compare the pairs of centrosymmetrically related invariants $\Phi[(-h,-k,-l), (h',k',l'), (h-h',k-k',l-l')]$ and $\Phi[(h,k,l), (-h',-k',-l'), (h'-h,k'-k,l'-l)]$. Figs. 2(*a*) and 2(*b*) show the experimental results for two pairs of triplets, which are in good agreement with the phases of the triplet invariants calculated on the basis of the coordinates listed in Table 1 (*cf.* Table 3). These results were confirmed for two different crystals and several pairs of triplets by experiments with synchrotron radiation and rotating-anode equipment using two different six-circle instruments; no discrepancies were observed. Thus the determination of the absolute structure is clear cut in spite of the poor quality of the crystals and their decay under X-ray irradiation.

Discussion

There are no unusual distances and angles in the molecule (see Table 2). The chiral atoms are C(4) and C(5); the distribution of their neighbours as given in Fig. 1 defines the absolute structure (*b*) *i.e.* (1*R*,5*S*).

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Structural Studies on the Biosides of *Digitalis lanata*: Bisdigitoxosides of Digitoxigenin, Gitoxigenin and Digoxigenin

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Abstract

The crystal structures and conformations of bisdigitoxosides of digitoxigenin (I), gitoxigenin (II) and digoxigenin (III and IV) have been determined using single-crystal X-ray crystallographic techniques. Crystals of (I), (II) and (IV) were grown from ethyl acetate solutions of the glycosides while (III) was grown from a solution of the digitoxoside in ethanol. As in other cardiac glycosides the ring junctions *A–B* and *C–D* are *cis*. The *D* ring in these structures shows different conformations while the *A*, *B* and *C* rings remain conformationally similar. Although digitoxigenin bisdigitoxoside and gitoxigenin bisdigitoxoside differ from each other in the absence and presence of a hydroxyl group at C(16) of the *D* ring, these two biosides crystallize in the space group $P2_12_12_1$ and are isomorphous. The presence of the hydroxyl group at C(16) does not affect the orientation of the lactone ring and the conformation of the molecule. Digoxigenin bisdigitoxoside crystallizes in two different crystal systems with four molecules of water in the orthorhombic form and one molecule of ethyl acetate in the triclinic form. In both forms the hydroxyl at C(3′) of the first sugar forms a hydrogen bond with the ring oxygen of the second sugar. This has also been observed in the trioside digoxin. The torsion angle C(13)–C(17)–C(20)–C(22) in the two forms differs by 7°. Crystal data at $T = 298$ K, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å: (I) $C_{35}H_{54}O_{10}.C_4H_8O_2$, $M_r = 722{\cdot}8$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}447$ (1), $b = 14{\cdot}303$ (1), $c = 23{\cdot}982$ (3) Å, $V = 3926$ Å^3, $Z = 4$, $D_x = 1{\cdot}223$ g cm^{-3}, $\mu = 6{\cdot}97$ cm^{-1}, $F(000) = 1568$, $R = 0{\cdot}071$ for 3006 observed reflections; (II) $C_{35}H_{54}O_{11}.C_4H_8O_2$, $M_r = 738{\cdot}8$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}351$ (2), $b = 14{\cdot}392$ (3), $c = 23{\cdot}738$ (6) Å, $V =$

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Table 1. *Crystal data and summary of experimental details*

	(I)	(II)	(III)	(IV)
Molecular formula	$C_{35}H_{54}O_{10}.C_4H_8O_2$	$C_{35}H_{54}O_{11}.C_4H_8O_2$	$C_{35}H_{54}O_{11}.4H_2O$	$C_{35}H_{54}O_{11}.C_4H_8O_2$
M_r	722·8	738·8	722·8	738·8
Crystallized from	Ethyl acetate	Ethyl acetate	Ethanol	Ethyl acetate
Crystal size (mm)	0·3 × 0·47 × 0·5	0·2 × 0·2 × 0·1	0·37 × 0·12 × 0·7	0·2 × 0·3 × 0·4
Cell dimensions				
a (Å)	11·447 (1)	11·351 (2)	35·715 (6)	7·458 (2)
b (Å)	14·303 (1)	14·392 (3)	14·422 (4)	10·646 (4)
c (Å)	23·982 (3)	23·738 (6)	7·526 (1)	13·064 (5)
α (°)				104·78 (3)
β (°)				105·23 (3)
γ (°)				83·07 (3)
Volume (Å^3)	3926	3878	3877	966
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12$	$P\bar{1}$
Z, D_x (g cm^{-3})	4, 1·223	4, 1·266	4, 1·239	1, 1·270
$F(000)$, μ (cm^{-1})	1568, 6·97	1600, 7·3	1568, 7·62	400, 7·38
T (K)	298	298	298	298
No. of reflections used for measuring cell parameters	25	25	25	25
θ range (°)	11–25	11–25	21–39	13–27
Absorption correction factors	0·9993–0·9650	0·9993–0·9722	0·9996–0·9222	0·9893–0·9573
$\lvert(\sin\theta)/\lambda\rvert_{max}$ (Å^{-1})	0·5614	0·5614	0·6317	0·6317
Range of hkl	±12, 16, 26	±12, 16, 26	−45, 18, ±9	±9, ±13, 16
Standard reflections	502, 061, 2,1,12	016, 302, 215	20,0,0, 080, 306	201, 030, 005
Intensity variation (%)	3	5	3	2
No. of unique reflections	3983	3275	4050	3909
Observed reflections	3006; $I > 2\sigma I$	1910; $I > 1{\cdot}2\sigma I$	2911; $I > 1{\cdot}5\sigma I$	3509; $I > 2\sigma I$
Final R, wR $\lvert w^{-1} = \sigma(F^2)\rvert$	0·071, 0·072	0·091, 0·087	0·087, 0·102	0·058, 0·059
Final shift/e.s.d.	0·03	0·01	0·02	0·02
Goodness of fit	1·98	2·51	2·53	0·64
Final $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0·69, −0·35	0·39, −0·42	0·55, −0·38	0·42, −0·31

