

twist-boat conformation with a (pseudo-)twofold axis through N(1) and C(4), while the benzo ring is near to a $^{2.5}B$ form, *i.e.* a true-boat conformation with C(7) and C(9a) as bowsprits. The distortion of an aromatic ring into a boat form rather than into a chair form is in keeping with force-constant calculations of Pulay, Fogarasi & Boggs (1981). Our present observation of the boat form adopted by a benzene moiety corroborates previous results (Lenstra & Petit, 1980; Van Havere, Lenstra & Geise, 1982; Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982) in sterically demanding situations created by substitutions on aromatic nuclei.

Finally, the planar carboxy group C(11),C(12),O(2),O(3) is almost perpendicular to the 'plane' of the pyrimido ring.

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Structure of Salicin, C₁₃H₁₈O₇

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Abstract. $M_r = 286.3$, orthorhombic, $P2_12_1$, $a = 8.314$ (1), $b = 21.169$ (3), $c = 7.650$ (1) Å, $U = 1346.4$ (3) Å³, $D_m = 1.41$, $D_x = 1.41$ Mg m⁻³, $Z = 4$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.12$ mm⁻¹, $F(000) = 608$, $T = 298$ K, $R = 0.038$ for 1552 observed reflexions. The torsion angle around the glucosidic C—O bond is 14.6 (4)°. The bond angle at the glucosidic O atom is 117.8 (2)°. The molecules are linked *via* hydrogen bonding to form strings along the twofold screw axes parallel to **a** and **c**.

Introduction. It has been proposed that the orientation of glucosyl bonds in dihydroxycoumarin β -glucoside be classified into two characteristic conformations: 'in-plane' and 'out-of-plane' with respect to the aromatic plane (Ueno, Shiraki, Sato & Saito, 1985). The in-plane conformation is commonly observed in other β -glucosides and even in the aromatic α -glucosides (Swaminathan, 1982). Although these structures result in considerable intramolecular repulsions, the repulsive energy is considered to be compensated by the

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resonance of π electrons of the glucosidic O atoms with the aromatic ring. The out-of-plane conformation, on the other hand, has neither of the above factors and is observed in 8-glucosyloxy-7-hydroxycoumarin (Ueno, Saito & Sato, 1978). Salicin [2-(hydroxymethyl)phenyl β -D-glucopyranoside], which is usually obtained from the bark of poplar and willow and has been used as an analgesic, has a glucosidic linkage to an aromatic ring with a bulky substituent, a —CH₂OH group, at its *ortho* position. The present paper deals with the structure of salicin in order to examine further details of the conformation of glucosyl bonds.

Experimental. Prismatic crystals from aqueous ethanol solution. Crystal 0.26 × 0.22 × 0.40 mm. D_m by flotation in a mixture of dichloromethane and chloroform. Nicolet P3/F automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell dimensions by least squares with 2θ values of 25 reflexions. Systematic absences $h00$, h odd, $0k0$, k odd, $00l$, l odd. Intensity data $4^\circ < 2\theta < 150^\circ$. $\omega/2\theta$

scan. h, k, l from 0 to 10, 27, 9. Scanning speed varied according to the prescanned peak intensities from 3° (150 counts s^{-1} or below) to 10° (3000 counts s^{-1} or above) min^{-1} in 2θ ; scan width 1° (ω) plus α_1 - α_2 divergence. Three standard reflexions every 100 reflexions showed no significant change in intensity. No absorption correction. 1576 independent reflexions measured, 1560 with net intensities ($|F_o| > 3\sigma|F_o|$). Direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). Anisotropic full-matrix least-squares program *SHELX76* (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F_o) + 0.036 \times (F_o)^2]^{-1}$. H atoms from difference Fourier map, refined with isotropic temperature factors. $wR = 0.024$, $S = 1.22$, $(\Delta/\sigma)_{\text{max}} = 0.2$, $\Delta\rho < 0.2 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters are listed in Table 1.* Bond distances and angles are in Table 2. An *ORTEP* (Johnson, 1965) drawing of the molecule with the numbering system used is shown in Fig. 1. The torsion angle C(6)-C(1)-C(7)-O(7) is $37.1(4)^\circ$. The glucopyranose ring is in the usual C_1 chair conformation. The conformation of the C(6')-O(6') bond is *trans-gauche* with respect to the C(5')-C(4') and C(5')-O(5') bonds. The conformation angle of the glucosyl linkage [C(3)-C(2)-O(1')-C(1'): φ] is only $14.6(4)^\circ$, which is close to those in the other aromatic glucosides with an in-plane conformation such as daphnetin 7-glucoside, 13.8° (Ueno, Sato & Saito, 1983), *p*-nitrophenyl β -D-glucosaminide, 16.4° (Brehm & Mout, 1975), and 1-naphthyl tetra-*O*-acetyl- β -D-glucoside, 11.2° (Makinen & Isaacs, 1978). These values correspond to one of the two favoured conformations of aromatic β -glucosides (Ueno *et al.*, 1985). Such a conformation causes short contacts between C(3) and C(1'), 2.827(5) \AA , and between H(C3) and C(1'), 2.54(3) \AA . Moreover, the angle C(3)-C(2)-O(1') is larger by $8.3(3)^\circ$ than C(1)-C(2)-O(1'). The strain brought about by the in-plane conformation is expected to be compensated by stabilization due to delocalization of the π electrons between the benzene ring and the glucosidic O atom. The bulky substituent, $-\text{CH}_2\text{OH}$, has little effect on the structure of the glucose moiety.

