Stereochemistry of the Cucurbitacins. Crystal and Molecular Structure and Absolute Configuration of Datiscoside Bis-(*p*-iodobenzoate) Dihydrate

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The molecular structure and absolute configuration of datiscoside (Ia) have been determined from a three-dimensional, single-crystal, *X*-ray analysis of its bis-(*p*-iodobenzoate) dihydrate (Ib).

Crystals have orthorhombic symmetry, space group $P2_12_12_1$, with a = 19·609(7), b = 31·485(17), c = 8·743(3) Å, Z = 4. The structure was solved by the heavy-atom method, and refined by least-squares methods to R 0·101 for 1627 independent reflections measured by counter diffractometry. The absolute configuration was determined by the method of anomalous dispersion.

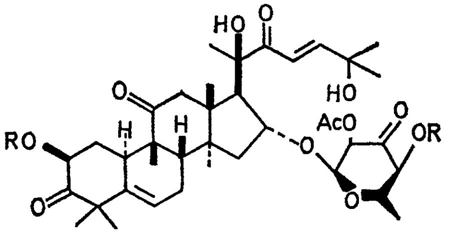
The steroidal nucleus of datiscoside has a folded conformation, with a cisoid fusion of rings B and C, and a *trans*-fusion of rings C and D. Rings A and C are in the chair conformation, while rings B and D are in the half-chair conformation. The previously uncertain configurations at C(2) and C(20) in the cucurbitacins have been unambiguously established. The sugar residue is 2-*O*-acetyl-6-deoxy-α-L-*gluco*-hex-3-ulopyranoside.

DATISCOSIDE, $C_{38}H_{54}O_{12}$, (Ia) is a cucurbitacin glycoside isolated from the roots of *Datisca glomerata* Baill., and showing significant anti-leukaemic activity; its isolation, and structural characterization by *X*-ray crystallographic analysis of its bis-(*p*-iodobenzoate) dihydrate (Ib) have been reported briefly.[1]

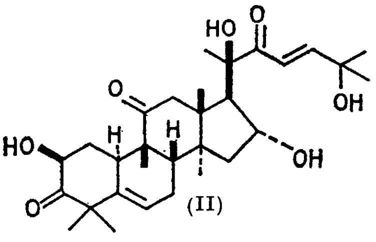
The *X*-ray study has established the molecular structure, stereochemistry, and absolute configuration of datiscoside, showing it to be a glycoside of cucurbitacin D (II). The study also establishes unambiguously the previously uncertain configurations of the cucurbitacins at C(20), assigned earlier only on biogenetic grounds,[2] and at C(2), for which contradictory evidence has been presented.[3] The 2β,3β-diol configuration in cucurbitacins O, P, and Q is also confirmed.[4]

EXPERIMENTAL

Crystals of the bis-(*p*-iodobenzoate) dihydrate (Ib) (m.p. 174—175 °C), prepared by treating datiscoside with an excess of *p*-iodobenzoyl chloride in pyridine, were obtained by recrystallisation from nitromethane.



(I) a; R = H
b; R = *p*-iodobenzoate



(II)

Crystal Data.—$C_{52}H_{60}I_2O_{14},2H_2O$, M = 1199. Orthorhombic, a = 19·609(7), b = 31·485(17), c = 8·743(3) Å, U = 5398 Å^3, D_m = 1·49(1), Z = 4, D_c = 1·475, F(000) = 2440. Space group, $P2_12_12_1$. Cu-K_α radiation, λ = 1·54178 Å; μ(Cu-K_α) = 99 cm^{-1}.

Preliminary unit-cell data were obtained from 25° precession photographs taken with Mo-K_α radiation (λ = 0·7107 Å). The final values of the cell edges were found by a least-squares fit of the preliminary values to the observed values of $\pm 2\theta$ for 13 strong general reflections carefully measured on a diffractometer.

Intensity Data.—The air-stable crystals of the dihydrate are needles elongated along c. Intensity measurements were obtained for a crystal 0·15 × 0·20 × 0·45 mm^3 mounted with the needle axis parallel to the ϕ axis of a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Our standard experimental procedures have been described in detail elsewhere.[5] Monochromatic Cu-K_α radiation was obtained by Bragg reflection of the direct beam from the (002) planes of a highly oriented graphite crystal.† Scintillation counting was used with pulse-height analysis.

