thiocyanates the anion was bound through N in an approximately linear manner ($M^{2+}\cdots NCS^-$ 180°) (Wei et al., 1987a,b). In the present structure the angle $Na^+\cdots NCS^- = 112\cdot4$ (3)° and, in addition to being coordinated to Na, the N atom is hydrogen bonded to a symmetry-related water molecule. Such non-linear arrangements are relatively uncommon but have already been reported for some alkali-metal thiocyanate complexes (Weber & Saenger, 1980; Suh, Weber, Kaftory, Saenger, Sieger & Vogtle, 1980). The other hydrogen atom of the water molecule is H-bonded to the ether oxygen O4. The distances are: O5—H51$\cdots$N (O5 $0\cdot5-x$, $0\cdot5+y$, $0\cdot5-z$): O$\cdots$N $2\cdot887$, H$\cdots$N $1\cdot98$ Å; O5—H52$\cdots$O4 (O5 $0\cdot5-x$, $0\cdot5+y$, $0\cdot5-z$): O$\cdots$O $3\cdot016$, H$\cdots$O $2\cdot33$ Å. A stereoscopic view of the hydrogen bonds between the complex units is presented in Fig. 3.

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# Structure of Catalpol Hexaacetate*

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**Abstract.** [$1S$-($1\alpha,4a\alpha,7\beta,7a\alpha$)]-5-Acetoxy-7-acetoxymethyl-$6\alpha,7\alpha$-epoxy-1-(2,3,4,6-tetra-$O$-acetyl-$\beta$-D-glucopyranosyloxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[c]pyran,‡ $C_{27}H_{34}O_{16}$, $M_r = 614\cdot6$, monoclinic, $P2_1$, $a = 5\cdot877$ (2), $b = 12\cdot735$ (5), $c = 20\cdot759$ (9) Å, $\beta = 95\cdot62$ (3)°, $V = 1546$ (1) Å$^3$, $Z = 2$, $D_x = 1\cdot32$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot103$ mm$^{-1}$, $F(000) = 648$, $T = 293$ K, $R = 0\cdot053$ for 2099 observed reflections. The X-ray analysis confirms the structure previously assigned on the basis of chemical and spectroscopic studies. The five-membered ring is intermediate between a half-chair and an $\alpha$-envelope, whilst the dihydropyran ring adopts a sofa conformation. The $\beta$-glucose moiety is a distorted $^4C_1$ chair. The packing in the crystal is entirely due to intermolecular C—H$\cdots$O contacts and van der Waals forces.

**Introduction.** Catalpol (1) is a naturally occurring iridoid glucoside which was isolated from the aerial parts of the plant Penstemon apateticus (Schrophulariaceae). The sample used was collected in Cofre de Perote (Estado de Veracruz, Mexico). This plant

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grows to a height of 60 cm and has a showy red flower. Catalpol serves as feeding attractants and stimulants for larvae and butterflies and protects them from insectivorous birds due to the unpalatability effect in the insects (Bowers, 1983; 1984; Bowers & Puttick, 1986; Stephenson, 1982; Franke, Rimpler & Schneider, 1987). This compound was first isolated by Claasen (1888) and a chemical structure of (1) was assigned by Duff, Bacon, Mundie, Farmer, Russell & Forrester (1965) from chemical and spectroscopic methods. In an effort to provide detailed structural information for iridoid glucosides, we have determined the crystal structure of (1a).
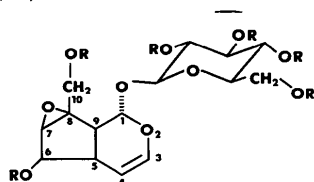