3878 Å^3, $Z = 4$, $D_x = 1{\cdot}266$ g cm^{-3}, $\mu = 7{\cdot}3$ cm^{-1}, $F(000) = 1600$, $R = 0{\cdot}091$ for 1910 observed reflections; (III) $C_{35}H_{54}O_{11}.4H_2O$, $M_r = 722{\cdot}8$, orthorhombic, $P2_12_12_1$, $a = 35{\cdot}715$ (6), $b = 14{\cdot}422$ (4), $c = 7{\cdot}526$ (1) Å, $V = 3877$ Å^3, $Z = 4$, $D_x = 1{\cdot}239$ g cm^{-3}, $\mu = 7{\cdot}62$ cm^{-1}, $F(000) = 1568$, $R = 0{\cdot}087$ for 2911 observed reflections; (IV) $C_{35}H_{54}O_{11}.C_4H_8O_2$, $M_r = 738{\cdot}8$, triclinic, $P\bar{1}$, $a = 7{\cdot}458$ (2), $b = 10{\cdot}646$ (4), $c = 13{\cdot}064$ (5) Å, $\alpha = 104{\cdot}78$ (3), $\beta = 105{\cdot}23$ (3), $\gamma = 83{\cdot}07$ (3)°, $V = 966$ Å^3, $Z = 1$, $D_x = 1{\cdot}270$ g cm^{-3}, $\mu = 7{\cdot}38$ cm^{-1}, $F(000) = 400$, $R = 0{\cdot}058$ for 3509 observed reflections.

Introduction

A major problem in drug design is to find an active conformation of the molecule of interest. One of the ways of arriving at an active conformation is to map out the common structural features of a number of analogues of the drug in question and relate them to their biological activity. We have been interested in the structural studies of cardiac glycosides and have reported the results of the analysis of several digitalis-like glycosides (Go, Kartha & Chen, 1980; Go & Kartha, 1980, 1981, 1982, 1983, 1984). In all these molecules the steroid nucleus has a *cis/trans/cis* conformation for the *A–B/B–C/C–D* ring junctions with the three rings *A*, *B* and *C* exhibiting the chair conformation while the five-membered *D* ring shows some conformational flexibility. In glycosides with one sugar and genin groups, the *D* ring of the steroid has an envelope conformation while in glycosides with two or more sugars a half-chair conformation seems to be the most predominant. The orientation of the lactone ring is determined by the torsion angle C(13)–C(17)–C(20)–C(22) which has values around 75 and −110°. Theoretical calculations have shown these values to be where these molecules have minimum energy (Rohrer, Fullerton, Yoshioka, From & Ahmed, 1979).

In this paper we report the crystal structures of the biosides of digitoxigenin (I), gitoxigenin (II) and digoxigenin (III and IV). In these four crystal structures we find that the *D* ring of the genin group is conformationally flexible while the *A*, *B* and *C* rings remain conformationally invariant as has been found in crystallographic studies of other analogues of cardiac glycosides (Karle & Karle, 1969; Przybylska & Ahmed, 1979; Rohrer & Fullerton, 1980). The three biosides differ in the presence or absence of a hydroxyl group on the steroid nucleus which does not seem to have any influence on the conformation of the molecule.

Experimental

The biosides of digitoxigenin and gitoxigenin were semisynthesized from commercially available digitoxin and gitoxin using the stepwise degradation procedure of Satoh & Aoyama (1970). Digoxigenin bisdigitoxoside was a gift from The Wellcome Foundation Ltd. Crystals suitable for crystallographic studies were grown by slow evaporation of a solution of each bioside in ethyl acetate. Digoxigenin bisdigitoxoside was also crystallized from a solution in ethanol. The crystals obtained from ethyl acetate had one molecule of ethyl acetate per molecule of the bioside as the solvent of crystallization while that crystallized from ethanol contained four water molecules per bioside as the solvent of crystallization. Preliminary examination and intensity-data

collections were carried out on an Enraf–Nonius computer-controlled CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ ($\lambda = 1.5418$ Å). Crystal data and pertinent experimental values are given in Table 1.

The structure of (I) was determined using the direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). From the crystal data it was observed that gitoxigenin bisdigitoxoside is isomorphous with the crystal structure of digitoxigenin bisdigitoxoside and hence the coordinates of (I) were used as the starting positions of atoms in (II) and the additional hydroxyl at C(16) was obtained from a difference map. The structure of (III) was solved by the direct-methods program *MULTAN*80 and that of (IV) by vector search methods (Nordman, 1966) using the coordinates of (III) as the starting model. All four structures were refined by full-matrix least squares on F with anisotropic thermal parameters for the non-H atoms of the glycosides and isotropic thermal parameters for the non-H atoms of the solvent molecules. H atoms were located from difference maps and were included in the structure-factor calculations but not refined. The final positional parameters of non-H atoms are given in Table 2.* Scattering-factor curves are taken from

* Lists of positional parameters for H atoms, anisotropic thermal parameters, structure factors, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51614 (97 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and isotropic thermal parameters*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\alpha)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\gamma)B(2,3)]$.

