

precession display suffers from ripples caused by series termination effects. However, if a precession angle of 15° were practical, this would allow the use of terms up to a resolution of 3 \AA which would result in map of much higher quality. We are exploring modifications necessary to make this feasible.

The real virtue of this electronic precession method is the rapid display, measurement and indexing of selected reflections with a reasonable allowance for crystal misalignment. Simulated precession images are displayed after 5 to 10 min of exposure. This allows the data collector to make a more informed judgement about the nature of a crystal, especially when heavy-atom derivatives are involved, before deciding to proceed with actual data collection. An occasional problem is the difficulty of finding a major axis with crystals of irregular morphology. We are investigating methods to align crystals in random orientations with only the benefit of their cell parameters as are other groups (Messerschmidt & Pflugrath, 1987). When this becomes practical, the time required to evaluate a heavy-atom-derivative crystal may approach the time it takes to mount a trial crystal.

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Structure of the Naturally Occurring Iridoid Glycosides 3,4-Dihydrounedoside Pentaacetate, $C_{24}H_{32}O_{14}$, and Pulchellose II Hydrate, $C_{17}H_{26}O_{12} \cdot H_2O$

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Abstract

3,4-Dihydrounedoside pentaacetate [compound (1)], 6-(acetoxy)octahydrooxireno[4,5]cyclopenta[1,2-*c*]pyran-2-yl- β -D-glucopyranoside tetraacetate, $C_{24}H_{32}O_{14}$, $M_r = 544.51$, orthorhombic, $P2_12_12_1$, D_m (floatation) = 1.3 Mg m^{-3} , $Z = 4$; at room temperature: $a = 34.217$ (9), $b = 10.822$ (5), $c = 7.572$ (3) \AA , $V = 2804$ (3) \AA^3 ; at 140 K: $a = 33.565$ (11), $b = 10.754$ (4), $c = 7.540$ (2) \AA , $V = 2722$ (3) \AA^3 , $D_x = 1.329 \text{ Mg m}^{-3}$, Ni-filtered $Cu K\alpha$, $\lambda = 1.5418 \text{ \AA}$, $\mu = 9.028 \text{ cm}^{-1}$, $F(000) = 1152$, $R = 0.040$ for 1896 observed reflections. In the iridoidal ring system the six-membered ring has a chair conformation and the five-membered ring an envelope conformation. Bridgehead H atoms, an acetoxy group and the epoxy group, all lie on the same side of the five-membered ring. Pulchellose II hydrate [compound (2)], methyl 1-(β -D-glucopyranosyloxy)-4a,5,6-trihydroxy-7-methyl-

1,4a,5,6,7,7a-hexahydrocyclopenta[*c*]pyran-4-carboxylate monohydrate, $C_{17}H_{26}O_{12} \cdot H_2O$, $M_r = 440.40$, orthorhombic, $P2_12_12_1$, $D_m = 1.4 \text{ Mg m}^{-3}$, $Z = 4$, $a = 26.943$ (6), $b = 9.235$ (4), $c = 7.902$ (4) \AA , $V = 1966$ (2) \AA^3 , $D_x = 1.488 \text{ Mg m}^{-3}$, Ni-filtered $Cu K\alpha$, $\lambda = 1.5418 \text{ \AA}$, $\mu = 10.697 \text{ cm}^{-1}$, $F(000) = 936$ at room temperature, $R = 0.035$ for 1921 observed reflections. In the iridoidal ring system the double bond flattens the six-membered ring to an envelope conformation. The non-H substituents and the only bridgehead H atom are all on the same side of the five-membered ring. The presence of the D-glucose ring, a 4C_1 chair in both structures, helped to determine the absolute configuration of the molecules.

Introduction

Chemotaxonomic studies are becoming increasingly important in the classification of plants. A charac-

teristic of the plants of the family Verbenaceae is the presence of compounds containing the bicyclic iridoid system. Both of the iridoid glucosides presented here were extracted from wild flowering plants of the family Verbenaceae. Chemical analyses and NMR studies on unedoside and closely related derivatives were conducted by Geisman, Knaak & Knight (1966) and also by Rimpler & Pistor (1974). Fig. 1 explains the resulting structural problem: the two research groups proposed different stereoisomers for unedoside, (a) being suggested by Geisman *et al.* and (b) by Rimpler & Pistor.

The X-ray structure analysis was undertaken on compound (1) to determine which of the two proposed structures, (a) or (b), is the correct one.

Pulchellosides I and II (Fig. 2) were isolated and characterized by Milz & Rimpler (1979). The X-ray analysis of pulchelloside II was intended to prove the correctness of the proposed stereoisomers and thereby examine the reliability of noncrystallographic methods for determining the stereochemistry of complex ring systems precisely.