A complete octant, to 2θ 90°, and a substantial part of another were examined. Significant scattered intensity was observed at 2829 reciprocal lattice points (1627 independent reflections). A reflection was taken as significant when the background-corrected peak intensity was greater than three times the square root of the total number of counts involved in the measurement.

Two reference reflections were monitored after every 50 measurement cycles and showed a linear decline to 94% of their original intensity over the course of the experiment.

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† Copper radiation was chosen, rather than molybdenum to avoid a possible lack of resolution on the diffractometer, caused by the length of the b axis. The high anomalous dispersion term for iodine with this radiation was also very useful in identifying the correct absolute configuration.

[1] S. M. Kupchan, C. W. Sigel, L. J. Guttman, R. J. Restivo, and R. F. Bryan, *J. Amer. Chem. Soc.*, 1972, **94**, 1353.

[2] D. H. R. Barton, C. F. Garbers, D. Giacopello, R. G. Harvey, J. Lessard, and D. R. Taylor, *J. Chem. Soc.* (*C*), 1969, 1050.

[3] (*a*) D. Lavie and B. S. Benjaminov, *J. Org. Chem.*, 1965, **30**, 607; (*b*) G. Snatzke, P. R. Enslin, C. W. Holzapfel, and K. B. Norton, *J. Chem. Soc.* (*C*), 1967, 972; (*c*) J. R. Bull and P. R. Enslin, *Tetrahedron*, 1970, **26**, 1525; see also ref. 2.

[4] S. M. Kupchan, *Pure and Appl. Chem.*, 1970, **21**, 227.

[5] G. A. Melson, P. T. Greene, and R. F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116.

This decline was probably due to the loss of a small amount of water of hydration from the crystal. An appropriate correction was applied to the structure amplitudes to compensate for this intensity loss. No absorption corrections were applied although μ is high. No serious errors arising from neglect of such a correction are apparent in the final results, though the use of anisotropic thermal parameters for the iodine atoms may have partially compensated for this systematic error.

Structure Determination and Refinement.—The structure was solved, without difficulty, by the heavy-atom method with phases originally based upon the co-ordinates of the iodine atoms, whose positions in the asymmetric unit were found from the three-dimensional Patterson function. With the two oxygen atoms of the molecules of water of hydration identified, but with all other light atoms treated as carbon and assigned isotropic thermal parameters of 4·0 Å^2, R was 0·26.

Preliminary refinement of this model by block-diagonal least-squares methods gave R 0·19 and showed 14 atoms with thermal parameters significantly lower than those of the remaining atoms. These 14 atoms were assigned as oxygen to give a chemically reasonable structure.

The choice of enantiomer could now be made by inspection of the agreement between observed and calculated structure amplitudes when the very large anomalous dispersion terms[6] for iodine were included in the structure-factor calculation.[7] A representative selection of the structure factors used in making the choice of enantiomer is given in Table 1.

TABLE 1

Representative Friedel pairs of reflections used in finding the absolute configuration. The superscripts + and − refer to the index triples hkl and $\bar{h}\bar{k}\bar{l}$, respectively

h	k	l	$\lvert F_o^+\rvert$	$\lvert F_o^-\rvert$	Δ_o	Δ_c
1	9	4	76·1	49·7	26·4	22·6
1	7	4	74·5	99·6	−25·1	−20·9
1	7	1	55·5	35·0	20·6	24·1
1	5	1	229·0	265·8	−36·8	−36·0
1	3	2	142·7	108·7	34·0	28·6
1	3	1	180·7	202·9	−22·2	−27·1
1	2	1	32·5	12·5	20·0	20·8
2	2	4	90·1	74·0	16·1	15·4
2	6	2	75·3	91·6	−16·3	−16·3
2	9	1	59·1	76·7	−17·6	−17·5
3	3	1	228·2	200·3	27·9	29·0
4	2	1	160·7	175·0	−14·3	−15·1
4	4	3	83·7	62·3	21·4	26·7
4	4	1	194·9	170·7	24·2	27·2
4	9	2	99·3	77·4	21·9	20·0
5	11	2	119·3	137·9	−18·6	−23·8
6	11	2	119·5	103·3	16·2	15·5
7	8	3	69·9	50·5	19·4	17·1

Further refinement of this model by least-squares methods gave, at convergence, R 0·101 and R' 0·131 {where $R' = \sqrt{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]}$}, and the standard deviation of an observation of unit weight was 1·06.

