	-0.1138 (3)	3.9 (1)
C(17)	0.5364 (2)	0.3728 (2)	-0.0516 (3)	3.8 (1)
C(18)	0.5703 (2)	0.4824 (2)	0.1446 (3)	3.9 (1)
C(19)	0.8018 (2)	0.7008 (3)	0.1191 (3)	4.8 (2)
C(20)	0.4847 (2)	0.3031 (2)	0.0347 (3)	4.3 (1)
C(21)	0.4982 (3)	0.1932 (3)	0.0049 (5)	6.3 (2)
C(22)	0.3945 (2)	0.3355 (2)	0.0096 (3)	4.1 (1)
C(23)	0.3337 (2)	0.3229 (3)	0.1191 (4)	5.5 (2)
C(24)	0.2499 (2)	0.3692 (3)	0.0829 (4)	5.7 (2)
C(25)	0.2602 (2)	0.4763 (3)	0.0401 (4)	5.3 (2)
C(26)	0.3255 (2)	0.4847 (2)	-0.0654 (4)	4.5 (1)
C(27)	0.1774 (2)	0.5203 (3)	-0.0043 (5)	6.9 (2)

tions, while the C and F rings are chairs. The five-membered D and E rings are in half-chair and envelope conformations respectively.

Introduction. During our synthetic studies directed towards a degradation of the indolizidine system in 3β-hydroxy-5α,6α-epoxysolanidane N-oxide (1) we isolated several new side-products. Their structures were proposed on the basis of chemical and spectroscopic evidence, but conclusive proof was lacking for one of them, solanida-2,4,6-triene (2). The X-ray determination of the crystal and molecular structure of (2) is now described.



Experimental. 3β-Hydroxy-5α,6α-epoxy-solanidane N-oxide (1) was obtained by oxidation of solanidine

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°) with their e.s.d.'s in parentheses