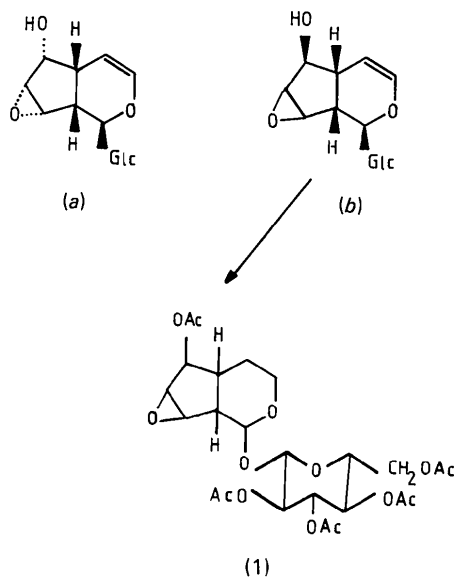


Fig. 1. Hypothetical stereoisomers for unedoside according to Geisman, Knaak & Knight (1966) (a) and Rimpler & Pistor (1974) (b); the unedoside of the present investigation (1).

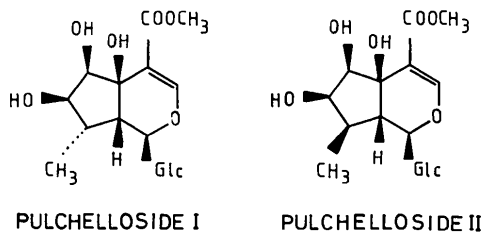


Fig. 2. Pulchelloside I and II as characterized by Milz & Rimpler (1979).

Experimental

The wild flower *Arbutus unedo* found near Delphi, Greece, is the plant source of unedoside. Pulchellosides I and II were obtained from *Verbena pulchella*, a South African wild flower chemically and morphologically related to the popular garden flower *Verbena*.

Unedoside and pulchelloside were extracted from dried, ground plant material with a hot ethanol-water mixture and isolated through column chromatography (Rimpler & Pistor, 1974; Milz & Rimpler, 1979). Compound (1) was obtained from unedoside by hydrogenation of the double bond and subsequent acetylation of all the hydroxyl groups. Both compounds (1) and (2) form colorless crystals.

Compound (1), 3,4-dihydrounedoside pentaacetate

A crystal approximately $0.2 \times 0.25 \times 0.6$ mm was used for the investigation. Data were first collected at room temperature and the structure solved and refined. Large thermal parameters, especially for the acetate groups, necessitated recollection of the data at low temperature. Of the 2022 reflections collected, 124 with intensities $I < 2\sigma(I)$ were termed unobserved. Ranges of the data are h 0–36, k 0–11 and l 0–7, $[(\sin\theta)/\lambda]_{\max} = 0.54 \text{ \AA}^{-1}$. Reflections 503 and 554 were rejected at the refinement stage because inspection of their profiles indicated errors in their measurement. Unit-cell dimensions were determined from 31 centered reflections in the range $36 < 2\theta < 47^\circ$. Data were collected with the ω - 2θ -scan method on a Stoe four-circle diffractometer. Low temperature was maintained with an N₂ gas-stream apparatus designed by Dietrich & Dierks (1970). The data were corrected for absorption with the Gaussian integration method of Busing & Levy (1957) using the program *ABSORB* of the *XTAL* (Stewart & Hall, 1986) program system. Factor A in $I_{\text{corr}} = (1/A)I_{\text{obs}}$ varied between 0.78 and 0.86. The mean path length for each reflection provided by the absorption program was used for extinction correction. The extinction factor for calculated structure factors varied between 1.0 and 0.88. The room-temperature structure was solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and the atom coordinates obtained served as starting set for the structure refinement of the low-temperature structure. Full-matrix least-squares refinement with the *SFLSX* program of the *XTAL* system minimized $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma(F_o)$ corresponding to $\sigma(I)$ from counting statistics.

Most H atoms were found from difference Fourier syntheses; six were calculated. Methyl H atoms were held fixed; non-methyl H atoms were refined isotropically, all other atoms anisotropically to final agreement factors $R = 0.040$ and $wR = 0.032$. In the final refinement cycle the maximum shift/e.s.d. was 0.06. The greatest residual electron density was

0.18 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Compound (2), pulchelloside II hydrate

Of the 1931 unique reflections measured for a crystal of approximate size 0.5 × 0.2 × 0.1 mm, 1921 with $I > 2\sigma(I)$ were used in the refinement. Unit-cell dimensions were determined from 18 centered reflections in the range $16 < 2\theta < 45^\circ$. Data were collected on a Stoe four-circle diffractometer to maximum $(\sin\theta)/\lambda = 0.564 \text{ \AA}^{-1}$ in the index ranges h 0–30, k 0–11 and l 0–10. No absorption or extinction corrections were applied. The structure was solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement with the *CRYLSQ* program of the *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) system minimized $\sum w(|F_o| - |F_c|)^2$ using $1/\sigma$ weights. The H atoms, all of which were found in difference Fourier syntheses, were refined isotropically, all other atoms anisotropically. The final agreement factors were $R=0.035$ and $wR=0.033$, max. (shift/e.s.d.) = 0.3; the greatest residual density in the final difference synthesis was 0.16 e Å⁻³.

Discussion

Coordinates and thermal parameters for compounds (1) and (2) are given in Tables 1 and 2.* The atom labels and bond angles and bond lengths are given in Figs. 3–6. Fig. 7 presents stereoviews of the molecules of the two compounds.

