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The Crystal Structure and Absolute Configuration of a Bromohexaacetyl Derivative of Vitexin*

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Crystals of a bromohexaacetyl derivative of vitexin have hexagonal symmetry with cell dimensions $a=21{\cdot}602$ (7) and $c=13{\cdot}869$ (7) Å and absolute configuration corresponding to space group $P6_5$. The crystal structure was determined by Fourier methods from X-ray diffraction data collected with an automatic diffractometer and refined by full-matrix least-squares calculations to a conventional $R_1=0{\cdot}099$. The results identify the material as a mixture of 70% 5-hydroxy-6-bromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{31}BrO_{16}$) and 30% 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{30}Br_2O_{16}$). It is confirmed that the sugar ring is a β-D-glucosyl moiety, attached through C–C bonds to the 8 position of the flavone nucleus and is approximately perpendicular to the flavone plane.

Introduction

Although the *C*-glycosyl flavone compounds occur widely in nature and were first isolated in 1851 (Haynes, 1963), the elucidation of the chemical structure was hampered by the nature of the *C*-glycosylic side chain. The resistance of the C–C bond to acid hydrolysis prevented the identification of the sugar moiety. Horowitz & Gentili (1964) first overcame these obstacles when they deduced the basic structure of vitexin from chemical and n.m.r. data. Later Eade, Hillis, Horn & Simes (1965) inferred the existence of two rotational isomers of acetylated vitexin from temperature-dependent n.m.r. studies. We undertook a study of a bromohexaacetylated derivative of vitexin to test these predictions and to investigate an initially difficult crystallographic problem. The chemical composition of the crystal under investigation was determined by X-ray analysis to be 70% 5-hydroxy-6-bromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{31}BrO_{16}$) and 30% 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{30}Br_2O_{16}$). Disorder was found in the occupation of the site bonded to the 3′ carbon atom.

Experimental procedure

Vitexin was isolated from the wood of *Vitex lucens.* A bromoheptaacetylated derivative of vitexin was made available by Dr R. Horowitz of the Fruit and Vegetable Chemistry Laboratory, Pasadena, California. Upon crystallization in a methanol–acetone solution, deacetylation at the 5 carbon position occurred. Pale yellow crystals of a vitexin derivative were given to us by Dr K. Palmer of the Western Regional Agricultural Research Laboratory, Albany, California. Pertinent crystallographic data are given in Table 1.

Table 1. *Physical data*

70% 5-Hydroxy-6-bromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{31}BrO_{16}$)
30% 5-Hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin ($C_{33}H_{30}Br_2O_{16}$)

Yellow hexagonal prisms	Space group $P6_5$
Systematic absences $00l$, $l \neq 6n$	
$a=21{\cdot}602$ (7) Å	$D_c=1{\cdot}40$ g cm^{-3}
$c=13{\cdot}869$ (7)	$D_m=1{\cdot}42$
$V=5604{\cdot}85$ Å^3	$\mu_{\text{Mo }K\alpha}=15{\cdot}8$ cm^{-1}

The density of 1·42 g cm^{-3} was measured by flotation of a batch of crystals in hexane and carbon tetrachloride. As the experimental density does not agree well with the calculated density of 1·40 g cm^{-3} assuming six molecules per unit cell, an estimation of the experimental error was attempted. The density was remeasured on the last available crystal in the same liquids. Over several hours, the density of the crystal slowly increased to 1·48 g cm^{-3} when the measurements were stopped.

Intensity data were collected for a crystal of size 0·144 × 0·200 × 0·221 mm on an automated Picker four-circle diffractometer at 23 °C. The Friedel pairs of three equivalent sets (h,k,l and $\overline{h+k},h,l$ and $\bar{k},h+k,l$) were measured out to a Bragg 2θ angle of 40° using graphite-monochromatized Mo $K\bar{\alpha}$ radiation ($\lambda=0{\cdot}71069$). Each reflection was scanned for 1·2° by the θ–2θ scan technique at a rate of 1·0° min^{-1}. The backgrounds were counted for 10 s at 0·4° above and below each end of the scan. The data were corrected only for Lorentz and polarization effects. The intensities of three standard reflections varied no more than 2·6% from average values during the data collection, without any systematic trend. Absorption is estimated to reduce the intensities by factors which range from 0·73 to 0·80, and an absorption correction was not applied. The equivalent reflections were averaged to give 3512 unique reflec-

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tions of which 2669 had $F^2 > \sigma(F^2)$. The total number of Friedel pairs was 1658 and approximately 1104 Friedel pairs had the average $F^2 > \sigma(F^2_{\text{ave}})$.