N—C(16)	1.461 (4)	C(11)—C(12)	1.531 (5)
N—C(22)	1.468 (4)	C(12)—C(13)	1.531 (4)
N—C(26)	1.458 (4)	C(13)—C(14)	1.543 (4)
C(1)—C(2)	1.497 (5)	C(13)—C(17)	1.566 (4)
C(1)—C(10)	1.553 (5)	C(13)—C(18)	1.551 (4)
C(2)—C(3)	1.336 (6)	C(14)—C(15)	1.543 (5)
C(3)—C(4)	1.444 (5)	C(15)—C(16)	1.543 (5)
C(4)—C(5)	1.347 (5)	C(16)—C(17)	1.561 (5)
C(5)—C(6)	1.444 (5)	C(17)—C(20)	1.543 (5)
C(5)—C(10)	1.538 (4)	C(20)—C(22)	1.536 (5)
C(6)—C(7)	1.332 (5)	C(20)—C(21)	1.539 (5)
C(7)—C(8)	1.497 (5)	C(22)—C(23)	1.505 (5)
C(8)—C(9)	1.551 (4)	C(23)—C(24)	1.534 (5)
C(8)—C(14)	1.545 (4)	C(24)—C(25)	1.528 (5)
C(9)—C(10)	1.548 (4)	C(25)—C(26)	1.517 (5)
C(9)—C(11)	1.541 (4)	C(25)—C(27)	1.529 (5)
C(10)—C(19)	1.547 (5)		
C(16)—N—C(22)	105.3 (4)	C(12)—C(13)—C(17)	114.5 (4)
C(16)—N—C(26)	115.8 (4)	C(12)—C(13)—C(18)	110.2 (4)
C(22)—N—C(26)	112.8 (4)	C(14)—C(13)—C(17)	99.8 (4)
C(2)—C(1)—C(10)	113.7 (5)	C(14)—C(13)—C(18)	112.4 (4)
C(1)—C(2)—C(3)	121.5 (6)	C(17)—C(13)—C(18)	111.3 (4)
C(2)—C(3)—C(4)	120.6 (6)	C(8)—C(14)—C(13)	111.8 (4)
C(3)—C(4)—C(5)	122.2 (6)	C(8)—C(14)—C(15)	120.0 (5)
C(4)—C(5)—C(6)	122.3 (5)	C(13)—C(14)—C(15)	104.4 (4)
C(4)—C(5)—C(10)	120.4 (5)	C(14)—C(15)—C(16)	102.8 (4)
C(6)—C(5)—C(10)	117.2 (5)	N—C(16)—C(15)	114.5 (5)
C(5)—C(6)—C(7)	124.3 (5)	N—C(16)—C(17)	101.8 (4)
C(6)—C(7)—C(8)	122.2 (5)	C(15)—C(16)—C(17)	107.7 (4)
C(7)—C(8)—C(9)	110.6 (4)	C(13)—C(17)—C(16)	103.4 (4)
C(7)—C(8)—C(14)	113.1 (4)	C(13)—C(17)—C(20)	119.3 (5)
C(9)—C(8)—C(14)	107.7 (4)	C(16)—C(17)—C(20)	105.8 (4)
C(8)—C(9)—C(10)	111.4 (4)	C(17)—C(20)—C(22)	103.5 (4)
C(8)—C(9)—C(11)	111.9 (4)	C(17)—C(20)—C(21)	113.7 (5)
C(10)—C(9)—C(11)	114.5 (4)	C(22)—C(20)—C(21)	112.1 (5)
C(1)—C(10)—C(5)	110.6 (4)	N—C(22)—C(20)	103.0 (4)
C(1)—C(10)—C(9)	110.0 (4)	N—C(22)—C(23)	110.0 (5)
C(1)—C(10)—C(19)	108.5 (5)	C(20)—C(22)—C(23)	116.9 (5)
C(5)—C(10)—C(9)	108.3 (4)	C(22)—C(23)—C(24)	109.9 (5)
C(5)—C(10)—C(19)	106.7 (4)	C(23)—C(24)—C(25)	111.4 (6)
C(9)—C(10)—C(19)	112.7 (4)	C(24)—C(25)—C(26)	110.8 (5)
C(9)—C(11)—C(12)	112.0 (5)	C(24)—C(25)—C(27)	111.4 (6)
C(11)—C(12)—C(13)	111.5 (5)	C(26)—C(25)—C(27)	110.9 (6)
C(12)—C(13)—C(14)	108.3 (4)	N—C(26)—C(25)	110.0 (5)
C(19)—C(10)—C(5)—C(4)	89.6 (5)	C(6)—C(5)—C(10)—C(1)	155.5 (6)
C(18)—C(13)—C(14)—C(8)	60.4 (4)	C(14)—C(8)—C(9)—C(10)	175.0 (5)
C(27)—C(25)—C(24)—C(23)	176.3 (7)	C(15)—C(14)—C(13)—C(12)	167.2 (5)
C(21)—C(20)—C(17)—C(16)	125.6 (6)	C(13)—C(17)—C(16)—N	-103.2 (4)
C(19)—C(10)—C(13)—C(18)	-3.3 (4)	C(23)—C(22)—N—C(16)	171.2 (6)

with monoperothalic acid in $\text{CHCl}_3/\text{Et}_2\text{O}$ at 277 K for 24 h (m.p. 545–546 K, analysis calculated for $\text{C}_{27}\text{H}_{43}\text{NO}_3 \cdot 2.5\text{H}_2\text{O}$: C 68.35, H 10.12%; found C 68.53, H 10.09%).

Solanida-2,4,6-triene (2) was obtained, in addition to other side-products (Stanković, Miljković, Gaši & Sakač, 1990) by refluxing compound (1) under an N_2 atmosphere in DMSO for 7 h. Purification on an alumina column (benzene), followed by recrystallization from acetone afforded pure transparent well shaped crystals (m.p. 441–442 K; calculated for $\text{C}_{27}\text{H}_{39}\text{N} \cdot \frac{1}{4}\text{H}_2\text{O}$: C 84.92, H 10.35%; found C 85.14, H 10.71%). A crystal with dimensions $1.31 \times 0.98 \times 0.52$ mm was mounted on a Siemens AED diffractometer. Data were collected using Ni-filtered $\text{Cu K}\alpha$

Table 3. Ring-puckering coordinates and asymmetry parameters

Ring	Q (Å)	φ (°)	θ (°)	ΔC_1 (pm)*	ΔC_2 (pm)*
Six-membered					
A	0.293 (4)	327.3 (8)	60.8 (7)	—	1.3[C(3)—C(4)]
B	0.377 (3)	253.1 (5)	51.4 (4)	9.4[C(6)]	15.5[C(6)—C(7)]
C	0.055 (3)	292 (3)	5.3 (3)	—	—
F	0.033 (4)	27 (7)	3.4 (4)	—	—
Five-membered					
D	0.463 (3)	193.9 (4)	—	—	4.7[C(16)]
E	0.427 (3)	139.2 (5)	—	4.8[N]	—

* pm indicates the location of the assumed symmetry in the ring.