Most bond lengths and angles in both compounds are in the expected range. The shortest C–C bond in compound (1) is C(7)–C(8) of the epoxy ring [1.464 (8) Å]. This bond is still longer than the 1.438 (4) Å found in the unsubstituted three-membered-ring ethylene oxide (Luger, Zaki, Buschmann & Rudert, 1986). The bond angles in both the substituted and unsubstituted triangular ring are between 59.5 and 60.5°.

In compound (2) the short bond C(4)–C(41), 1.476 (5) Å, is the result of resonance, *i.e.*, partial conjugation in the atom sequence O(41)–C(41)–C(4)–C(3)–O(2). The unusually long bond C(5)–C(6), 1.581 (5) Å, is the result of repulsion between the O atoms O(5) and O(6), since they are almost eclipsed, [O(5)–C(5)–C(6)–O(6) = 10.8 (4)°]. This repulsion cannot be relieved because of the structural rigidity at C(5), the most highly strained part of the molecule.

* Lists of structure factors, bond lengths and angles, torsional angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44538 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters (U_{eq} and U in Å² × 10²) of 3,4-dihydroenedoside pentacetate at 140 K

U_{eq} values were calculated according to Hamilton (1959).

	x	y	z	U_{eq}/U
C(1)	0.8143 (1)	0.1792 (4)	0.2835 (7)	3.8 (2)
H(1)	0.827 (1)	0.236 (3)	0.175 (6)	2. (1)
O(2)	0.8140 (1)	0.0515 (3)	0.2364 (5)	4.2 (1)
C(3)	0.7896 (1)	0.0357 (5)	0.0803 (8)	4.2 (2)
H(31)	0.791 (1)	–0.066 (4)	0.037 (6)	4. (1)
H(32)	0.803 (9)	0.087 (3)	–0.016 (5)	1. (1)
C(4)	0.7467 (2)	0.0652 (5)	0.1224 (8)	3.9 (2)
H(41)	0.736 (1)	0.008 (4)	0.200 (6)	2. (1)
H(42)	0.729 (1)	0.057 (5)	0.005 (8)	6. (2)
C(5)	0.7419 (1)	0.1931 (4)	0.2072 (7)	3.4 (2)
H(5)	0.715 (9)	0.202 (3)	0.272 (5)	0.9 (9)
C(6)	0.7447 (1)	0.3061 (5)	0.0829 (7)	3.7 (2)
H(6)	0.768 (1)	0.290 (3)	–0.020 (6)	2. (1)
C(7)	0.7552 (2)	0.4124 (4)	0.2003 (8)	4.2 (2)
H(7)	0.757 (1)	0.501 (4)	0.150 (6)	4. (1)
O(10)	0.7331 (1)	0.4126 (3)	0.3663 (5)	4.6 (1)
C(8)	0.7731 (1)	0.3616 (4)	0.3620 (8)	4.1 (2)
H(8)	0.792 (1)	0.412 (4)	0.434 (6)	4. (1)
C(9)	0.7737 (1)	0.2215 (4)	0.3500 (7)	3.2 (2)
H(9)	0.767 (1)	0.174 (4)	0.451 (6)	2. (1)
O(6)	0.7074 (1)	0.3263 (3)	–0.0081 (5)	4.5 (1)
C(61)	0.7059 (2)	0.2897 (5)	–0.1796 (7)	4.4 (2)