The crystal structure viewed along the c axis is shown in Fig. 2. The hydrogen bonds O(6')H \cdots O(2')-H \cdots O(6')H- and O(4')H \cdots O(7)H \cdots O(4')H- form

* Lists of structure factors, anisotropic thermal parameters, atomic parameters of H atoms, the least-squares plane of the coumarin ring and hydrogen-bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39536 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic temperature factors

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

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	0.4536 (4)	0.09695 (14)	0.6781 (4)	2.96
C(2)	0.4133 (4)	0.14988 (14)	0.5790 (5)	2.63
C(3)	0.3567 (4)	0.14456 (14)	0.4019 (5)	3.24
C(4)	0.3349 (4)	0.08489 (16)	0.3369 (5)	3.77
C(5)	0.3736 (5)	0.03170 (15)	0.4335 (6)	4.37
C(6)	0.4325 (4)	0.03788 (14)	0.6022 (6)	3.97
C(7)	0.5174 (4)	0.10410 (14)	0.8628 (5)	3.80
O(7)	0.6382 (3)	0.05930 (10)	0.9079 (3)	3.97
C(1')	0.3690 (4)	0.26177 (13)	0.5856 (5)	2.60
C(2')	0.3680 (4)	0.31319 (13)	0.7228 (4)	2.59
C(3')	0.3091 (4)	0.37477 (14)	0.6426 (4)	2.77
C(4')	0.4105 (4)	0.39095 (13)	0.4827 (4)	2.67
C(5')	0.4097 (4)	0.33483 (13)	0.3566 (5)	2.67
C(6')	0.5165 (5)	0.34383 (15)	0.1998 (4)	3.42
O(1')	0.4379 (3)	0.20748 (10)	0.6619 (3)	3.11
O(2')	0.2646 (3)	0.29634 (10)	0.8655 (3)	3.24
O(3')	0.3264 (3)	0.42527 (9)	0.7649 (3)	3.65
O(4')	0.3472 (3)	0.44406 (9)	0.3902 (3)	3.54
O(5')	0.4717 (3)	0.28039 (9)	0.4467 (3)	2.69
O(6')	0.5124 (3)	0.28946 (10)	0.0887 (3)	4.16