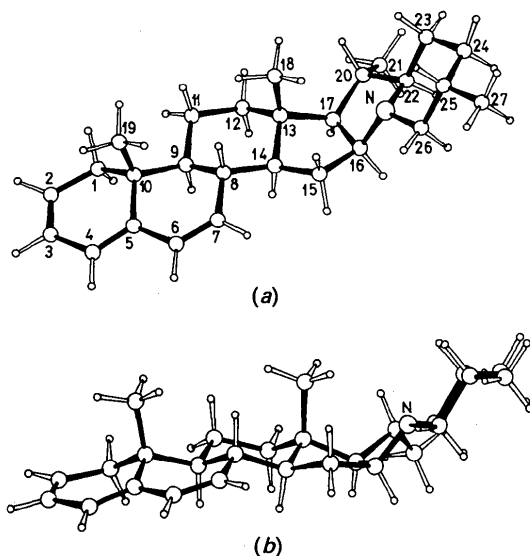


Fig. 1. (a) A perspective view of molecule showing atomic labeling. Carbon atoms are indicated by number only. (b) The conformation of the steroid skeleton. A view of the molecule parallel to the least-squares plane of C(1)–C(17) atoms.

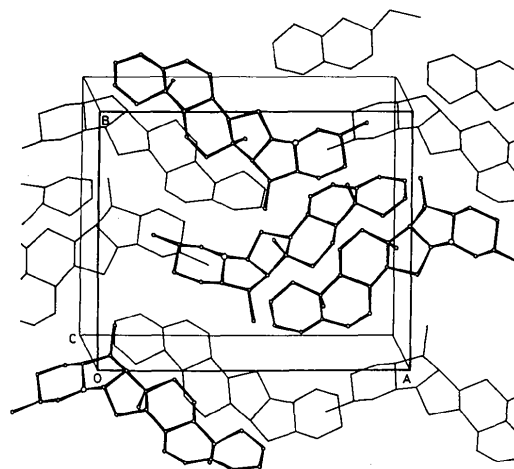


Fig. 2. The packing arrangement looking down the c axis.

radiation. The refined lattice parameters were obtained by a least-squares procedure from the setting angles of 30 reflections with $10 < \theta < 30^\circ$. The intensities were collected in the range $3 < \theta < 70^\circ$, θ - 2θ step-scanning mode, minimum scan speed $0.05^\circ \text{ s}^{-1}$, profile analysis with the method of Lehmann & Larsen (1974), scan amplitude $\theta - 0.6^\circ < \theta < \theta + 0.6^\circ + (\Delta\lambda/\lambda)\tan\theta$, h 0 to 19, k 0 to 16, l 0 to 11. A standard reflection was measured after every 50 reflections and remained constant throughout the experiment. Of 2439 independent reflections, 2253 with $F_o > 5\sigma(F_o)$ were considered as observed and used for calculation. Data were corrected for Lorentz and polarization effects but not for absorption. A correction was also performed for extinction ($f_{\text{ext}} = 2.945 \times 10^{-5}$).

The phase problem was solved with the *SHELX* (Sheldrick, 1976) program. The best E map gave all non-H atoms ($R = 0.24$). Full-matrix least-squares refinement, $\sum w(\Delta F^2)$ minimized, 254 parameters

refined. The refinement was terminated at $R = 0.042$, $wR = 0.051$, $R_{\text{tot}} = 0.044$, $S = 0.69$, $w = [\sigma^2(F_o) + 0.25 \times 10^{-4} F_o^2]^{-1}$. Maximum peak heights in final $\Delta\rho$ map within $\pm 0.13 \text{ e } \text{Å}^{-3}$. The H-atom positions were generated from assumed geometries and were taken into account without refinement in structure-factor calculations with isotropic temperature factors $B_{\text{H}} = B_{\text{C}} + 1 \text{ Å}^2$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962, Vol. III).