O(61)	0.7333 (1)	0.2460 (3)	–0.2593 (5)	5.5 (1)
C(62)	0.6655 (2)	0.319 (1)	–0.257 (1)	8.3 (4)
H(621)	0.650 (3)	0.395 (9)	–0.18 (2)	23. (6)
H(622)	0.651 (2)	0.245 (5)	–0.23 (1)	10. (3)
H(623)	0.662 (2)	0.311 (7)	–0.37 (1)	11. (3)
O(1)	0.8417 (1)	0.1934 (3)	0.4266 (4)	3.9 (1)
C(10)	0.8809 (1)	0.1917 (4)	0.3703 (8)	4.0 (2)
H(10)	0.887 (1)	0.119 (4)	0.283 (6)	3. (1)
C(20)	0.9074 (1)	0.1795 (4)	0.5319 (8)	3.9 (2)
H(20)	0.899 (1)	0.243 (3)	0.618 (6)	2. (1)
O(20)	0.9014 (1)	0.0556 (3)	0.6033 (6)	4.5 (1)
C(210)	0.8874 (2)	0.0467 (6)	0.773 (1)	6.3 (3)
O(210)	0.8814 (2)	0.1321 (4)	0.8649 (7)	11.0 (3)
C(220)	0.8816 (2)	–0.0864 (6)	0.820 (1)	8.4 (3)
H(2210)	0.862 (0)	–0.125 (0)	0.738 (0)	10. (3)
H(2220)	0.908 (0)	–0.132 (0)	0.811 (0)	7. (2)
H(2230)	0.871 (0)	–0.094 (0)	0.945 (0)	22. (5)
C(30)	0.9510 (1)	0.1894 (5)	0.4767 (7)	3.9 (2)
H(30)	0.964 (1)	0.106 (4)	0.424 (8)	8. (2)
O(30)	0.9749 (1)	0.2074 (3)	0.6325 (5)	4.7 (1)
C(310)	0.9956 (2)	0.1099 (6)	0.6992 (9)	5.5 (2)
O(310)	0.9933 (1)	0.0072 (4)	0.6399 (6)	6.6 (2)
C(320)	1.0202 (2)	0.1527 (6)	0.8548 (9)	7.0 (2)
H(3210)	1.039 (0)	0.220 (0)	0.814 (0)	13. (3)
H(3220)	1.002 (0)	0.189 (0)	0.948 (0)	17. (4)
H(3230)	1.035 (0)	0.082 (0)	0.904 (0)	11. (3)
C(40)	0.9589 (1)	0.3004 (5)	0.3585 (8)	4.2 (2)
H(40)	0.960 (2)	0.373 (5)	0.427 (9)	8. (2)
O(40)	0.9980 (1)	0.2808 (3)	0.2820 (5)	4.6 (1)
C(410)	1.0246 (1)	0.3745 (5)	0.2920 (8)	4.7 (2)
O(410)	1.0173 (1)	0.4741 (4)	0.3500 (7)	6.7 (2)
C(420)	1.0642 (2)	0.3328 (7)	0.220 (1)	6.0 (3)
H(4210)	1.074 (2)	0.260 (6)	0.24 (1)	12. (3)
H(4220)	1.062 (2)	0.330 (8)	0.10 (1)	15. (4)
H(4230)	1.092 (1)	0.398 (5)	0.227 (8)	8. (2)
C(50)	0.9278 (1)	0.3095 (5)	0.2096 (8)	4.5 (2)
H(50)	0.931 (1)	0.242 (4)	0.115 (7)	5. (1)
O(50)	0.8892 (1)	0.3097 (3)	0.2914 (5)	4.3 (1)
C(60)	0.9313 (2)	0.4288 (6)	0.111 (1)	5.9 (2)
H(6010)	0.922 (1)	0.495 (4)	0.174 (8)	5. (2)
H(6020)	0.960 (2)	0.435 (5)	0.058 (8)	9. (2)
O(60)	0.9032 (1)	0.4217 (3)	–0.0346 (6)	6.3 (2)
C(610)	0.8923 (2)	0.5292 (6)	–0.110 (1)	6.4 (3)
O(610)	0.9050 (1)	0.6281 (4)	–0.0617 (7)	7.8 (2)
C(620)	0.8630 (3)	0.5071 (9)	–0.256 (1)	8.7 (4)
H(6210)	0.845 (2)	0.572 (6)	–0.25 (1)	11. (3)
H(6220)	0.881 (3)	0.51 (1)	–0.37 (2)	28. (7)
H(6230)	0.850 (2)	0.430 (6)	–0.23 (1)	10. (3)