	x	y	z	B_{eq} (Å^2)		x	y	z	B_{eq} (Å^2)
(I)									
C(1)	−0·0767 (9)	0·3710 (8)	0·7849 (5)	5·5 (3)	C(1′)	−0·031 (1)	0·1679 (8)	0·9119 (5)	5·8 (3)
C(2)	−0·011 (1)	0·3771 (8)	0·8403 (6)	6·1 (3)	C(2′)	−0·057 (1)	0·0694 (8)	0·8930 (5)	6·4 (3)
C(3)	−0·074 (1)	0·3289 (8)	0·8874 (5)	6·0 (3)	C(3′)	0·010 (1)	0·0002 (7)	0·9294 (5)	6·4 (3)
C(4)	−0·195 (1)	0·3695 (7)	0·8935 (4)	5·0 (3)	C(4′)	0·138 (1)	0·0266 (7)	0·9322 (5)	5·4 (3)
C(5)	−0·2663 (9)	0·3668 (7)	0·8384 (4)	4·6 (2)	C(5′)	0·153 (1)	0·1293 (7)	0·9500 (5)	5·3 (3)
C(6)	−0·388 (1)	0·4091 (8)	0·8473 (5)	5·6 (3)	C(6′)	0·280 (1)	0·158 (1)	0·9491 (5)	7·1 (4)
C(7)	−0·3831 (9)	0·5151 (7)	0·8554 (5)	5·2 (3)	C(1″)	0·278 (1)	−0·0889 (8)	0·9491 (5)	5·7 (3)
C(8)	−0·3184 (8)	0·5655 (7)	0·8080 (4)	4·2 (2)	C(2″)	0·354 (1)	−0·1260 (9)	0·9994 (4)	6·8 (3)
C(9)	−0·1968 (9)	0·5216 (7)	0·7975 (4)	4·4 (2)	C(3″)	0·434 (1)	−0·2078 (8)	0·9795 (5)	6·0 (3)
C(10)	−0·2009 (9)	0·4133 (7)	0·7878 (4)	4·7 (2)	C(4″)	0·361 (1)	−0·2795 (7)	0·9487 (5)	5·4 (3)
C(11)	−0·139 (1)	0·5734 (8)	0·7495 (5)	5·7 (3)	C(5″)	0·290 (1)	−0·2346 (8)	0·9027 (5)	5·3 (3)
C(12)	−0·130 (1)	0·6784 (8)	0·7607 (5)	5·5 (3)	C(6″)	0·206 (1)	−0·3042 (9)	0·8754 (6)	7·6 (4)
C(13)	−0·2507 (9)	0·7257 (7)	0·7710 (4)	4·4 (2)	O(5′)	0·0902 (6)	0·1867 (5)	0·9100 (3)	5·4 (2)
C(14)	−0·3154 (9)	0·6697 (7)	0·8175 (4)	4·1 (2)	O(3′)	−0·0397 (8)	0·0004 (6)	0·9827 (4)	8·7 (3)
C(15)	−0·253 (1)	0·7008 (7)	0·8712 (4)	4·5 (2)	O(4′)	0·1985 (7)	−0·0269 (5)	0·9716 (3)	6·2 (2)
C(16)	−0·210 (1)	0·8012 (8)	0·8620 (5)	6·4 (3)	O(5″)	0·2133 (7)	−0·1652 (5)	0·9253 (3)	5·9 (2)
C(17)	−0·2222 (9)	0·8224 (8)	0·7992 (5)	5·6 (3)	O(3″)	0·5223 (7)	−0·1710 (6)	0·9434 (4)	7·3 (2)
C(18)	−0·317 (1)	0·7348 (9)	0·7171 (4)	6·0 (3)	O(4″)	0·4361 (8)	−0·3508 (5)	0·9261 (4)	7·2 (2)
C(19)	−0·261 (1)	0·3871 (8)	0·7339 (5)	6·0 (3)					
C(20)	−0·3031 (9)	0·9024 (8)	0·7881 (4)	4·8 (3)	O(24)	0·351 (1)	0·032 (1)	1·0082 (6)	22·1 (5)*
C(21)	−0·425 (1)	0·9096 (7)	0·8092 (5)	5·6 (3)	O(26)	−0·3193 (9)	0·1040 (7)	0·9937 (4)	8·9 (3)*
C(22)	−0·277 (1)	0·9814 (7)	0·7617 (5)	5·7 (3)	C(24)	−0·221 (2)	0·068 (1)	1·0797 (7)	10·1 (5)*
C(23)	−0·375 (1)	1·0442 (8)	0·7638 (5)	6·1 (3)	C(25)	−0·294 (2)	0·041 (1)	1·0385 (8)	12·1 (6)*
O(3)	−0·0849 (7)	0·2285 (5)	0·8738 (3)	6·4 (2)	C(26)	−0·390 (2)	0·067 (1)	0·9422 (7)	11·6 (5)*
O(14)	−0·4337 (6)	0·7036 (4)	0·8222 (3)	4·4 (2)	C(27)	−0·402 (2)	0·155 (1)	0·9158 (7)	11·1 (5)*
O(21)	−0·4621 (7)	1·0024 (5)	0·7929 (3)	6·1 (2)					
O(23)	−0·3883 (8)	1·1225 (6)	0·7445 (4)	8·2 (2)					