(1) R = H
(1a) R = Ac

**Experimental.** Colourless crystal $0.32 \times 0.30 \times 0.40$ mm. Nicolet R3 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $3.9 < 2\theta < 20.7°$, 2835 reflections with $3 < 2\theta < 50°$ for two octants, 2099 independent with $I > 2.5\sigma(I)$, index range $h \pm 6$, $k\ 0\rightarrow15$, $l\ 0\rightarrow24$, $\omega$-scan mode, variable scan speed, scan width $1.0°$ ($\theta$), two standard reflections (0$\bar{2}$2, 040) monitored every 50 measurements, Lp correction applied and absorption ignored. Structure solved by combination of direct methods and partial structure expansion by an iterative $E$-Fourier procedure using SHELXTL5 (Sheldrick, 1985). Blocked-cascade least-squares refinement of all non-H atoms with anisotropic thermal parameters; H atoms of CH, $CH_2$ and $CH_3$ groups riding on bonded C with fixed isotropic temperature factor $U = 0.06$ Å$^2$, and splitting the structure into more than one refinement
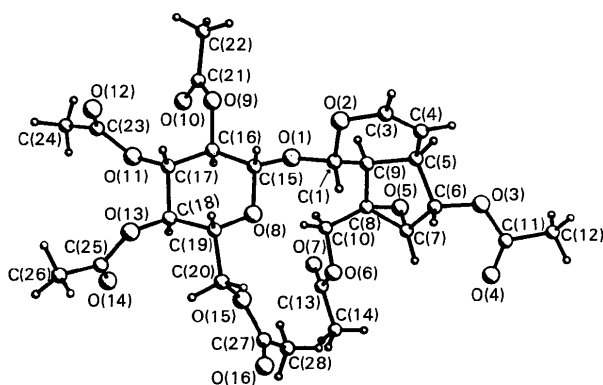
Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| O(1) | 8236 (5) | 7021 (3) | 2786 (1) | 43 (1) |
| C(1) | 9783 (8) | 7078 (4) | 3339 (2) | 40 (2) |
| O(2) | 10963 (6) | 6090 (3) | 3372 (2) | 59 (1) |
| C(3) | 12301 (10) | 5927 (5) | 3942 (3) | 60 (2) |
| C(4) | 11947 (10) | 6394 (4) | 4484 (3) | 59 (2) |
| C(5) | 10025 (9) | 7134 (4) | 4555 (2) | 51 (2) |
| C(6) | 10727 (9) | 8254 (4) | 4773 (2) | 50 (2) |
| C(7) | 8870 (9) | 8957 (5) | 4476 (2) | 50 (2) |
| C(8) | 7585 (8) | 8395 (4) | 3947 (2) | 45 (2) |
| C(9) | 8461 (8) | 7270 (4) | 3913 (2) | 43 (2) |
| C(10) | 6442 (9) | 8941 (4) | 3363 (3) | 58 (2) |
| O(3) | 11031 (7) | 8258 (3) | 5472 (2) | 68 (1) |
| C(11) | 12149 (11) | 9099 (5) | 5752 (3) | 67 (2) |
| O(4) | 12824 (7) | 9808 (4) | 5454 (2) | 70 (2) |
| C(12) | 12369 (15) | 8975 (7) | 6472 (3) | 101 (3) |
| O(5) | 6596 (6) | 8565 (3) | 4548 (2) | 64 (1) |
| O(6) | 5871 (6) | 10009 (3) | 3530 (2) | 66 (2) |
| C(13) | 3681 (10) | 10233 (5) | 3570 (3) | 56 (2) |
| O(7) | 2162 (7) | 9639 (4) | 3426 (3) | 91 (2) |
| C(14) | 3431 (12) | 11312 (6) | 3806 (3) | 91 (3) |
| C(15) | 9264 (8) | 7085 (4) | 2194 (2) | 44 (2) |
| C(16) | 7470 (8) | 6767 (4) | 1657 (2) | 40 (2) |
| C(17) | 8230 (8) | 7017 (4) | 997 (2) | 42 (2) |
| C(18) | 9032 (8) | 8153 (4) | 961 (2) | 46 (2) |
| C(19) | 10844 (8) | 8360 (4) | 1536 (2) | 49 (2) |
| C(20) | 11740 (9) | 9468 (4) | 1577 (3) | 59 (2) |
| O(8) | 9850 (6) | 8148 (3) | 2124 (2) | 48 (1) |
| O(9) | 7124 (5) | 5651 (3) | 1701 (2) | 45 (1) |
| C(21) | 4997 (10) | 5266 (4) | 1713 (2) | 49 (2) |
| O(10) | 3320 (7) | 5823 (3) | 1643 (2) | 80 (2) |
| C(22) | 4990 (11) | 4111 (5) | 1795 (3) | 66 (2) |
| O(11) | 6261 (5) | 6864 (3) | 533 (2) | 51 (1) |
| C(23) | 6573 (10) | 6360 (4) | −25 (2) | 56 (2) |
| O(12) | 8348 (8) | 6006 (4) | −143 (2) | 94 (2) |
| C(24) | 4361 (10) | 6321 (6) | −444 (3) | 75 (2) |
| O(13) | 10152 (6) | 8311 (3) | 395 (2) | 52 (1) |
| C(25) | 8949 (11) | 8744 (4) | −137 (3) | 56 (2) |
| O(14) | 6995 (8) | 9014 (4) | −141 (2) | 78 (2) |
| C(26) | 10433 (11) | 8816 (5) | −674 (3) | 75 (2) |
| O(15) | 9928 (6) | 10141 (3) | 1738 (2) | 63 (1) |
| C(27) | 10516 (13) | 11076 (5) | 1990 (3) | 71 (2) |
| O(16) | 12437 (10) | 11400 (4) | 2030 (3) | 109 (2) |
| C(28) | 8560 (12) | 11616 (6) | 2238 (4) | 102 (3) |