The glycosidic linkage in compound (1) is equatorial at C(1) [C(3)–O(2)–C(1)–O(1) = 174.3 (4)°] and also at C(10) [C(50)–O(50)–C(10)–O(1) = 172.4 (4)°]. The anomeric torsion angles O(2)–C(1)–O(1)–C(10) = –77.2 (4)° and O(50)–C(10)–O(1)–C(1) = –76.3 (5)° show a minus *gauche* arrangement

Table 2. Atomic parameters (U_{eq} and U in $\text{\AA}^2 \times 10^3$) of pulchelloside II hydrate

U_{eq} values were calculated according to Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U
O(3)	0.7008 (1)	-0.0346 (3)	0.1592 (3)	3.4 (1)
H(311)	0.731 (1)	-0.038 (4)	0.112 (5)	5. (1)
H(312)	0.686 (2)	-0.116 (4)	0.153 (6)	9. (2)
C(11)	0.6275 (1)	-0.0893 (3)	0.5827 (4)	2.7 (1)
H(19)	0.643 (9)	-0.166 (3)	0.656 (3)	1.5 (7)
C(21)	0.6611 (1)	0.0431 (3)	0.5683 (4)	2.7 (1)
H(21)	0.643 (9)	0.110 (3)	0.497 (3)	1.4 (7)
O(21)	0.7080 (1)	0.0080 (3)	0.4992 (3)	3.7 (1)
H(201)	0.705 (1)	-0.007 (4)	0.400 (5)	6. (1)
C(31)	0.6695 (1)	0.1017 (3)	0.7461 (4)	2.9 (1)
H(31)	0.690 (9)	0.033 (3)	0.819 (3)	1.4 (7)
O(31)	0.6949 (1)	0.2385 (3)	0.7461 (4)	4.6 (1)
H(301)	0.707 (2)	0.250 (5)	0.669 (6)	10. (2)
C(49)	0.6213 (1)	0.1215 (3)	0.8416 (4)	2.7 (1)
H(41)	0.603 (9)	0.197 (3)	0.788 (3)	2.1 (8)
O(49)	0.6301 (1)	0.1554 (3)	1.0151 (3)	3.6 (1)
H(401)	0.651 (1)	0.104 (3)	1.043 (4)	3. (1)
C(51)	0.5870 (1)	-0.0089 (3)	0.8270 (4)	2.7 (1)
H(51)	0.603 (1)	-0.092 (3)	0.884 (4)	2.5 (8)
O(51)	0.5813 (1)	-0.0476 (2)	0.6509 (2)	2.7 (1)
C(61)	0.5362 (1)	-0.0210 (4)	0.8995 (5)	4.3 (1)
H(611)	0.511 (1)	-0.068 (3)	0.867 (4)	3.8 (9)
H(621)	0.539 (1)	0.030 (4)	1.044 (5)	7. (1)
O(61)	0.5181 (1)	0.1606 (3)	0.8567 (4)	5.1 (1)
H(601)	0.495 (2)	0.143 (6)	0.763 (8)	14. (2)
O(1)	0.6202 (1)	-0.1459 (2)	0.4198 (3)	2.9 (1)
C(1)	0.5848 (1)	-0.2597 (3)	0.4072 (4)	2.7 (1)
H(1)	0.550 (1)	-0.222 (3)	0.445 (3)	2.5 (8)
O(2)	0.5963 (1)	-0.3731 (2)	0.5264 (3)	3.1 (1)
C(3)	0.6347 (1)	-0.4606 (4)	0.4829 (4)	3.3 (1)
H(3)	0.648 (1)	-0.510 (3)	0.580 (4)	2.8 (8)
C(4)	0.6542 (1)	-0.4744 (3)	0.3307 (4)	2.8 (1)
C(41)	0.6974 (1)	-0.5723 (4)	0.3183 (5)	3.5 (1)
O(41)	0.7184 (1)	-0.6293 (3)	0.4353 (3)	5.5 (1)
O(42)	0.7120 (1)	-0.5905 (3)	0.1575 (3)	3.9 (1)
C(42)	0.7532 (2)	-0.6891 (5)	0.1320 (6)	4.9 (2)
H(421)	0.758 (1)	-0.696 (4)	-0.002 (5)	7. (1)
H(422)	0.783 (1)	-0.641 (4)	0.157 (6)	7. (1)
H(423)	0.745 (2)	-0.791 (5)	0.204 (6)	11. (2)
C(5)	0.6325 (1)	-0.4006 (3)	0.1777 (4)	2.6 (1)
O(5)	0.6680 (1)	-0.3083 (3)	0.0975 (3)	3.5 (1)
H(50)	0.686 (1)	-0.350 (4)	0.022 (5)	7. (1)
C(6)	0.6123 (1)	-0.5157 (4)	0.0467 (4)	3.3 (1)
H(6)	0.615 (1)	-0.614 (3)	0.113 (4)	3.6 (9)
O(6)	0.6405 (1)	-0.5167 (3)	-0.1054 (3)	4.1 (1)
H(60)	0.658 (1)	-0.592 (4)	-0.100 (5)	6. (1)
C(7)	0.5585 (1)	-0.4742 (4)	0.0111 (4)	3.4 (1)
H(7)	0.536 (1)	-0.562 (3)	-0.031 (4)	3.8 (9)
O(7)	0.5568 (1)	-0.3644 (3)	-0.1185 (3)	3.7 (1)
H(70)	0.581 (2)	-0.401 (6)	-0.193 (6)	11. (2)
C(8)	0.5411 (1)	-0.4066 (4)	0.1779 (4)	3.2 (1)
H(8)	0.539 (1)	-0.489 (3)	0.271 (4)	2.7 (8)
C(10)	0.4917 (1)	-0.3295 (5)	0.1676 (6)	4.4 (1)
H(11)	0.462 (1)	-0.401 (5)	0.138 (5)	8. (1)
H(12)	0.493 (1)	-0.251 (4)	0.077 (5)	7. (1)
H(13)	0.484 (1)	-0.301 (4)	0.286 (5)	5. (1)
C(9)	0.5858 (1)	-0.3127 (3)	0.2264 (4)	2.6 (1)
H(9)	0.585 (1)	-0.236 (3)	0.157 (4)	3.0 (9)

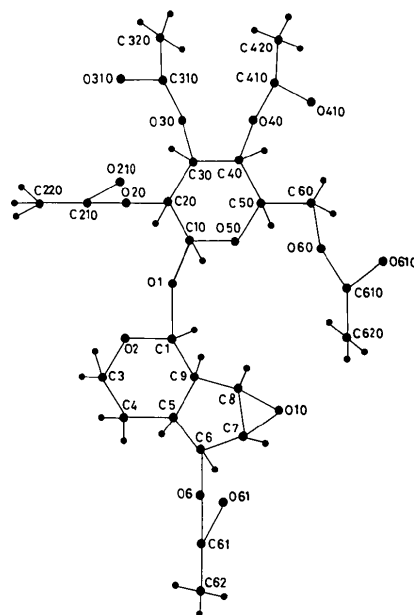


Fig. 3. Schematic drawing with atom labels of the molecule of 3,4-dihydroenedoside pentaacetate [compound (1)].