(II)									
C(1)	−0·077 (1)	0·3930 (8)	0·7904 (6)	4·1 (3)	C(1′)	−0·047 (1)	0·1804 (9)	0·9088 (5)	4·2 (3)
C(2)	−0·019 (1)	0·3923 (9)	0·8494 (6)	4·7 (3)	C(2′)	−0·067 (1)	0·0880 (9)	0·8811 (5)	3·7 (3)
C(3)	−0·092 (1)	0·3430 (8)	0·8916 (5)	3·6 (3)	C(3′)	0·000 (1)	0·0107 (9)	0·9115 (6)	4·2 (3)
C(4)	−0·213 (1)	0·3863 (8)	0·8950 (5)	3·7 (3)	C(4′)	0·126 (1)	0·0427 (7)	0·9244 (5)	3·7 (3)
C(5)	−0·273 (1)	0·3881 (8)	0·8372 (5)	3·1 (3)	C(5′)	0·135 (1)	0·1417 (7)	0·9491 (4)	3·4 (3)
C(6)	−0·397 (1)	0·4301 (8)	0·8430 (5)	3·3 (3)	C(6′)	0·260 (1)	0·1778 (8)	0·9542 (5)	4·8 (3)
C(7)	−0·393 (1)	0·5346 (8)	0·8545 (5)	3·4 (3)	C(1″)	0·2637 (9)	−0·0822 (8)	0·9465 (8)	3·4 (3)
C(8)	−0·3228 (9)	0·5842 (8)	0·8075 (5)	2·3 (3)	C(2″)	0·329 (1)	−0·1175 (9)	0·9956 (5)	4·5 (3)
C(9)	−0·198 (1)	0·5425 (8)	0·7996 (5)	2·3 (3)	C(3″)	0·412 (1)	−0·1975 (8)	0·9801 (5)	4·4 (3)
C(10)	−0·205 (1)	0·4373 (8)	0·7900 (5)	3·2 (3)	C(4″)	0·3426 (9)	−0·2671 (8)	0·9485 (5)	4·1 (3)
C(11)	−0·135 (1)	0·5951 (8)	0·7525 (6)	3·8 (3)	C(5″)	0·274 (1)	−0·2264 (8)	0·9004 (5)	4·1 (3)
C(12)	−0·127 (1)	0·6974 (8)	0·7657 (5)	3·6 (3)	C(6″)	0·194 (1)	−0·2938 (9)	0·8712 (6)	5·5 (3)
C(13)	−0·246 (1)	0·7471 (9)	0·7731 (5)	3·1 (3)	O(5′)	0·0738 (6)	0·2018 (5)	0·9109 (3)	4·0 (2)
C(14)	−0·3169 (9)	0·6917 (8)	0·8177 (5)	2·9 (3)	O(3′)	−0·0581 (7)	−0·0144 (6)	0·9620 (4)	5·4 (2)
C(15)	−0·263 (1)	0·7230 (9)	0·8763 (5)	3·5 (3)	O(4′)	0·1793 (7)	−0·0170 (5)	0·9656 (3)	4·3 (2)
C(16)	−0·204 (1)	0·8185 (9)	0·8676 (5)	3·3 (3)	O(5″)	0·1963 (6)	−0·1547 (5)	0·9199 (3)	4·4 (2)
C(17)	−0·223 (1)	0·8432 (8)	0·8034 (5)	3·3 (3)	O(3″)	0·5029 (7)	−0·1637 (6)	0·9448 (4)	5·3 (2)
C(18)	−0·311 (1)	0·7550 (9)	0·7167 (5)	4·4 (4)	O(4″)	0·4164 (7)	−0·3402 (5)	0·9270 (4)	6·0 (2)
C(19)	−0·257 (1)	0·4132 (8)	0·7314 (5)	3·9 (3)					
C(20)	−0·304 (1)	0·9220 (9)	0·7934 (5)	3·8 (3)	O(24)	−0·128 (1)	1·0385 (7)	0·5237 (4)	9·3 (3)*
C(21)	−0·430 (1)	0·9247 (8)	0·8122 (5)	3·5 (3)	O(26)	−0·1758 (7)	0·9005 (6)	0·4905 (4)	5·7 (2)*
C(22)	−0·275 (1)	1·0001 (9)	0·7688 (6)	4·2 (4)	C(24)	−0·191 (1)	0·9679 (9)	0·5306 (6)	6·8 (4)*
C(23)	−0·378 (1)	1·0599 (7)	0·7704 (5)	3·8 (3)	C(25)	−0·281 (1)	0·945 (1)	0·5730 (6)	7·4 (4)*
O(3)	−0·1007 (7)	0·2460 (5)	0·8734 (3)	4·6 (2)	C(26)	−0·089 (1)	0·916 (1)	0·4469 (6)	6·7 (4)*
O(14)	−0·4370 (6)	0·7247 (4)	0·8201 (3)	2·9 (2)	C(27)	−0·081 (1)	0·8285 (9)	0·4157 (6)	6·7 (4)*
O(16)	−0·2469 (6)	0·8858 (5)	0·9041 (3)	4·4 (2)					
O(21)	−0·4693 (6)	1·0173 (5)	0·7979 (3)	4·1 (2)					
O(23)	−0·3944 (7)	1·1378 (5)	0·7532 (4)	6·0 (2)					