Solution and refinement

One bromine atom position was determined by a three-dimensional Patterson synthesis and refined by the method of least squares to $R_1 = \sum|\Delta F|/\sum|F_o| = 0{\cdot}42$. The remaining carbon and oxygen atoms were located by a series of least-squares refinements and three-dimensional difference Fourier syntheses. The atoms refined to $R_1 = 0{\cdot}17$ with isotropic thermal parameters.

A subsequent difference Fourier map revealed a large peak 1·8 Å from the phenyl ring. Refinement of an oxygen atom at this position yielded a negative isotropic thermal parameter of $-0{\cdot}12$ Å^2. The peak was then assigned to a bromine atom with a partial occupancy factor. In the refinements of a bromine atom Br(2), with 40, 35 or 30% occupancy, the isotropic thermal parameter decreased as the occupancy factor was decreased. At 30% occupancy, the thermal parameter of 6·20 Å^2 was consistent with two expectations. First, it was only slightly larger than 5·63 Å^2 for the carbon atom, C(3′), to which this atom is bound. Second, it was closest in value to the thermal parameter of 6·98 Å^2 for the fully occupied bromine atom, Br(1). A subsequent n.m.r. study (Horowitz & Lundin, personal communication) of the crystalline sample confirmed that there was less than 100% proton occupancy at the C(3′) position, but indicated at least 85%. It was not definitive concerning the total absence of hydrogen at the C(6) position. Another refinement was calculated with occupancy factors of 15% for Br(2) and 85% for Br(1). The latter bromine atom was assigned a lower occupancy factor to reduce the relatively high thermal parameter. In the refinement, the isotropic thermal parameter for Br(2) became negative, indicating that the occupancy factor for Br(2) was too low to account for the electron density. For Br(1), the isotropic value of 5·69 Å^2 was slightly smaller than 5·94 Å^2 for the carbon atom, C(6), to which it is bound. This seemed unreasonable because the bromine atom is less constrained than the C(6) in the benzopyrone ring. In subsequent refinements, Br(1) and Br(2) were assigned the occupancy factors which we considered to be most reasonable, 100 and 30%, respectively.

The measured density, 1·42 g cm^{-3}, corresponds to 1·45 bromine atoms per molecule. Our interpretation of the diffraction data requires a density of 1·40 g cm^{-3}. If each molecule contains only one bromine atom, the calculated density is 1·36 g cm^{-3}; it is 1·50 g cm^{-3} for two bromine atoms per molecule. The density measurement supports the conclusion that we have a mixture of compounds. Because the material may not have been uniform in composition, we do not regard the density as a reliable basis for determining the bromine content of the data crystal.

Three of the six acetate groups exhibited large thermal motion. Evidence for partial but not complete rotation about the O–C bond in the acetate groups was found in difference Fourier maps. Several attempts were made to refine each of the strongly anisotropic acetate groups as two groups with partial occupancy. However, these disorder models did not significantly lower R_1 or improve the pertinent bond distances. In subsequent refinements, the acetate atoms were treated as fully occupied, despite the large temperature parameters that resulted.

All non-hydrogen atoms were refined anisotropically in $P6_1$ to $R_1 = 0{\cdot}100$ and in $P6_5$ to $R_1 = 0{\cdot}089$. A comparison of the observed and calculated Friedel pairs with the largest anomalous dispersion differences also confirmed $P6_5$ as the correct space group. The absolute configuration which we find in $P6_5$ is the expected D configuration of the sugar moiety.

In the anisotropic refinements, several atoms in the benzopyrone ring were found not to have positive definite temperature factors. Elimination of the weak data between $\sigma(F^2)$ and $3\sigma(F^3)$ in further refinements did not improve the temperature factors. It was not surprising to obtain unreasonable temperature factors using only 1104 Friedel pairs to determine 460 parameters. To reduce the number of variables, only the bromine atoms were refined anisotropically in subsequent refinements.