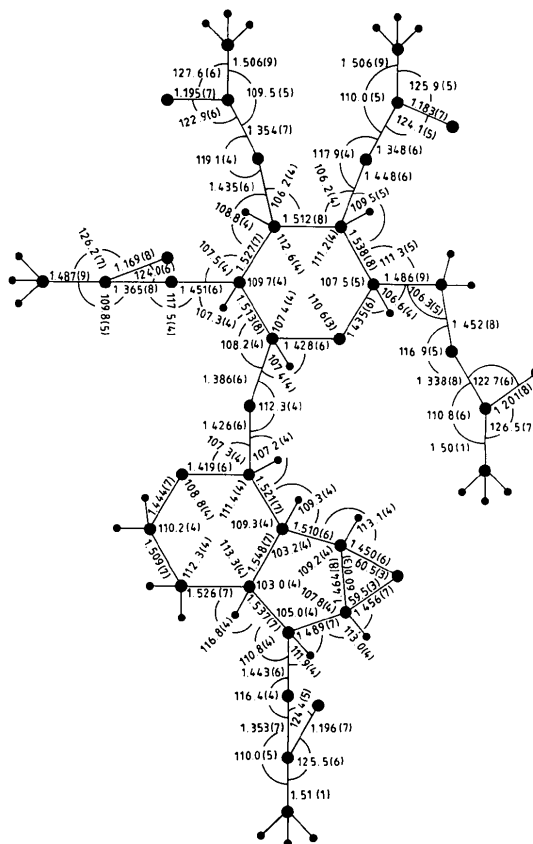


Fig. 4. Bond lengths (Å) and angles (°) of compound (1).

for the atom pairs $O(2)\cdots C(10)$ and $O(50)\cdots C(1)$. These are in the range generally found for equatorial glycosidic linkages (-80 to -70°) and close to the -70 to -60° predicted by theoretical calculations (Jeffrey & Taylor, 1980).

The glycosidic linkage in compound (2) is nearly axial at $C(1)$ [$C(3)-O(2)-C(1)-O(1) = -76.0(3)^\circ$], and equatorial at $C(11)$ [$C(51)-O(51)-C(11)-O(1) = 171.7(2)^\circ$], with anomeric torsion angles $O(2)-C(1)-O(1)-C(11) = -53.0(3)^\circ$ and $O(51)-C(11)-O(1)-C(1) = -53.5(3)^\circ$. The arrangement for $O(2)\cdots C(11)$ and $O(51)\cdots C(1)$ is also minus *gauche*, the preferred conformation for glycosidic linkages.

Ring configuration and conformation

Absolute configurations could be determined by the presence of the known absolute configuration of the naturally occurring D-glucose. The β -D-glucopyranose rings in both structures take up a nearly ideal 4C_1 chair conformation. Puckering parameters for all six-membered rings were calculated according to Cremer & Pople (1975) and are listed in Table 3.

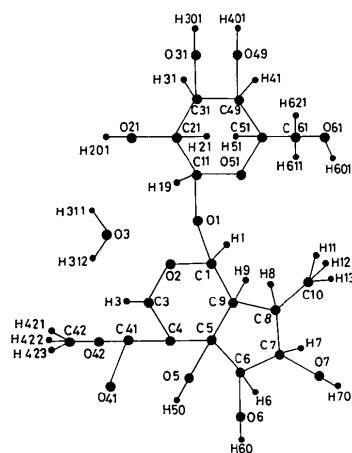


Fig. 5. Schematic drawing with atom labels of the molecule of pulchelloside II hydrate [compound (2)].

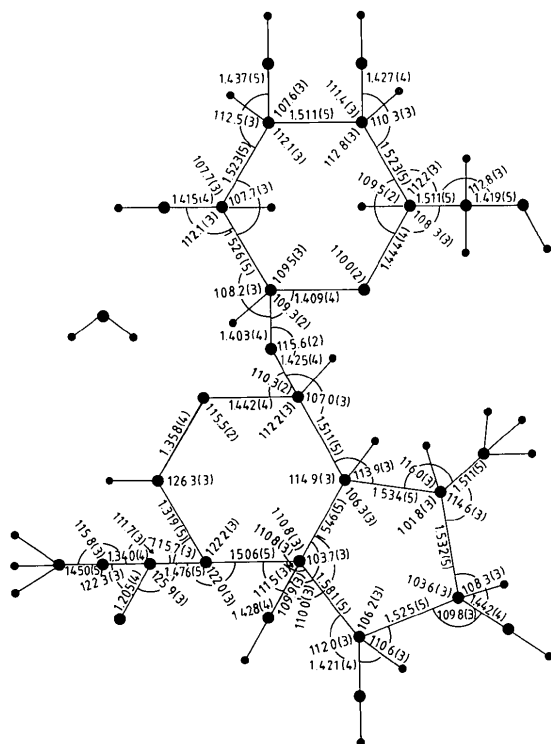


Fig. 6. Bond lengths (Å) and angles ($^{\circ}$) of compound (2).