Anisotropic thermal parameters were assumed only for the iodine atoms and one of the molecules of water of hydration was assumed to be present with only half occupancy because of its large thermal parameter when complete occupancy was assumed.

A final three-dimensional difference electron-density map showed no structurally significant features and no convincing evidence of the presence of hydrogen atoms.

Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20607 (3 pp., 1 microfiche).† Four strong, low-order reflections which seemed to be affected by secondary extinction were omitted from the final cycles of the refinement. The scattering functions used were those for the neutral atoms.[8] The weighting scheme used was based on counting statistics with some allowance for the presence of errors of a non-statistical nature in the measurement of the stronger intensities.[9] All calculations were carried out on the XDS Sigma 2 computer used to control the diffractometer, with programs written in this laboratory.

RESULTS AND DISCUSSION

The atomic parameters defining the crystal structure of (Ib) are given, together with their estimated standard deviations,[10] in Table 2.

TABLE 2

Positional parameters, given as fractions of the cell edges ($\times 10^4$), and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
I(1)	3344(1)	8594(1)	5975(4)	*
I(2)	2365(2)	563(1)	735(5)	*
C(1)	4383(16)	6012(9)	2135(39)	4·9(7)
C(2)	4636(11)	6110(7)	3678(30)	2·5(5)
C(3)	5383(13)	6102(8)	3752(34)	3·6(6)
C(4)	5701(13)	5651(8)	3397(33)	3·3(6)
C(5)	5356(15)	5486(9)	2016(38)	4·8(7)
C(6)	5706(13)	5229(8)	1035(37)	3·9(6)
C(7)	5421(12)	5020(7)	−328(29)	2·5(5)
C(8)	4640(13)	4978(8)	−476(33)	3·5(6)
C(9)	4339(12)	5422(8)	1710(31)	2·8(5)
C(10)	4581(11)	5553(7)	1790(28)	1·9(5)
C(11)	3578(13)	5371(8)	340(33)	3·4(6)
C(12)	3216(10)	4974(7)	1004(29)	1·7(4)
C(13)	3529(11)	4597(7)	45(28)	2·0(5)
C(14)	4294(11)	4588(7)	303(30)	2·4(5)
C(15)	4507(12)	4164(8)	−622(32)	3·1(6)
C(16)	3922(12)	3865(8)	−195(32)	2·6(5)
C(17)	3319(12)	4149(8)	470(31)	3·0(5)
C(18)	3339(15)	4686(10)	−1680(37)	5·1(7)
C(19)	4489(13)	5763(8)	−1123(34)	3·8(6)
C(20)	2643(14)	3983(9)	98(35)	3·9(6)
C(21)	2035(13)	4256(8)	781(36)	3·7(6)
C(22)	2555(12)	3519(8)	925(34)	3·8(6)
C(23)	2537(12)	3514(8)	2521(31)	3·0(6)
C(24)	2314(12)	3132(8)	3160(32)	3·0(6)
C(25)	2148(15)	3110(10)	4921(37)	4·7(7)
C(26)	1401(14)	3046(9)	5123(34)	4·1(6)
C(27)	2612(15)	2731(10)	5622(39)	5·5(7)
C(28)	6483(16)	5664(10)	3425(40)	5·6(8)
C(29)	5501(15)	5330(10)	4721(38)	4·9(7)
C(30)	4521(13)	4528(8)	1977(33)	3·3(6)
C(31)	4625(14)	3277(9)	648(40)	4·3(6)
C(32)	4945(13)	3163(8)	2163(33)	3·3(8)
C(33)	4496(12)	2896(7)	3066(30)	2·4(5)
C(34)	4247(12)	2477(8)	2116(31)	2·8(5)
C(35)	3854(13)	2655(8)	822(36)	4·0(6)
C(36)	3640(14)	2287(9)	−233(36)	4·0(6)
C(37)	5583(17)	3508(10)	3940(44)	6·7(8)

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† See note about Supplementary Publications in Notice to Authors, No. 7 in *J. Chem. Soc.* (*A*), Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, p. 215.