Discussion. The final atomic positions and equivalent isotropic temperature factors for non-H atoms are given with their e.s.d.'s in Table 1.* Bond lengths, angles and relevant torsion angles are listed in Table 2. A perspective view of the molecule with the atom-labelling system is shown in Fig. 1(a). The conformation of all six rings can be seen clearly from Fig. 1(b). The puckering parameters (Cremer & Pople, 1975)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53040 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and asymmetry parameters (Duax, Weeks & Rohrer, 1976) are listed in Table 3. Ring *A* has a $1\alpha,10\beta$ half-chair conformation, ring *B* exhibits a transition form between 9α envelope (sofa) and $9\alpha,10\beta$ half-chair, while rings *C* and *F* adopt a chair conformation. The five-membered *D* ring has a $13\beta,14\alpha$ half-chair conformation, while ring *E* is in an envelope form with the N atom at the flap. The β -axial C(18) methyl group is almost eclipsed with the C(19) methyl moiety as shown by the non-bonded torsion angle $C(19)-C(10)\cdots C(13)-C(18) = -3.3(4)^\circ$. The position of the C(27) methyl group is equatorial, while C(21) assumes an α -pseudo-equatorial position.

The packing arrangement along *c* is presented in Fig. 2. The interactions between molecules, which lie

almost parallel to the diagonals of the *ab* plane, occur only through van der Waals contacts.

We thank Dr F. Ugozzoli for collecting intensities and Dr Gy Argay for some computing facilities.

References

- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, pp. 271–383. New York: John Wiley.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STANKOVIĆ, S., MILJKOVIĆ, D., GAŠI, K. & SAKAČ, Z. (1990). In preparation.

Acta Cryst. (1990). **C46**, 2205–2207

Structure and Conformation of a Novel *N*-Glycosylimidazole Nucleoside: Ethyl 5-Amino-1-(2,3-*O*-isopropylidene- β -ribofuranosyl)imidazole-4-carboxylate

BY C. E. BRIANT AND D. W. JONES

Chemistry and Chemical Technology, University of Bradford, Bradford BD7 1DP, England

(Received 26 September 1989; accepted 9 February 1990)

Abstract. $C_{14}H_{21}N_3O_6$, $M_r = 327.7$, tetragonal, $P4_3$, $a = 9.154(2)$, $c = 19.066(5)$ Å, $V = 1597.7(7)$ Å³, $Z = 4$, $D_m = 1.35(1)$, $D_x = 1.361$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.68$ cm⁻¹, $F(000) = 696$, $T = 298$ K, final $R = 0.030$ for 1062 observed reflections. In the crystal structure the imidazole base planes are mutually perpendicular rather than parallel and the only intermolecular hydrogen-bonding distance is 2.90(2) Å from the ribofuranosyl O(5') to N(3) in the imidazole ring. Close intramolecular approaches are 2.84(2) Å from the imidazole amino N(5) to ethoxy O(7) [rather than to carboxy O(6)] and 3.14(2) Å from N(5) to the sugar O(5'). The bicyclic furanodioxalane group has a flattened 'W' shape with both rings in an envelope form (sugar pucker 0T_1) and the conformation of the glycosidic linkage C(2)—N(1)—C(1')—O(1') is within the *syn* range.

Introduction. For the synthesis of aminoimidazole nucleosides, related to active intermediates in *de novo* purine nucleotide biosynthesis and to natural nucleosides with anti-tumour activity, the use of 2,3-*O*-isopropylidene-D-ribofuranosylamine (I) has been developed by G. Shaw and co-workers (e.g. Mackenzie, Shaw & Thomas, 1976). Thus, its

toluene-*p*-sulfonate in ethanolic NaOH can react with the imidate formed from refluxing ethyl α -amino- α -cyanoacetate and triorthoformate in acetonitrile to give a gum from which the title β -nucleoside, EARIC, was eventually recrystallized from ethanol (Cusak, Hildick, Robinson, Rugg & Shaw, 1973). 220 MHz ¹H NMR spectroscopy (Jones, Mokoena, Robinson & Shaw, 1981) shows that in DMSO solution EARIC assumes a dynamic conformational equilibrium between *N*- and *S*-type furanose ring-puckering modes; the preferred glycosidic rotational conformation is *anti* and the preferred exocyclic CH₂OH is *gg*. A single-crystal X-ray analysis performed on EARIC now indicates an *S*-type conformation in the solid state.