Table 3. Puckering parameters for six-membered rings

	Total puckering Q (Å)	Position on conformational sphere ($^{\circ}$)		Designation
		φ	θ	
Tetrahydropyran ring of compound (1)	0.56	1	15	4C_1
Dihydropyran ring of compound (2)	0.391	253	123	1E
Bridged tetrahydropyran ring of compound (1)	1.074	0	74	${}^{3,0}B-E$
Glucose ring of compound (1)	0.553	7	34	4C_1
Glucose ring of compound (2)	0.586	12	12	4C_1

There are three rings to be considered in the iridoid moiety of compound (1). The first one is the tetrahydropyran ring that in clockwise numbering looking from 'above' [0 = O(2), 1 = C(1), 2 = C(9), 3 = C(5), 4 = C(4) and 5 = C(3)] takes on a 4C_1 chair conformation. The five-membered ring is *cis*-connected at C(5) and C(9), leaving H(5) quasi-equatorial and H(9) quasi-axial with respect to the plane of the six-membered ring. The cyclopentane ring adopts an envelope conformation with C(5) out of the plane through C(6), C(7), C(8) and C(9). The third ring is the above-mentioned epoxy ring [O(10)–C(7)–C(8)] or a bridged tetrahydropyran ring that the cyclopentane forms together with the epoxy ring. In clockwise numbering [0 = O(10), 1 = C(7), 2 = C(6), 3 = C(5), 4 = C(9), 5 = C(8)], the conformation is halfway between a ${}^{3,0}B$ boat and an 0E envelope conformation, *i.e.* O(10) is situated 1.201 (6) Å above the plane formed by C(6), C(7), C(8) and C(9) (see Table 3). The H(5) and H(6) atoms are *trans* to each other.

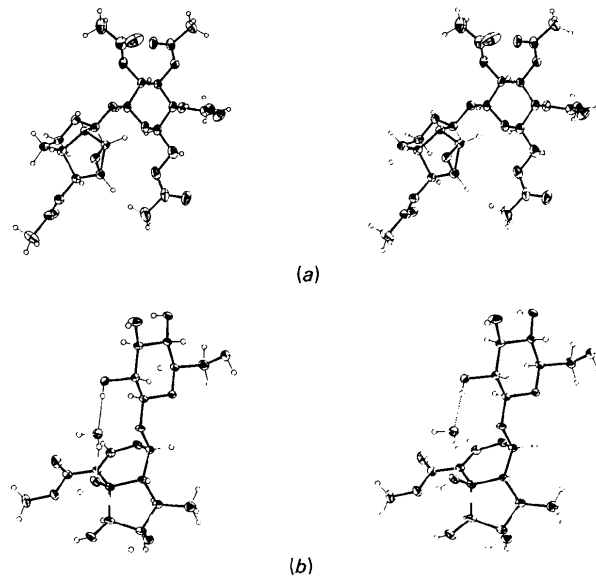
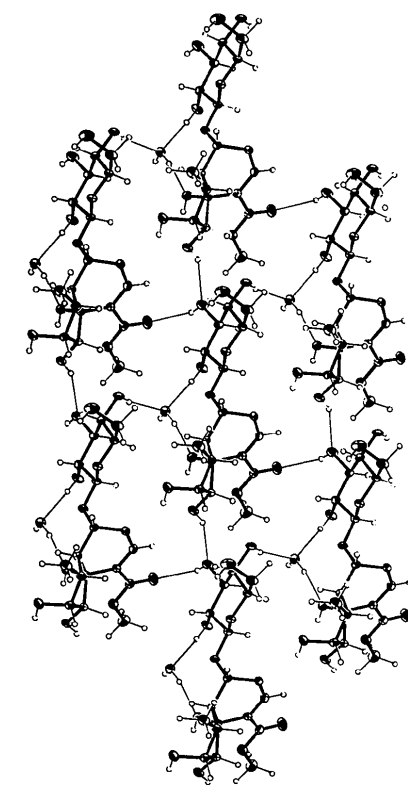
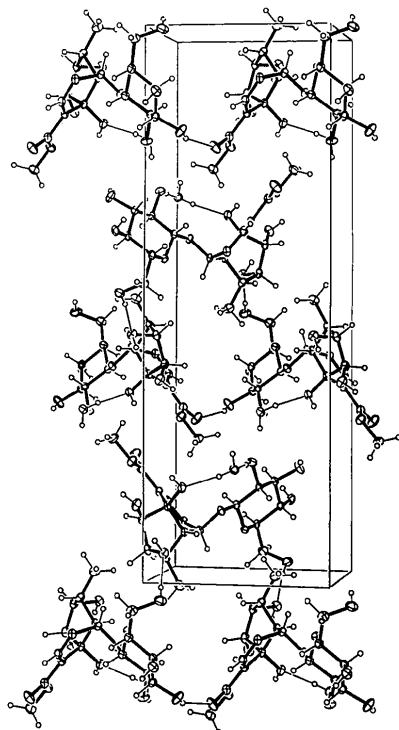


Fig. 7. Stereoviews of the molecule of 3,4-dihydrounedoside pentaacetate (a) and pulchelloside II hydrate (b).