[7] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, 1951, **168**, 271; J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781; W. C. Hamilton, *ibid.*, 1965, **18**, 502.

[8] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1969, **B,25**, 374.

[9] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, **B,25**, 374.

[10] L. I. Hodgson and J. S. Rollett, *Acta Cryst.*, 1963, **16**, 329.

TABLE 2 (*Continued*)

Atom	x	y	z	$B/\text{Å}_2$
C(38)	5619(21)	3939(13)	4919(53)	8·6(9)
C(39)	3767(15)	7973(10)	5893(42)	5·3(7)
C(40)	4125(16)	7807(10)	7020(42)	5·3(8)
C(41)	4408(15)	7403(9)	6770(38)	4·7(7)
C(42)	4171(13)	7168(9)	5568(37)	4·0(7)
C(43)	3757(14)	7302(9)	4451(38)	4·6(7)
C(44)	3473(16)	7752(11)	4501(42)	5·9(8)
C(45)	4442(14)	6692(9)	5382(38)	4·7(7)
C(46)	2920(18)	1072(11)	6343(47)	7·0(9)
C(47)	3554(17)	1157(11)	7017(45)	6·4(8)
C(48)	3935(17)	1491(11)	6328(42)	6·4(8)
C(49)	3656(13)	1686(8)	4944(33)	5·7(6)
C(50)	3054(15)	1591(10)	4427(42)	5·5(8)
C(51)	2652(16)	1251(11)	5172(42)	6·2(8)
C(52)	4131(10)	1980(7)	4180(30)	2·2(5)
O(2)	4424(9)	6564(6)	4018(24)	4·7(4)
O(3)	5782(9)	6388(6)	3923(24)	5·3(5)
O(11)	3183(9)	5675(6)	16(23)	4·7(4)
O(16)	4083(8)	3563(5)	1050(20)	3·4(3)
O(20)	2490(10)	3923(6)	−1457(24)	5·1(5)
O(22)	2492(9)	3218(6)	2(22)	4·4(4)
O(25)	2388(9)	3474(6)	5697(25)	5·3(4)
O(31)	4350(9)	2901(6)	−32(23)	4·6(4)
O(32)	5101(9)	3535(6)	2985(24)	5·0(4)
O(33)	4314(9)	2942(5)	4333(24)	4·3(4)
O(34)	3837(8)	2224(5)	3115(22)	3·7(4)
O(35)	5961(12)	3208(8)	4336(34)	8·2(7)
O(45)	4688(10)	6506(6)	6436(25)	5·9(5)
O(52)	4730(9)	2012(6)	4431(23)	4·3(4)
$H_2O(1)$	3841(12)	3768(8)	5617(33)	8·2(7)
$H_2O(2)$	3258(17)	4514(11)	4448(43)	3·9(8)

* The iodine atoms were assigned anisotropic thermal parameters in the form: $\exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$; the values of β_{ij} ($\times 10^4$) given in that order are:

I(1)	64(1)	9(0)	368(7)	5(1)	33(3)	−12(1)
I(2)	104(2)	19(0)	381(8)	−24(8)	−4(4)	33(2)

A view of the molecule as found in the crystal, and in the correct absolute configuration with respect to a right-handed axial system, is shown in Figure 1. Bond lengths, bond angles, and torsion angles in the cucurbitacin glycoside part of the molecule are shown in Figure 2. The dimensions of the two *p*-iodobenzoate residues are not given, but both groups are planar within the limits of error, and the mean C–C distance is 1·40(5) Å. These geometrical parameters lead directly to the chemical structure and stereochemistry for (Ib) and hence for datiscoside itself (Ia).

A realistic estimate of the accuracy of the determination is given by the root-mean-square deviation from the mean C–C single-bond distance of 1·55 Å.[11] This deviation is 0·05 Å, compared to the estimated standard deviations of 0·03—0·04 Å calculated when the parameter errors of Table 2 are used. The error in a C–C–C bond angle is, likewise, probably closer to 3° than to the estimates of 2—2·5° obtained from the errors given in Table 2. Within these limits of error the molecule shows no unusual geometric features.