block affording a method of origin-fixing. $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$, where $\sigma$ is the standard deviation of observed amplitudes, based on counting statistics; isotropic extinction parameter $X = 0.0006$. In the last cycle $(\Delta/\sigma)_{max} = 0.53$; $\Delta\rho$ from $-0.20$ to $0.18$ e Å$^{-3}$, $S = 1.20$, final $R = 0.053$, $wR = 0.059$; scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the SHELXTL5 system of programs.

**Discussion.** Fig. 1 shows the molecular conformation of (1a). Final atomic coordinates are in Table 1* and bond distances and angles in Table 2.

The absolute configuration of (1a) was not determined directly, but was inferred from the known

Fig. 1. The molecular structure of (1a) showing the atom labelling.

Table 2. *Bond lengths (Å) and angles (°), e.s.d.'s are given in parentheses*

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·395 (5) | O(1)–C(15) | 1·423 (6) |
| C(1)–O(2) | 1·435 (6) | C(1)–C(9) | 1·505 (7) |
| O(2)–C(3) | 1·371 (6) | C(3)–C(4) | 1·308 (8) |
| C(4)–C(5) | 1·490 (8) | C(5)–C(6) | 1·540 (8) |
| C(5)–C(9) | 1·552 (6) | C(6)–C(7) | 1·498 (7) |
| C(6)–O(3) | 1·444 (6) | C(7)–C(8) | 1·458 (7) |
| C(7)–O(5) | 1·448 (6) | C(8)–C(9) | 1·527 (7) |
| C(8)–C(10) | 1·498 (7) | C(8)–O(5) | 1·443 (6) |
| C(10)–O(6) | 1·451 (7) | O(3)–C(11) | 1·357 (8) |
| C(11)–O(4) | 1·185 (8) | C(11)–C(12) | 1·495 (9) |
| O(6)–C(13) | 1·329 (7) | C(13)–O(7) | 1·185 (8) |
| C(13)–C(14) | 1·472 (10) | C(15)–C(16) | 1·512 (6) |
| C(15)–O(8) | 1·408 (6) | C(16)–C(17) | 1·517 (7) |
| C(16)–O(9) | 1·440 (6) | C(17)–C(18) | 1·525 (7) |
| C(17)–C(11) | 1·444 (5) | C(18)–C(19) | 1·541 (7) |
| C(18)–O(13) | 1·416 (6) | C(19)–C(20) | 1·505 (8) |
| C(19)–O(8) | 1·430 (6) | C(20)–O(15) | 1·431 (7) |
| O(9)–C(21) | 1·345 (6) | C(21)–O(10) | 1·211 (7) |
| C(21)–C(22) | 1·481 (8) | O(11)–C(23) | 1·352 (6) |
| C(23)–O(12) | 1·184 (7) | C(23)–C(24) | 1·493 (8) |
| O(13)–C(25) | 1·368 (6) | C(25)–O(14) | 1·198 (8) |
| C(25)–C(26) | 1·484 (9) | O(15)–C(27) | 1·334 (7) |
| C(27)–O(16) | 1·197 (9) | C(27)–C(28) | 1·474 (11) |