Table 2 (*cont.*)

	x	*y*	*z*	B_{eq}(Å^2)
(III)				
C(1)	0·5211 (2)	0·7549 (6)	0·850 (1)	4·3 (2)
C(2)	0·5319 (2)	0·8522 (7)	0·837 (1)	5·1 (2)
C(3)	0·5581 (2)	0·8829 (7)	0·989 (1)	5·3 (2)
C(4)	0·5407 (2)	0·8582 (6)	1·166 (1)	4·9 (2)
C(5)	0·5287 (2)	0·7576 (6)	1·179 (1)	4·5 (2)
C(6)	0·5113 (2)	0·7366 (8)	1·365 (1)	5·8 (2)
C(7)	0·4738 (2)	0·7849 (8)	1·386 (1)	5·7 (2)
C(8)	0·4457 (2)	0·7603 (6)	1·239 (1)	4·4 (2)
C(9)	0·4632 (2)	0·7771 (6)	1·052 (1)	4·1 (2)
C(10)	0·5020 (2)	0·7286 (6)	1·029 (1)	4·4 (2)
C(11)	0·4343 (2)	0·7512 (7)	0·909 (1)	5·0 (2)
C(12)	0·4003 (2)	0·8102 (7)	0·926 (1)	5·2 (2)
C(13)	0·3793 (2)	0·7984 (6)	1·111 (1)	4·0 (2)
C(14)	0·4084 (2)	0·8090 (6)	1·265 (1)	4·1 (2)
C(15)	0·4093 (2)	0·9142 (6)	1·295 (1)	4·9 (2)
C(16)	0·3701 (3)	0·9452 (6)	1·278 (1)	6·2 (2)
C(17)	0·3523 (2)	0·8842 (6)	1·129 (1)	4·5 (2)
C(18)	0·3600 (2)	0·7035 (6)	1·114 (1)	5·1 (2)
C(19)	0·4977 (2)	0·6231 (7)	1·031 (1)	6·1 (2)
C(20)	0·3124 (2)	0·8618 (6)	1·159 (1)	4·8 (2)
C(21)	0·2948 (2)	0·8479 (8)	1·338 (1)	6·9 (3)
C(22)	0·2862 (2)	0·8530 (7)	1·042 (1)	6·1 (2)
C(23)	0·2498 (2)	0·8310 (7)	1·117 (1)	6·2 (2)
C(1′)	0·6180 (2)	0·8638 (6)	0·850 (1)	4·5 (2)
C(2′)	0·6581 (2)	0·8640 (6)	0·919 (1)	4·9 (2)
C(3′)	0·6837 (2)	0·8912 (7)	0·769 (1)	5·0 (2)
C(4′)	0·6774 (2)	0·8311 (6)	0·606 (1)	4·5 (2)
C(5′)	0·6361 (2)	0·8223 (6)	0·561 (1)	4·7 (2)
C(6′)	0·6304 (3)	0·7493 (8)	0·417 (1)	7·3 (3)
C(1″)	0·7338 (2)	0·8589 (7)	0·444 (1)	5·6 (2)
C(2″)	0·7469 (3)	0·8736 (7)	0·253 (1)	7·0 (3)
C(3″)	0·7880 (2)	0·8796 (8)	0·242 (1)	7·1 (3)
C(4″)	0·8005 (2)	0·9654 (7)	0·351 (1)	7·0 (3)
C(5″)	0·7852 (2)	0·9603 (8)	0·543 (2)	7·7 (3)
C(6″)	0·7930 (3)	1·0439 (9)	0·655 (2)	9·4 (4)
O(3)	0·5942 (1)	0·8362 (4)	0·9865 (8)	5·1 (1)
O(12)	0·3729 (1)	0·7898 (5)	0·7921 (7)	6·2 (2)
O(14)	0·3915 (1)	0·7733 (4)	1·4231 (7)	5·1 (1)
O(21)	0·2552 (2)	0·8264 (5)	1·296 (1)	7·5 (2)
O(23)	0·2193 (2)	0·8211 (6)	1·056 (1)	9·5 (2)
O(5′)	0·6154 (1)	0·7960 (4)	0·7123 (7)	4·8 (1)
O(3′)	0·6783 (2)	0·9879 (4)	0·7298 (9)	6·5 (2)
O(4′)	0·6943 (1)	0·8702 (4)	0·4477 (8)	5·3 (1)
O(5″)	0·7462 (2)	0·9516 (4)	0·5337 (9)	6·2 (2)
O(3″)	0·8042 (2)	0·7986 (5)	0·314 (1)	8·2 (2)
O(4″)	0·8411 (2)	0·9703 (6)	0·350 (1)	10·1 (2)
O(*W*1)	0·1414 (3)	0·8801 (7)	1·135 (1)	12·9 (3)*
O(*W*2)	0·3987 (3)	0·5777 (7)	1·447 (2)	13·6 (3)*
O(*W*3)	0·3958 (5)	0·454 (1)	1·148 (3)	19·7 (6)*
O(*W*4)	0·4578 (5)	0·497 (1)	1·616 (3)	16·0 (6)*
(IV)				
C(1)	0·3759	−0·1540	−0·0393	2·9 (1)
C(2)	0·3799 (6)	−0·0252 (5)	0·0449 (4)	3·4 (1)
C(3)	0·5121 (7)	0·0646 (5)	0·0329 (4)	3·4 (1)
C(4)	0·7040 (6)	−0·0051 (4)	0·0331 (4)	3·3 (1)
C(5)	0·6959 (5)	−0·1309 (4)	−0·0540 (3)	2·6 (1)
C(6)	0·8921 (6)	−0·1942 (5)	−0·0564 (4)	3·6 (1)
C(7)	0·9777 (6)	−0·2497 (5)	0·0437 (4)	3·4 (1)
C(8)	0·8499 (6)	−0·3490 (4)	0·0525 (3)	2·4 (1)
C(9)	0·6570 (6)	−0·2827 (4)	0·0604 (3)	2·4 (1)
C(10)	0·5654 (5)	−0·2278 (4)	−0·0432 (3)	2·4 (1)
C(11)	0·5351 (6)	0·3747 (4)	0·0809 (4)	2·9 (1)
C(12)	0·6329 (6)	−0·4285 (4)	0·1793 (4)	2·8 (1)
C(13)	0·8170 (6)	−0·5081 (4)	0·1651 (3)	2·3 (1)
C(14)	0·9460 (5)	−0·4174 (4)	0·1443 (3)	2·3 (1)
C(15)	1·0234 (6)	−0·3319 (4)	0·2556 (4)	3·0 (1)
C(16)	1·0706 (7)	−0·4273 (5)	0·3304 (4)	3·3 (1)
C(17)	0·9243 (6)	−0·5331 (4)	0·2809 (4)	2·8 (1)
C(18)	0·7784 (7)	−0·6310 (5)	0·0759 (4)	3·1 (1)
C(19)	0·5282 (7)	−0·3389 (5)	−0·1468 (4)	3·5 (1)
C(20)	1·0025 (7)	−0·6681 (5)	0·2816 (4)	3·1 (1)
C(21)	1·1806 (8)	−0·7229 (5)	0·2503 (5)	4·7 (1)
C(22)	0·9299 (8)	−0·7597 (5)	0·3083 (4)	4·4 (1)
C(23)	1·048 (1)	−0·8800 (5)	0·2934 (5)	5·1 (2)
O(3)	0·4576 (5)	0·1024 (3)	−0·0709 (3)	3·5 (1)
O(12)	0·5161 (4)	−0·5120 (3)	0·2016 (3)	3·8 (1)
O(14)	1·1077 (4)	−0·4966 (3)	0·1151 (2)	3·0 (1)
O(21)	1·1963 (6)	−0·8562 (4)	0·2595 (4)	5·6 (1)
O(23)	1·0327 (6)	−0·9841 (4)	0·3076 (5)	7·9 (2)
C(1′)	0·2998 (7)	0·1829 (5)	−0·0900 (4)	3·3 (1)
C(2′)	0·3297 (7)	0·2681 (5)	−0·1603 (4)	3·4 (1)
C(3′)	0·1542 (7)	0·3456 (4)	−0·2051 (4)	3·1 (1)
C(4′)	−0·0078 (6)	0·2571 (4)	−0·2552 (3)	2·9 (1)
C(5′)	−0·0263 (7)	0·1759 (5)	−0·1774 (4)	3·6 (1)
C(6′)	−0·1728 (8)	0·0787 (6)	−0·2297 (5)	5·6 (1)
C(1″)	−0·2159 (7)	0·3888 (5)	−0·3640 (4)	3·1 (1)
C(2″)	−0·4232 (7)	0·4161 (5)	−0·4033 (4)	3·7 (1)
C(3″)	−0·4590 (7)	0·4988 (5)	−0·4876 (4)	3·9 (1)
C(4″)	−0·3404 (8)	0·6162 (5)	−0·4485 (4)	4·2 (1)
C(5″)	−0·1361 (8)	0·5752 (5)	−0·4086 (4)	3·9 (1)
C(6″)	−0·009 (1)	0·6885 (6)	−0·3570 (5)	6·3 (2)
O(5′)	0·1467 (5)	0·1035 (3)	−0·1486 (3)	3·5 (1)
O(3′)	0·1125 (5)	0·4495 (4)	−0·1187 (3)	4·2 (1)
O(4′)	−0·1840 (4)	0·3287 (3)	−0·2770 (2)	3·2 (1)
O(5″)	−0·1229 (5)	0·5094 (3)	−0·3227 (3)	3·6 (1)
O(3″)	−0·4237 (6)	0·4165 (4)	−0·5863 (3)	4·4 (1)
O(4″)	−0·3566 (7)	0·6763 (4)	−0·5367 (3)	6·2 (1)
O(24)	0·326 (1)	0·1250 (9)	−0·04406 (7)	13·6 (3)*
O(26)	0·471 (1)	−0·0499 (7)	−0·5068 (6)	9·9 (2)*
C(24)	0·342 (2)	0·001 (1)	−0·457 (1)	11·6 (3)*
C(25)	0·248 (2)	−0·078 (1)	−0·421 (1)	13·5 (4)*
C(26)	0·569 (2)	0·036 (1)	−0·548 (1)	11·3 (3)*
C(27)	0·656 (2)	−0·039 (2)	−0·616 (1)	17·1 (6)*