The final full-matrix least-squares refinement on F includes 2662 reflections with $F^2 > \sigma(F^2)$. Seven reflections with $\sin\theta/\lambda < 0{\cdot}06$ had bad background counts and were deleted. Carbon and oxygen atoms were refined with isotropic and bromine atoms with anisotropic thermal parameters. Ring hydrogen-atom positions were calculated, assuming a C–H distance of 1·0 Å. The hydrogen-atom temperature factors were assigned the values of the atoms to which they were bonded and the atoms were then included as fixed contributions to the calculated structure factors. The final discrepancy indices are $R_1 = 0{\cdot}099$ and $R_2 = \{\sum w(\Delta F)^2/\sum w(F_o)^2\}^{1/2} = 0{\cdot}083$: $R_1 = 0{\cdot}129$ including zero-weighted data. In the final refinement, $\sigma(I)$ was increased to $[\sigma(I)^2 + 0{\cdot}06(I)^2]^{1/2}$ to avoid over-weighting the stronger reflections. The final error in observation of unit weight is 1·26 and is defined by $\{\sum w(\Delta F)^2/(N_o - N_v)\}^{1/2}$ where w is given by $4F^2/\sigma^2(F^2)$. The scattering factors of Doyle & Turner (1968) were used for oxygen, carbon and bromine, those of Stewart, Davidson & Simpson (1965) for spherical hydrogen, and the anomalous scattering factors of Cromer & Liberman (1970) for the bromine atom. The final observed structure factors and calculated differences are given in Table 2.* The final positional and thermal parameters are given in Tables 3 and 4.

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30839 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Atomic parameters*

Positional parameters are × 10^4, isotropic thermal parameters × 10.

	x	*y*	*z*	*B*
Br(1)	4964 (1)	1375 (1)	0000	*
Br(2)	5786 (3)	2486 (3)	−3746 (5)	*
O(1)	4698 (5)	−1289 (5)	−1660 (7)	38 (2)
C(2)	4061 (8)	−1865 (8)	−1992 (11)	35 (4)
C(3)	3454 (8)	−1852 (9)	−1793 (12)	42 (4)
C(4)	3423 (10)	−1258 (10)	−1393 (13)	61 (5)
C(5)	4213 (9)	−0032 (9)	−0773 (12)	35 (4)
C(6)	4858 (10)	0519 (9)	−0519 (13)	48 (4)
C(7)	5439 (8)	0423 (8)	−0554 (11)	29 (3)
C(8)	5412 (8)	−0176 (8)	−0940 (11)	27 (3)
C(9)	4734 (7)	−0721 (7)	−1236 (10)	22 (3)
C(10)	4143 (8)	−0647 (9)	−1128 (11)	30 (4)
C(1′)	4144 (8)	−2422 (8)	−2478 (11)	37 (4)
C(2′)	4815 (8)	−2231 (8)	−2789 (11)	35 (4)
C(3′)	4902 (9)	−2719 (9)	−3283 (14)	51 (4)
C(4′)	4319 (10)	−3408 (10)	−3537 (13)	55 (4)
C(5′)	3690 (8)	−3564 (8)	−3186 (12)	41 (4)
C(6′)	3563 (8)	−3081 (9)	−2654 (12)	35 (4)
C(1″)	6074 (8)	−0228 (8)	−1101 (11)	31 (4)
C(2″)	6080 (8)	−0838 (9)	−0578 (13)	39 (4)
C(3″)	6792 (8)	−0825 (8)	−0841 (11)	34 (4)
C(4″)	6864 (8)	−0856 (8)	−1944 (12)	46 (4)
C(5″)	6832 (8)	−0219 (8)	−2363 (11)	34 (4)
C(6″)	6886 (9)	−0212 (9)	−3489 (13)	50 (4)
O(7″)	6148 (5)	−0290 (5)	−2129 (7)	32 (2)
O(11)	2881 (7)	−1211 (6)	−1294 (8)	61 (3)
O(12)	3602 (6)	0055 (6)	−0692 (8)	51 (3)
O(13)	6109 (5)	0978 (5)	−0298 (8)	36 (2)
C(14)	6285 (10)	1051 (10)	0651 (14)	54 (4)
O(15)	5914 (7)	0651 (7)	1262 (10)	74 (4)
C(16)	7010 (10)	1691 (10)	0828 (13)	60 (5)
O(17)	6139 (5)	−0695 (5)	0441 (8)	40 (2)
C(18)	5655 (12)	−1243 (12)	0999 (16)	68 (5)
O(19)	5145 (7)	−1767 (7)	0704 (9)	64 (3)
C(20)	5823 (11)	−1067 (11)	2066 (16)	81 (6)
O(21)	6782 (6)	−1436 (6)	−0433 (8)	50 (3)
C(22)	7275 (13)	−1318 (13)	0208 (18)	89 (6)
O(23)	7736 (10)	−0736 (10)	0457 (13)	123 (5)
C(24)	7241 (12)	−2058 (12)	0470 (18)	88 (7)
O(25)	7572 (6)	−0746 (6)	−2125 (8)	51 (3)
C(26)	7655 (16)	−1257 (16)	−2520 (20)	110 (8)
O(27)	7122 (12)	−1802 (12)	−2726 (16)	146 (7)
C(28)	8428 (14)	−1031 (14)	−2788 (19)	109 (8)
O(29)	−2741 (9)	0553 (9)	−3773 (11)	95 (4)
C(30)	−2057 (27)	0890 (25)	−3913 (32)	186 (14)
O(31)	8252 (18)	0639 (17)	−3732 (24)	241 (12)
C(32)	8168 (17)	1662 (19)	−4091 (23)	148 (10)
O(33)	4457 (6)	−3889 (6)	−3950 (9)	54 (3)
C(34)	4628 (10)	−3805 (12)	−4919 (16)	75 (5)
O(35)	4628 (7)	−3344 (8)	−5395 (10)	82 (4)
C(36)	4879 (9)	−4325 (9)	−5209 (13)	50 (4)