(a)



(b)

Table 4. Hydrogen-bond lengths (Å) and angles (°)

	O...O	O...H	∠O-H...O
O(21)-H(201)...O(3)	2.722 (4)	1.93 (4)	175.10 (1)
O(3)-H(312)...O(5)	2.722 (4)	1.90 (4)	165.50 (2)
O(61)-H(601)...O(7)	2.769 (4)	1.80 (6)	164.20 (0)
O(49)-H(401)...O(3)	2.829 (4)	2.07 (4)	169.90 (1)
O(31)-H(301)...O(41)	2.814 (5)	2.18 (5)	154.00 (2)
O(6)-H(60)...O(31)	2.940 (4)	2.21 (4)	144.30 (4)

The pyran ring of the iridoid moiety of compound (2), in clockwise numbering [$0 = O(2)$, $1 = C(1)$, $2 = C(9)$, $3 = C(5)$, $4 = C(4)$ and $5 = C(3)$], has very nearly a ¹*E* conformation, *i.e.* an envelope with C(1) out of the plane through the rest of the atoms in the ring. The flattening of the ring is the result of the C(3)-C(4) double bond.

The conformation of compound (2) is further stabilized by the inclusion of a solvent water molecule that forms one hydrogen bond with the iridoid moiety at O(5) and another with the sugar moiety at O(21). Another weaker hydrogen bond reaches to O(49) of a neighboring molecule (Table 4); Fig. 8 characterizes the hydrogen bridges.

In compound (2), as in compound (1), the cyclopentane ring is attached *cis* to the six-membered ring, leaving H(9) and O(5) on the same side of the ring. This five-membered ring adopts an envelope conformation with C(8) out of the plane through C(5), C(6), C(7) and C(9). Atoms H(8) and H(9) are *trans* to each other while H(7) and H(6) are *cis*. The three hydroxyl groups and the methyl group are therefore all on one side, above the ring. The crystallographic study thus proves that structure proposal (b), given in the *Introduction*, as suggested by Rimpler & Pistor (1974), is the correct one for unedoside.

For pulchelloside II one can conclude that the stereochemical features proposed by Milz & Rimpler (1979) on the basis of NMR studies were all correct.

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Fig. 8. Hydrogen bridges in pulchelloside II hydrate in the layer parallel to *bc* (a) and between pairs of these layers (b).

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A Model for the Hydrogen-Bond-Length Probability Distributions in the Crystal Structures of Small-Molecule Components of the Nucleic Acids

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Abstract

The probability distributions of the N—H...O=C and O—H...O=C hydrogen-bond lengths observed in the crystal structures of the purines, pyrimidines, nucleosides and nucleotides have been fitted to a one-dimensional hydrogen-bond potential-energy function. In order to obtain a quantitative correspondence between the experimental and theoretical distributions, it is necessary to include with the usual hydrogen-bond-type potential-energy function, an effective crystal-packing force and two thermodynamical parameters of the crystal lattice, the Debye temperature and the Gruneisen constant.

Introduction

The statistical analysis of results of crystal structure determinations has had some notable successes. Examples are the exploration of the permitted regions of polypeptide chain conformations by Ramachandran & Sasisekharan (1968) and the determination of the permitted ring conformations and glycosidic torsion angles in the components of the nucleic acids by Altona & Sundaralingam (1972). Over the past five years, a number of statistical studies have been made of the hydrogen-bond geometry observed in the crystal structures of small biological molecules. These studies have been made possible by access to crystal structural data through the computer-readable Cambridge Structural Database (Allen, Kennard & Taylor, 1983).

Taylor, Kennard & Versichel (1983, 1984*a,b*) studied the geometry of 1509 N—H...O=C and N⁺—H...O⁻—C bonds in a variety of compounds.

Ceccarelli, Jeffrey & Taylor (1981) examined the O—H...O bonds in the pyranose and pyranoside sugars using neutron diffraction data. A similar study was made by Jeffrey & Maluszynska (1982) of neutron diffraction analyses of amino acids. The analyses have been extended to the small-molecule components of nucleic acids, nucleosides and nucleotides, and purines and pyrimidines by Jeffrey, Maluszynska & Mitra (1985) and Jeffrey & Maluszynska (1986). The following general observations were made from these studies.

(i) Hydrogen-bond lengths are group-pair properties, rather than atom-pair properties. Based on the observed hydrogen-bond lengths, acceptor and donor groups can be ordered according to the strengths of the hydrogen bonds that they form (Taylor, Kennard & Versichel, 1984*b*). In the nucleosides and nucleotides, for example, the hydrogen-bond strengths of the donor groups are P—OH > C—OH > >NH > O_wH > N(H)H, whereas for the acceptor groups, they are O=P > O_wH₂ > O=C > O(H)C > N << > O < (Jeffrey, Maluszynska & Mitra, 1985).

(ii) For any particular group pair, the observed hydrogen-bond lengths, *i.e.* H...A, have a distribution which is qualitatively 'an inverse' of a Morse type of hydrogen-bond potential-energy curve, *i.e.*, ρ_{exp} vs V_{hb} in Fig. 1.

In this paper, we seek to obtain a relationship between the bond-length probability distribution, ρ_{exp} , and an effective potential-energy relationship for the two-centered† N—H...O=C and O—H...O=C hydrogen bonds observed in the crystal structures of the

† A two-centered hydrogen bond is defined as a configuration in which there is only one electronegative acceptor atom within 3.0 Å from the H atom in the forward direction with respect to the covalent X—H bond, *i.e.*, with $D—H...A \geq 90^\circ$.

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