* Atoms refined isotropically.

International Tables for X-ray Crystallography (1974). All calculations were performed using the structure determination program package *SDP* (B. A. Frenz & Associates Inc., 1986) and local programs. The high R values for (II) and (III) were due to poor data.

Discussion

Fig. 1 gives a pictorial representation of the biosides with the numbering of the atoms and ring designations. The steroid nucleus in these compounds is the most conformationally stable portion of the molecule with ring junctions *A–B* and *C–D* in the *cis* configuration giving the steroid nucleus a *cis/trans/cis* conformation and thus a bent shape. As in other structures the *A*, *B* and *C* rings have a chair conformation. The five-membered *D* ring shows a variety of conformations: (I) has a conformation close to a distorted 13α,14β-half-chair, (II) is a 13β-envelope, (III) is in between a distorted 14β,15α-half-chair and a 15α-envelope and (IV) is a distorted 14β,15α-half-chair (Altona, Geise & Romers, 1968). From these results it is not possible to classify the conformation of the *D* ring, although a distorted half-chair conformation seems to be preferred.

The lactone ring orientation at C(17), which determines the relative position of the carbonyl oxygen, has been thought to be an important factor in determining the relative biological activity of these glycosides and

their analogues (Rohrer, Kihara, Deffo, Rathore, Ahmed, From & Fullerton, 1984). Although we have not carried out any biological-activity assays on these compounds, a discussion of the relative position of the carbonyl oxygen of the lactone ring seems to be in order. In all the studies correlating the carbonyl oxygen distance to biological activity digitoxigenin has been taken to be the prototype (Rohrer & Fullerton, 1980). A superposition of the present structures on the prototype digitoxigenin is shown in Fig. 2. Molecular fit was carried out using the *FIT* command of the *SYBYL* (Tripos Associates Inc., 1988) molecular modelling system. Atoms C(1) to C(17) and O(3) of the steroid nucleus were used for the purpose and the atoms of the steroid nucleus of the four structures were fitted on to the steroid nucleus of digitoxigenin. The orientation of the lactone ring is determined by the torsion angle C(13)–C(17)–C(20)–C(22), χ, which has been shown theoretically to have two possible minimum-energy conformations around 80 and −100°. The torsion angle χ in (I) and (II) is −116° while it is −93° in (III) and −100° in (IV). The lactone oxygen–oxygen separations between digitoxigenin and the biosides calculated from the superposition figure are 1·92, 1·64, 3·75 and 2·93 Å for structures (I) to (IV), respectively. When the lactone ring of the biosides is rotated to the alternate minimum-energy conformation with the positive torsion angle $(180-\chi°)$, the O(23)–O(23) separation reduces to 0·89, 1·09, 1·25 and 0·67 Å. Although these values are close to the 'active' orientation for digitoxigenin (Rohrer *et al.*, 1984) the values obtained for the two forms of biosides of digoxigenin, 1·25 and 0·67 Å, indicate that one should accept these values with caution when linking the oxygen–oxygen separation to activity.

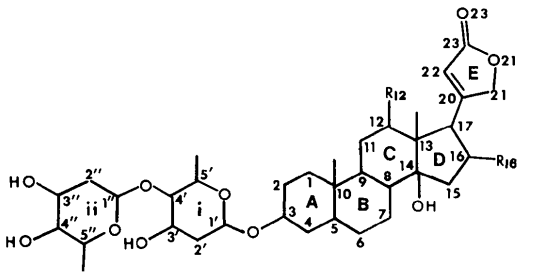

Fig. 1. Schematic drawing of the biosides of digitalis showing the numbering of the atoms and ring designations. R_{12} = H for (I) and (II); OH for (III) and (IV). R_{16} = H for (I), (III) and (IV); OH for (II).

Table 3. *Steroid–sugar and sugar–sugar linkage torsion angles* (°) *with e.s.d.'s in parentheses*

		φ_1: C(2)–C(3)–O(3)–C(1′)	φ_2: C(3)–O(3)–C(1′)–C(2′)
Steroid to first sugar			
Triosides:	digoxin	67·5 (3)	149·8 (3)
	gitoxin	128·6 (3)	169·9 (3)
Biosides of:	digitoxigenin (I)	119·8 (10)	176·9 (10)
	gitoxigenin (II)	114·3 (13)	180·7 (13)
	digoxigenin (III)	71·8 (9)	143·7 (9)
	digoxigenin (IV)	68·7 (4)	147·4 (4)
Monoside of:	digoxigenin	161·7 (5)	165·1 (5)
		φ_1': C(3′)–C(4′)–O(4′)–C(1″)	φ_2': C(4′)–O(4′)–C(1″)–C(2″)
First to second sugar			
Triosides:	digoxin	71·9 (3)	163·0 (3)
	gitoxin	80·4 (3)	159·5 (3)
Biosides of:	digitoxigenin (I)	111·1 (10)	168·6 (10)
	gitoxigenin (II)	104·2 (13)	166·0 (13)
	digoxigenin (III)	69·9 (9)	157·2 (9)
	digoxigenin (IV)	71·8 (4)	159·4 (4)
		φ_1'': C(3″)–C(4″)–O(4″)–C(1‴)	σ_2'': C(4″)–O(4″)–C(1‴)–C(2‴)
Second to third sugar			
Triosides:	digoxin	123·8 (3)	178·5 (3)
	gitoxin	111·8 (3)	177·5 (3)