| | | | |
|---|---|---|---|
| C(1)–O(1)–C(15) | 114·2 (3) | O(1)–C(1)–O(2) | 105·5 (4) |
| O(1)–C(1)–C(9) | 108·4 (4) | O(2)–C(1)–C(9) | 112·9 (4) |
| C(1)–O(2)–C(3) | 114·1 (4) | O(2)–C(3)–C(4) | 123·2 (5) |
| C(3)–C(4)–C(5) | 124·0 (5) | C(4)–C(5)–C(6) | 115·5 (4) |
| C(4)–C(5)–C(9) | 112·1 (4) | C(6)–C(5)–C(9) | 105·6 (4) |
| C(5)–C(6)–C(7) | 105·6 (4) | C(5)–C(6)–O(3) | 107·6 (4) |
| C(7)–C(6)–O(3) | 115·2 (4) | C(6)–C(7)–C(8) | 108·7 (5) |
| C(6)–C(7)–O(5) | 113·2 (4) | C(8)–C(7)–O(5) | 59·6 (3) |
| C(7)–C(8)–C(9) | 110·0 (4) | C(7)–C(8)–C(10) | 122·7 (5) |
| C(9)–C(8)–C(10) | 121·7 (4) | C(7)–C(8)–O(5) | 59·9 (3) |
| C(9)–C(8)–O(5) | 110·3 (4) | C(10)–C(8)–O(5) | 116·3 (4) |
| C(1)–C(9)–C(5) | 110·7 (4) | C(1)–C(9)–C(8) | 113·0 (4) |
| C(5)–C(9)–C(8) | 103·8 (4) | C(8)–C(10)–O(6) | 109·7 (4) |
| C(6)–O(3)–C(11) | 116·2 (4) | O(3)–C(11)–O(4) | 123·4 (5) |
| O(3)–C(11)–C(12) | 109·6 (6) | O(4)–C(11)–C(12) | 127·0 (6) |
| C(7)–O(5)–C(8) | 60·5 (3) | C(10)–O(6)–C(13) | 117·7 (4) |
| O(6)–C(13)–O(7) | 123·9 (6) | O(6)–C(13)–C(14) | 110·5 (5) |
| O(7)–C(13)–C(14) | 125·6 (6) | O(1)–C(15)–C(16) | 107·2 (4) |
| O(1)–C(15)–O(8) | 105·9 (4) | C(16)–C(15)–O(8) | 109·9 (4) |
| C(15)–C(16)–C(17) | 111·3 (4) | C(15)–C(16)–O(9) | 108·1 (4) |
| C(17)–C(16)–O(9) | 108·7 (4) | C(16)–C(17)–C(18) | 111·2 (4) |
| C(16)–C(17)–O(11) | 106·7 (4) | C(18)–C(17)–O(11) | 109·1 (4) |
| C(17)–C(18)–C(19) | 108·6 (4) | C(17)–C(18)–O(13) | 110·2 (4) |
| C(19)–C(18)–O(13) | 106·0 (4) | C(18)–C(19)–C(20) | 114·6 (4) |
| C(18)–C(19)–O(8) | 108·6 (4) | C(20)–C(19)–O(8) | 107·3 (4) |
| C(19)–C(20)–O(15) | 108·1 (4) | C(15)–O(8)–C(19) | 113·2 (4) |
| C(16)–O(9)–C(21) | 119·9 (4) | O(9)–C(21)–O(10) | 122·1 (5) |
| O(9)–C(21)–C(22) | 112·1 (5) | O(10)–C(21)–O(10) | 125·7 (5) |
| C(17)–O(11)–C(23) | 117·9 (4) | O(11)–C(23)–O(12) | 123·7 (5) |
| O(11)–C(23)–C(24) | 109·4 (5) | O(12)–C(23)–C(24) | 127·0 (5) |
| C(18)–O(13)–C(25) | 118·8 (4) | O(13)–C(25)–O(14) | 122·7 (5) |
| O(13)–C(25)–C(26) | 109·6 (5) | O(14)–C(25)–C(26) | 127·7 (5) |
| C(20)–O(15)–C(27) | 117·2 (5) | O(15)–C(27)–O(16) | 122·7 (6) |
| O(15)–C(27)–C(28) | 111·9 (6) | O(16)–C(27)–C(28) | 125·3 (6) |