Datiscoside has been identified chemically[1] as a glycoside of cucurbitacin D (II), and because of the known relationships between the cucurbitacins[12] this *X*-ray analysis resolves several outstanding problems in the stereochemistry of these compounds.

The equations of the least-squares mean planes through the atoms of the rings and the side chain at C(17) are given in Table 3, which together with the torsion angles

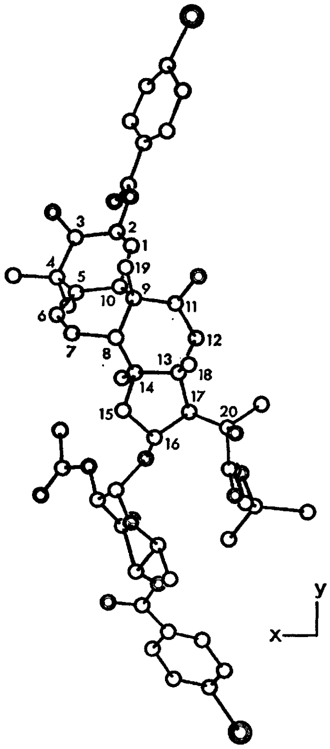

FIGURE 1 View of the molecular structure of datiscoside bis-(*p*-iodobenzoate) as found in the crystal. Oxygen atoms are indicated by double circles and iodine atoms by larger circles. The molecule is shown in its correct absolute configuration with respect to a right-handed axial system

TABLE 3

Least-squares mean planes through various groups of atoms

(*a*) Coefficients are given for the normalized equations in the form $aX + bY + cZ = d$, where X, Y, and Z are in Å with respect to the cell axial system.

Plane	a	b	c	d
(1) Ring *A*	−0·3975	−0·5832	0·7092	−12·8363
(2) Ring *B*	−0·2463	−0·7572	0·6050	−14·6370
(3) Ring *C*	0·2899	−0·0410	0·9562	1·7847
(4) Ring *D*	0·2519	−0·1422	0·9573	0·0215
(5) Sugar	−0·7840	0·5544	0·2792	−1·3913
(6) Side-chain	0·9799	−0·1572	0·1229	3·2236

(*b*) Deviations (Å)

(1) C(1) 0·28, C(2) −0·30, C(3) 0·22, C(4) −0·14, C(5) 0·15, C(10) −0·20

(2) C(5) −0·04, C(6) 0·04, C(7) 0·12, C(8) −0·28, C(9) 0·29, C(10) −0·14

(3) C(8) 0·19, C(9) −0·12, C(10) 0·16, C(12) −0·24, C(13) 0·33, C(14) −0·32

(4) C(13) 0·30, C(14) −0·30, C(15) 0·18, C(16) −0·03, C(17) −0·15

(5) C(31) −0·16, C(32) 0·16, C(33) −0·24, C(34) 0·30, C(35) −0·30, O(31) 0·24

(6) C(20) 0·11, C(22) −0·04, O(22) 0·02, C(23) −0·18, C(24) −0·01, C(25) 0·11

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[11] A. McL. Mathieson, *Perspectives in Structural Chemistry*, 1967, **1**, 44.

[12] D. Lavie, Y. Shvo, D. Willner, P. R. Enslin, J. M. Hugo, and K. B. Norton, *Chem. and Ind.*, 1959, 951.