Table 4. *Hydrogen-bonding distances* (Å) *in the biosides*

	(I)	(II)	(III)	(IV)
O(14)···O(23) (−1 − *x*, −0·5 + *y*, 1·5 − *z*)	2·84 (1)	2·87 (1)	—	—
O(4″)···O(14) (1 + *x*, −1 + *y*, *z*)	3·01 (1)	3·18 (1)	—	—
O(3″)···O(24) (1 + *x*, *y*, *z*)	2·91 (2)	2·96 (1)	—	—
O(3′)···O(4″) (−0·5 + *x*, −0·5 − *y*, 2 − *z*)	3·07 (1)	—	—	—
O(16)···O(3′) (*x*, 1 + *y*, *z*)	—	2·92 (1)	—	—
O(16)···O(3″) (−1 + *x*, 1 + *y*, *z*)	—	3·08 (1)	—	—
O(3′)···O(5″) (*x*, *y*, *z*)	—	—	2·889 (8)	2·955 (6)
O(3″)···O(12) (0·5 + *x*, 1·5 − *y*, 1 − *z*)	—	—	2·877 (8)	—
O(3″)···O(12) (−1 + *x*, 1 + *y*, 1 + *z*)	—	—	—	2·966 (5)
O(12)···O(14) (*x*, *y*, 1 + *z*)	—	—	2·866 (7)	—
O(12)···O(14) (−1 + *x*, *y*, *z*)	—	—	—	2·958 (5)
O(14)···O(*W*2) (*x*, *y*, *z*)	—	—	2·84 (1)	—
O(*W*2)···O(4″) (0·5 + *x*, 1·5 − *y*, 2 − *z*)	—	—	2·65 (1)	—
O(4″)···O(*W*1) (1 − *x*, 2 − *y*, −1 + *z*)	—	—	2·77 (1)	—
O(*W*1)···O(23) (*x*, *y*, *z*)	—	—	2·97 (1)	—
O(*W*3)···O(*W*1) (0·5 − *x*, 0·5 + *y*, 2 − *z*)	—	—	2·73 (2)	—
O(*W*2)···O(*W*3) (*x*, *y*, *z*)	—	—	2·80 (1)	—
O(14)···O(3′) (1 + *x*, −1 + *y*, *z*)	—	—	—	2·969 (5)
O(4″)···O(26) (−1 + *x*, 1 + *y*, *z*)	—	—	—	3·014 (9)

It has been shown (Yoda, Yoda & Sarrif, 1973) that the first sugar attached to the steroid has the greatest effect on binding and activity, which suggests that the relative orientation of the first sugar to the steroid nucleus is important in understanding the activity of

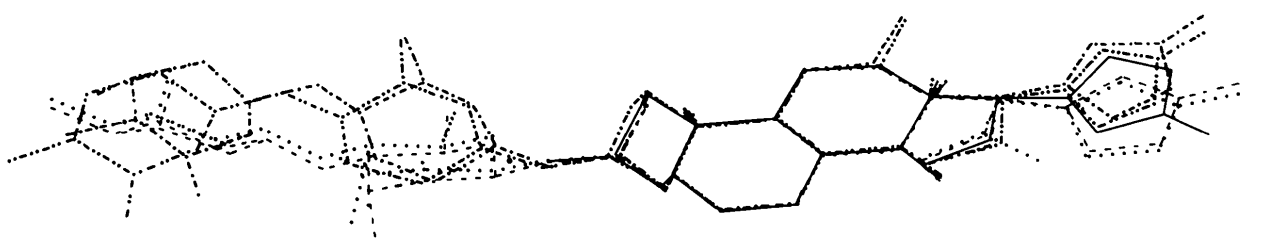

Fig. 2. Superposition of the four structures on the prototype digitoxigenin. Key: — digitoxigenin, ----- digitoxigenin bisdigitoxoside, ... gitoxigenin bisdigitoxoside, ·····- digoxigenin bisdigitoxoside (orthorhombic form); ····· digoxigenin bisdigitoxoside (triclinic form).

these compounds (Fullerton, Ahmed, From, McParland, Rohrer & Griffin, 1986). Owing to steric hindrance more than two-thirds of the possible conformations obtained by rotation of 360° about the two bonds linking the steroid and the sugar moieties are found to be unfavorable (Rohrer *et al.*, 1984). Torsion angles around the glycosidic linkages are listed in Table 3 with those found in the structures of the triosides and monoside. In this series of compounds the torsion angle about C(3)–O(3) [*i.e.* φ_1: C(2)–C(3)–O(3)–C(1′)] varies from 67 to 162° while the torsion angle φ_2 [C(3)–O(3)–C(1′)–C(2′)] varies from 144 to 181°. The range of values has been observed in other analogues of glycosides and indicates high flexibility around the glycosidic linkage C(3)–O(3). The φ_1' torsion angle about the linkage between the first and second sugars shows a variation similar to those about the steroid first sugar linkage although the range is smaller. The second and third sugar linkage has φ_1 and φ_2 values around 116° and close to 180° respectively.