Table 2. Bond lengths (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

C(1)-C(2)	1.394 (4)	C(1')-O(5')	1.419 (4)
C(1)-C(6)	1.390 (5)	C(2')-C(3')	1.522 (4)
C(1)-C(7)	1.516 (4)	C(2')-O(2')	1.435 (4)
C(2)-C(3)	1.388 (5)	C(3')-C(4')	1.525 (4)
C(2)-O(1')	1.389 (4)	C(3')-O(3')	1.428 (4)
C(3)-C(4)	1.390 (5)	C(4')-C(5')	1.530 (4)
C(4)-C(5)	1.385 (5)	C(4')-O(4')	1.429 (4)
C(5)-C(6)	1.384 (5)	C(5')-C(6')	1.505 (4)
C(7)-O(7)	1.424 (4)	C(5')-O(5')	1.439 (4)
C(1')-C(2')	1.512 (4)	C(6')-O(6')	1.431 (4)
C(1')-O(1')	1.410 (4)		
C(2)-C(1)-C(6)	117.7 (3)	C(1')-C(2')-O(2')	110.6 (2)
C(2)-C(1)-C(7)	120.7 (3)	C(3')-C(2')-O(2')	109.1 (2)
C(6)-C(1)-C(7)	121.6 (3)	C(2')-C(3')-C(4')	109.7 (3)
C(1)-C(2)-C(3)	121.7 (3)	C(2')-C(3')-O(3')	110.2 (3)
C(1)-C(2)-O(1')	115.0 (3)	C(4')-C(3')-O(3')	107.6 (3)
C(3)-C(2)-O(1')	123.3 (3)	C(3')-C(4')-C(5')	109.2 (3)
C(2)-C(3)-C(4)	119.3 (3)	C(3')-C(4')-O(4')	111.7 (2)
C(3)-C(4)-C(5)	119.8 (3)	C(5')-C(4')-O(4')	107.3 (2)
C(4)-C(5)-C(6)	120.1 (3)	C(4')-C(5')-C(6')	113.7 (3)
C(1)-C(6)-C(5)	121.2 (3)	C(4')-C(5')-O(5')	108.5 (2)
C(1)-C(7)-O(7)	113.9 (3)	C(6')-C(5')-O(5')	105.8 (2)
C(2')-C(1')-O(1')	107.6 (2)	C(5')-C(6')-O(6')	110.9 (3)
C(2')-C(1')-O(5')	108.8 (2)	C(2)-O(1')-C(1')	117.8 (2)
O(1')-C(1')-O(5')	107.0 (2)	C(1')-O(5')-C(5')	111.4 (2)
C(1')-C(2')-C(3')	109.8 (3)		

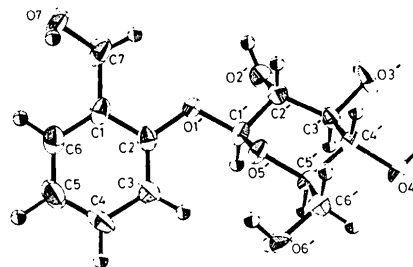


Fig. 1. Perspective drawing of the molecule showing the numbering system of the atoms.

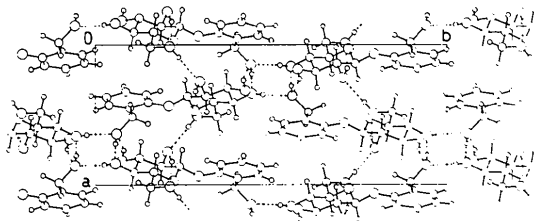


Fig. 2. The crystal structure viewed along the *c* axis. The hydrogen bonds are indicated by broken lines.

infinite strings along the twofold screw axes parallel to the *a* and *c* axes, respectively.

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2-Pyridine-*ONN*-azoxycyanide, C₆H₄N₄O: a Heterocyclic Analogue of Calvatic Acid

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Abstract. C₆H₄N₄O, *M_r* = 148.1, m.p. 347–348 K, triclinic, *P* $\bar{1}$, *a* = 6.368 (2), *b* = 7.856 (2), *c* = 7.902 (2) Å, α = 115.41 (2), β = 75.32 (2), γ = 105.42 (2)°, *U* = 339.8 (2) Å³, *Z* = 2, *D_x* = 1.45 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.12 mm⁻¹, *F*(000) = 152, room temperature, *R* = 0.052 for 1173 reflexions. The O atom of the azoxy group is bonded to the N atom adjacent to the pyridine ring; the cyano and pyridine moieties are in *anti* orientation. The synthesis of the title compound has been confirmed to be regiospecific and also stereospecific.

Introduction. The structure and stereoisomerism of calvatic acid (1), *p*-carboxybenzeneazoxycyanide, an antibacterial and antifungal compound from *Calvatia lilacina* (Gasco, Serafino, Mortarini, Menziani, Bianco & Ceruti-Scurti, 1974), has been described by Viterbo, Gasco, Serafino & Mortarini (1975). As part of an extensive chemical and pharmaceutical investigation on

R-ONN-azoxycyanides, a new direct synthesis to obtain alkyl, aryl and heteroaryl derivatives has recently been proposed (Fruttero, Mulatero, Calvino & Gasco, 1984). In the present article, as an example of the heteroaryl class, we describe the crystal and molecular structure of 2-pyridine-*ONN*-azoxycyanide (2), with the aim of confirming the regiospecificity and clarifying the stereospecificity of the above synthesis.