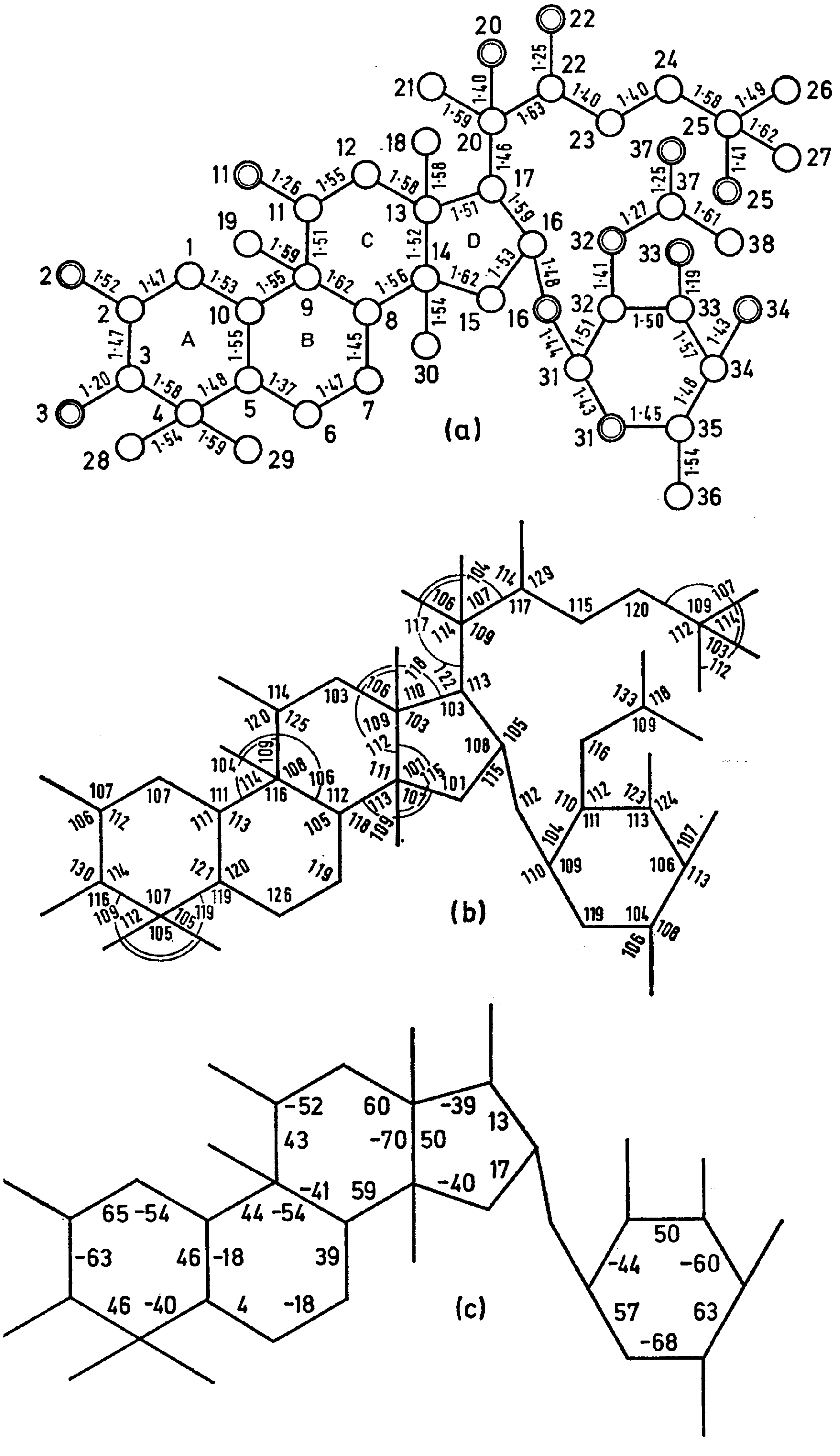

FIGURE 2 (a) Bond lengths in the cucurbitacin glycoside part of the molecule showing the numbering scheme for the atoms. The *p*-iodobenzoate residues contain atoms C(39) through C(52), O(45), and O(52). (b) Bond angles in the same region of the molecule. (c) Torsion angles about the bonds in the rings in the cucurbitacin glycoside region. The sequence of angles is counter-clockwise around a given ring. A torsion angle is taken as positive for the angle *A*–*B*–*C*–*D* when the view is down *B*–*C* with *A* above *D* and a clockwise rotation of *A* is required to eclipse *C*–*D*

(Figure 2) and the Newman projections about the bonds at the ring junctions (Figure 3) give a precise definition of the molecular stereochemistry.