configuration of the glucose moiety and from chemical and spectroscopic studies (Duff, Bacon, Mundie, Farmer, Russell & Forrester, 1965).

The conformation of the five-membered ring C(5)–C(9) may be described by the parameters $\Delta = -17\cdot1$ (5) and $\varphi_m = 25\cdot6$ (5)° (Altona, Geise & Romers, 1968), indicating a conformation between a half-chair and an α-envelope. The five-membered conformation in loganin (Jones, Sheldrick, Glüsenkamp & Tietze, 1980), in boschnaloside monohydrate (Soriano-García, Toscano, Jiménez & Lira-Rocha, 1986), in 3,4-dihydrounedoside pentaacetate and in pulchelloside II hydrate (Strumpel, Chen, Buschmann & Ruban, 1988) is an envelope. The fusion to the dihydropyran ring is *cis*, with torsion angles about the

common bond of $-22\cdot4$ (5) and $-27\cdot4$ (6)° in the five- and six-membered rings, respectively. The angle between the mean planes through the five- and six-membered rings is $41\cdot4$ (2)°.

The dihydropyran ring is a sofa with C(1) as the flap, $0\cdot60$ (1) Å out of the plane of the other five atoms. The torsion angles differ from those of an ideal sofa [0, 0, 28, $-56$, 54, $-27°$ cyclically starting from the double bond (Bucourt & Hainaut, 1965)] by an average of 2°. This type of conformation has been observed in loganin, boschnaloside monohydrate and pulchelloside II hydrate, whereas in 3,4-dihydrounedoside penta-acetate the ring adopts a chair conformation. The epoxy ring is oriented to minimize transannular repulsions between its O atom and the acetoxymethyl group. The angle between the epoxy plane and the mean plane of the acetoxymethyl group is $65\cdot8$ (3)°.

The β-glucose moiety slightly deviates from $^4C_1$ conformation. The Cremer & Pople (1975) criteria give values for the puckering parameters [$\theta = 174\cdot2$ (5), $\varphi = 78$ (1)°, $Q = 0\cdot574$ (5) Å] which correspond to a chair conformation as in most D-pyranoses (Ohanessian, Longchambon & Arene, 1978). The endocyclic C—O—C angle $= 113\cdot2$ (4)° and is similar to the exocyclic C(1)–O(1)–C(15) $= 114\cdot2$ (3)°. The endocyclic angles involving ring C atoms range from $108\cdot6$ (4) to $111\cdot3$ (4)°. The conformation around the glycosidic bond is defined by the torsion angle C(15)–O(1)–C(1)–C(9) $= 166\cdot2$ (4)° and all ring substituents are equatorial.