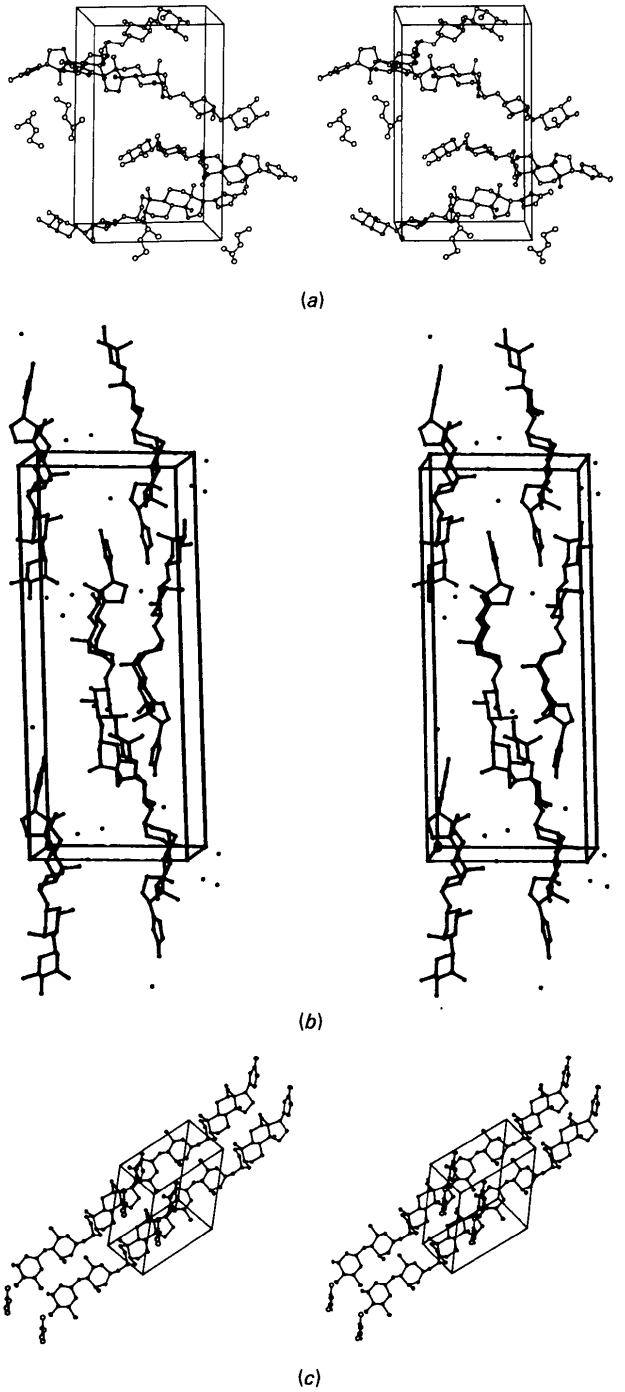

Fig. 3. Stereoviews of the crystal packing in the crystal structures of (*a*) digitoxigenin bisdigitoxoside, (*b*) digoxigenin bisdigitoxoside (orthorhombic form) and (*c*) digoxigenin bisdigitoxoside (triclinic form).

The three biosides differ from each other in the presence or absence of a hydroxyl group: (II) has a hydroxyl at C(16) while (III) and (IV) have hydroxyls at C(12). (I) lacks a hydroxyl group at both C(16) and C(12). The additional hydroxyl at C(16) does not seem to have any influence on the orientation of the lactone ring with respect to the steroid nucleus. One interesting observation in this series of structures is the presence of a hydrogen bond between the OH at C(3′) of the first sugar and the ring oxygen (O5″) of the second sugar observed in the two crystalline forms (III and IV) of digoxigenin bisdigitoxoside. This hydrogen bond has also been observed in the structure of digoxin (Go, Kartha & Chen, 1980). Gitoxin (Go & Kartha, 1980) and the biosides (I) and (II) do not possess this hydrogen bond; the O···O distance is over 3·28 Å, which is too long to be considered as a hydrogen bond. Hydrogen-bonding distances in the four structures are given in Table 4. From this table it can be seen that the orthorhombic form of digoxigenin bisdigitoxoside (III) has more hydrogen bonds than the other three structures. The hydrogen-bonding pattern may be a reason for the observed differences between the two forms. Stereoviews of the crystal packing of (I) (II is isomorphous to I), (III) and (IV) are shown in Fig. 3.

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Conformational Polymorphism of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate. I. Structures and Atomic Displacement Parameters between 100 and 350 K for Three Crystal Forms

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Abstract

Atomic coordinates and displacement parameters have been obtained for the previously described crystal structures [Byrn, Curtin & Paul (1972). *J. Am. Chem. Soc.* **94**, 890–898] of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate at 105, 180, 230, 296 and 353 K for the yellow form [Y-(I)], and at 98, 296 and 353 K for the white form [W-(I)]. Crystals of Y-(I) deuterated at the hydroxyl groups have been studied at 230 and 289 K. We have also determined the structure at 97, 179, 226, 296 and 343 K of a third, light-yellow [LY-(I)] crystal form that seems to have escaped detection up till now. The molecules have different conformations in the three polymorphic forms: the twist angle of the ester grouping with respect to the mean plane of the benzene ring is about 5° in Y-(I), about 40° in LY-(I), and about 85° and 70° for the two symmetry-independent molecules in W-(I). These differences are associated with different hydrogen-bonding patterns. Analysis of the anisotropic displacement parameters shows that the molecules do not behave as rigid bodies in the crystals. The ester groups have an additional librational motion with respect to the rest of the molecule. The temperature dependence of $\langle\omega^2\rangle$, the mean-square amplitude of this libration, is much larger for Y-(I) than for the other two forms. The results are discussed in terms of a mean-field potential model. Crystal data at 296 K [$C_{10}H_8Cl_2O_6$, $M_r = 295{\cdot}1$, λ(Mo $K\alpha$) = 0·7107 Å]: Y-(I) form, $a = 9{\cdot}582$ (2), $b = 4{\cdot}292$ (1), $c = 7{\cdot}950$ (2) Å, $\alpha = 114{\cdot}23$ (2), $\beta = 94{\cdot}93$ (2), $\gamma = 106{\cdot}22°$, $V = 278{\cdot}67$ Å^3, $R = 0{\cdot}028$ for 940 observed reflections; W-(I) form, $a = 9{\cdot}843$ (1), $b = 7{\cdot}847$ (2), $c = 10{\cdot}573$ (2) Å, $\alpha = 116{\cdot}40$ (2), $\beta = 124{\cdot}18$ (1), $\gamma = 88{\cdot}96$ (2)°, $V = 574{\cdot}76$ Å^3, $R = 0{\cdot}026$ for 1832 observed reflections; LY-(I) form, $a = 3{\cdot}8980$ (4), $b = 8{\cdot}034$ (2), $c = 9{\cdot}491$ (2) Å, $\alpha = 70{\cdot}42$ (2), $\beta = 89{\cdot}09$ (1), $\gamma = 86{\cdot}68°$, $V = 279{\cdot}57$ Å^3, $R = 0{\cdot}026$ for 1039 observed reflections.

Introduction

The work to be described here and in a forthcoming paper (Richardson, Yang, Bregger & Dunitz, 1989) is a contribution towards the solution of a problem that is more than 100 years old, the problem of the colour

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