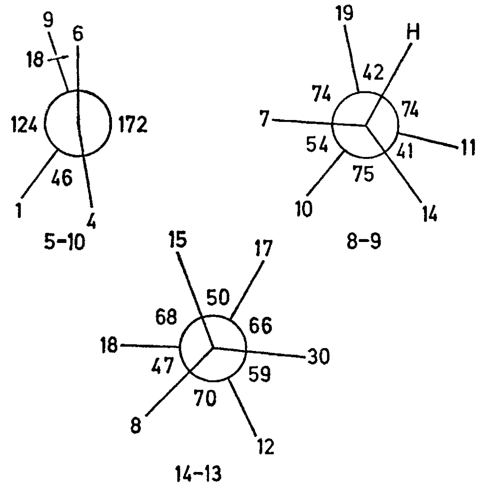

FIGURE 3 Newman projections showing the arrangement of substituent atoms about the bonds at the junctions of the rings in the steroidal nucleus

Ring A is in a flattened chair conformation.[13] This arrangement involves 1,3-diaxial interactions between the 4α-methyl group and the 2α- and 10α-hydrogen atoms, as well as an eclipsed arrangement of the 4β-methyl group and the hydrogen atom at C(6).

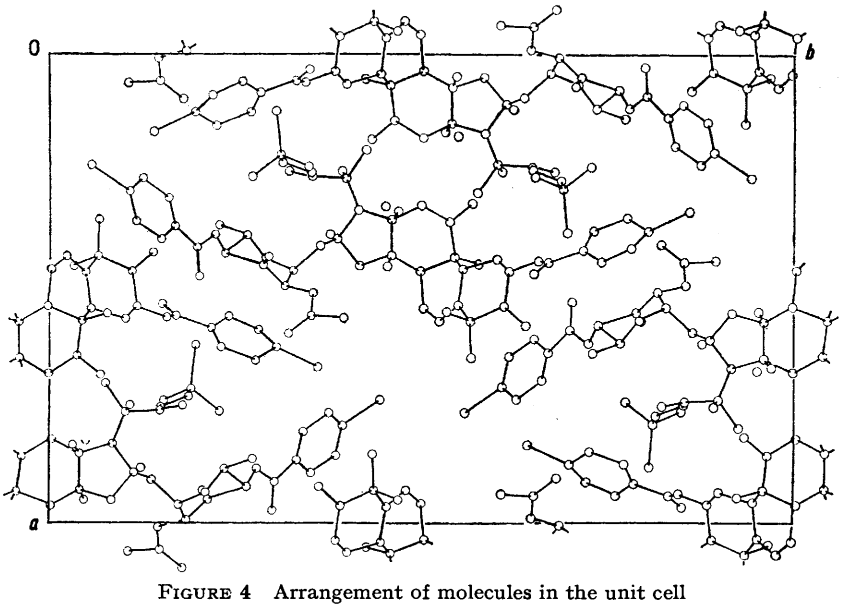

FIGURE 4 Arrangement of molecules in the unit cell

The oxygen atom at C(2) has a β-configuration. A correct assignment of the configuration of the substituent at C(2) in dihydrocucurbitacin was made[3a] on the basis of the n.m.r. signal of the C(2) proton, but the opposite configuration has also been suggested on the basis of c.d. experiments.[3b] A corresponding signal to that described in ref. 3*a* appears in the n.m.r. spectrum of datiscoside diacetate[1] so that this *X*-ray study unambiguously establishes the configuration for the C(2) substituent in the cucurbitacins, and the results of the c.d. experiments must be re-interpreted.

The $2\beta,3\beta$-diol configuration[4] in cucurbitacins O, P, and Q is also confirmed by this *X*-ray study, in view of the demonstrated *cis*-configuration of their 2,3-diol system, and of their inter-relation with cucurbitacin B, which, in turn, has been correlated with cucurbitacin D.[12,14]

The cyclohexene ring B has a half-chair conformation very close to the theoretical minimum-energy conformation of type 6f of Bucourt and Hainaut.[15] Both C(5) and C(10) are involved in close approaches to the 14α-methyl group (3·43 and 3·23 Å).

Ring C has a chair conformation[13] somewhat flattened to relieve stress from interactions between the 14α-methyl group, C(5), and the 10α-hydrogen atom.