The arrangement of the molecules in the unit cell is shown in Fig. 2. Excluding H atoms there are nine intermolecular approaches < 3·40 Å: C(7)···O(7), C(15)···O(10), C(8)···O(7) (1+x, y, z), 3·17 (1), 3·18 (1), 3·39 (1); C(5)···O(4) (2−x, −0·5+y, 1−z) 3·40 (1); C(12)···O(2) (2−x, 0·5+y, 1−z) 3·37 (1); C(3)···O(4) (3−x, −0·5+y, 1−z) 3·33 (1); C(25)··· O(12), C(26)···O(12) (2−x, 0·5+y, −z), 3·13 (1),
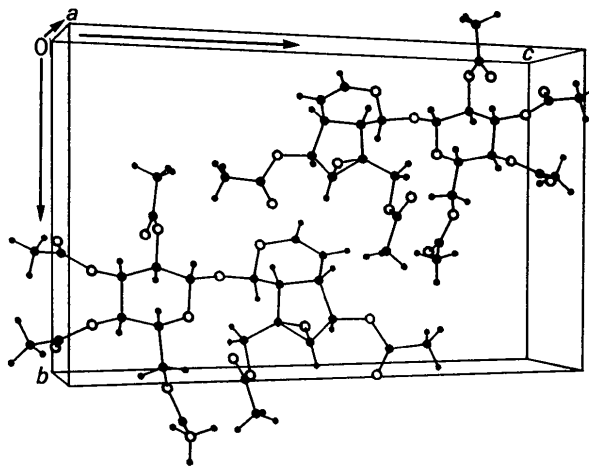


Fig. 2. A perspective drawing of the packing arrangement.

3·30 (1), and C(24)···O(14) (1−*x*, −0·5+*y*, −*z*) 3·31 (1) Å. No suitable donors for H-bond formation are available. The molecules are held in the crystal by van der Waals forces.

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# Structure of 1-Cyano-3,3-dimethyl-2-thiatricyclo[3.2.1.1⁶,⁸]nonane 2,2-Dioxide

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**Abstract.** $C_{11}H_{15}NO_2S$, $M_r = 225\cdot3$, monoclinic, $P2_1/n$, $a = 6\cdot382$ (3), $b = 14\cdot586$ (6), $c = 12\cdot049$ (13) Å, $\beta = 98\cdot20$ (6)°, $V = 1100$ (2) Å³, $Z = 4$, $D_x = 1\cdot348$ g cm⁻³, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 2\cdot6$ cm⁻¹, $F(000) = 480$, $T = 296$ K, $R = 0\cdot035$ for 1031 observed diffractometer data. The three five-membered rings adopt an envelope conformation. The S atom has the usual distorted tetrahedral configuration with mean S=O bond length 1·443 (3) Å. The cyano group is almost linear with C—C≡N angle 177·2 (4)° and C≡N bond 1·144 (5) Å. The structure of the title compound is compared with that of its precursor, 5-*exo*-cyano-5-*endo*-isopropylsulfonyl-2-norbornene, an efficient new radical clock.

**Introduction.** A convenient approach to check for the presence of radical intermediates during organic reactions is to use a radical clock (Griller & Ingold, 1980).

Recently, the 5-cyano-substituted 5-*endo*-isopropylsulfonyl-2-norbornene (I) has been synthetized (Vacher, Samat & Chanon, 1985), and the corresponding α-sulfonyl-C-centred radical (II) undergoes an intramolecular addition at the double bond, leading to the tricyclo compound (III).
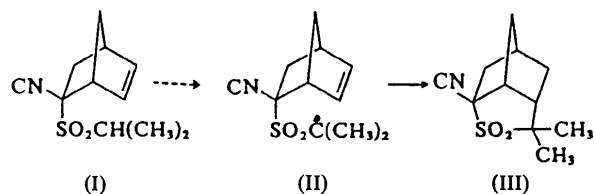


In connection with the structure of (I), already reported (Vacher, Samat, Allouche, Laknifli, Baldy & Chanon, 1988), we decided to undertake an X-ray study of (III).