Ring D is in a half-chair conformation[15] very similar to that found in 3α-hydroxy-5α-androstan-17-one[16] and that in 4-bromo-$9\beta,10\alpha$-pregna-4,6-diene-3,20-dione.[17] The fusion of rings C and D to form a *trans*-hydrindane is very similar to the theoretical model of Bucourt and Hainaut.[15] The opening of the C(13)–C(14) torsion angle in ring C to 70°, and the corresponding closure of the corresponding torsion angle in ring D to 50°, especially confirms the goodness of the model.[15] The fusion of rings B and C is cisoid, with a β-configuration for both the hydrogen atom at C(8) and the methyl group at C(9). The stereochemistry at the ring junctions is illustrated

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[13] H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 1967, **23**, 439.

[14] S. M. Kupchan, R. M. Smith, Y. Aynehchi, and M. Maruyama, *J. Org. Chem.*, 1970, **35**, 2891.

[15] R. Bucourt and D. Hainaut, *Bull. Soc. chim. France*, 1965, 1366.

[16] D. F. High and J. Kraut, *Acta Cryst.*, 1966, **21**, 88.

[17] C. Romers, B. Hesper, E. van Heijkoop, and H. J. Geise, *Acta Cryst.*, 1966, **20**, 363.

by the Newman projections (Figure 3). Overall, the steroidal nucleus has a folded conformation.

The β-configuration of the oxygen atom at C(20) in the side-chain has previously been assigned only on biogenetic grounds,[2] but is now confirmed unambiguously by this *X*-ray work.

The glycoside residue (16α) is a novel sugar, 2-*O*-acetyl-6-deoxy-α-L-*gluco*-hex-3′-ulopyranoside.[18] The aldohexose ring is in a chair conformation with both the 2-acetoxy-group [at C(32)] and the 6-methyl group [at C(35)] equatorial.

Molecular Packing.—A view of the arrangement of molecules within the unit cell is shown in Figure 4. Shorter interatomic approach distances between molecules are listed in Table 4. The O · · · O separations are within the range of such distances associated with hydrogen bonding, but in the absence of any definite identification of hydrogen atom positions the actual pattern of hydrogen bonding, if any, is unclear.

The hydroxy-oxygen, O(25), and the ketonic oxygen, O(11), of a neighbouring molecule are 2·96 Å apart, and the angles O(25) · · · O(11)–C(11) and O(11) · · · O(25)–C(25) are 151 and 121°. This geometry suggests a suitable orientation for a weak hydrogen bond. However, a similar geometry exist for O(25) and the ketonic O(20) of a neighbouring molecule with O · · · O 2·87 Å and the angle C(25)–O(25) · · · O(20) 147°. This geometry is less favourable for hydrogen-bond formation.

The $H_2O(1)$ · · · O(33)–C(33), $H_2O(1)$ · · · O(28)–C(28), and $H_2O(2)$ · · · O(11)–C(11) angles of 128, 124, and 118°, with corresponding O · · · O separations of 2·98, 3·00, and 2·93 Å, suggest additional weak hydrogen bonding. The two water molecules may also be hydrogen bonded one to another.

TABLE 4

Selected shorter intermolecular contacts (Å)

C(18) · · · O(20^{I})	3·43	O(11) · · · O(25^{IV})	2·96
C(19) · · · O(17^{I})	3·19	O(11) · · · $H_2O(2^{IV})$	2·93
C(27) · · · O(27^{II})	3·31	O(20) · · · O(25^{I})	2·87
C(34) · · · O(3^{III})	3·55	O(25) · · · $H_2O(1)$	3·00
C(36) · · · O(3^{III})	3·26	$H_2O(1)$ · · · $H_2O(2)$	2·81
		$H_2O(1)$ · · · O(33)	2·98

Roman numerals as superscripts refer to the following transformation relative to the reference molecule at x, y, z:

I $x, y, z - 1$
II $x - 0{\cdot}5, 0{\cdot}5 - y, 1 - z$
III $1 - x, y - 0{\cdot}5, 0{\cdot}5 - z$
IV $0{\cdot}5 - x, 1 - y, z - 0{\cdot}5$

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[18] For sugar nomenclature see 'The Carbohydrates,' eds. W. Pigman and D. Horton, Academic Press, New York, 2nd edn., 1970, vol. IIB, pp. 809—833.