* Anisotropic thermal parameters for Br(1), Br(2) are: B_{11}=7·1 (1), 5·3 (4); B_{22}=4·2 (1), 5·8 (4); B_{33}=8·4 (1), 7·4 (4); B_{12}=2·9 (1), 3·8 (3); B_{13}=1·7 (1), 0·0 (3); B_{23}=−1·6 (1), −0·2 (3).

Table 4. *Parameters for hydrogen atoms*

The atoms are numbered like the adjacent carbon atoms. Positional parameters are × 10^3.

	x	*y*	*z*	*B* (Å^2)
H(3)	304	−227	−199	4·1
H(2′)	520	−175	−264	3·6
H(3′)	536	−251	−353	5·1
H(5′)	324	−400	−330	4·2
H(6′)	309	−325	−239	3·9
H(1″)	632	017	−074	2·9
H(2″)	580	125	−088	4·0
H(3″)	705	−031	−091	3·4
H(4″)	642	−121	−213	4·5
H(5″)	719	023	−224	3·4
H(6″*a*)	714	−045	−370	5·3
H(6″*b*)	645	−047	−369	5·3

Table 5. *Bond lengths* (Å) *in 5-hydroxy-*3′,6*-dibromo-*2″,3″,4′,4″,6″,7*-hexaacetylvitexin*

Benzopyrone ring			
O(1)-C(2)	1·393 (16)	C(6)—C(7)	1·372 (19)
O(1)-C(9)	1·327 (14)	C(6)—Br(1)	1·887 (17)
C(2)-C(3)	1·356 (18)	C(7)—C(8)	1·375 (17)
C(2)-C(1′)	1·466 (19)	C(7)—O(13)	1·386 (15)
C(3)-C(4)	1·429 (21)	C(8)—C(9)	1·406 (17)
C(4)-C(10)	1·497 (21)	C(8)—C(1″)	1·505 (19)
C(4)-O(11)	1·232 (18)	C(9)—C(10)	1·372 (18)
C(5)-C(6)	1·351 (21)	O(13)-C(14)	1·358 (18)
C(5)-C(10)	1·352 (19)	C(14)-O(15)	1·189 (18)
C(5)-O(12)	1·427 (17)	C(14)-C(16)	1·503 (22)
β-D-Glucose ring			
C(1″)-C(8)	1·505 (19)	O(17)-C(18)	1·363 (20)
C(1″)-C(2″)	1·510 (19)	C(18)-O(19)	1·190 (20)
C(1″)-O(7″)	1·448 (15)	C(18)-C(20)	1·525 (25)
C(2″)-C(3″)	1·565 (18)	O(21)-C(22)	1·311 (23)
C(2″)-O(17)	1·438 (17)	C(22)-O(23)	1·199 (23)
C(3″)-C(4″)	1·543 (21)	C(22)-C(24)	1·604 (29)
C(3″)-O(21)	1·427 (16)	O(25)-C(26)	1·322 (27)
C(4″)-C(5″)	1·526 (20)	C(26)-O(27)	1·198 (27)
C(4″)-O(25)	1·447 (17)	C(26)-C(28)	1·534 (30)
C(5″)-C(6″)	1·565 (22)	O(29)-C(30)	1·294 (44)
C(6″)-O(29)	1·483 (20)	C(30)-C(32)	1·505 (43)
		C(30)-O(31)	1·080 (48)
Phenyl ring			
C(1′)-C(2)	1·466 (19)	C(4′)-C(5′)	1·318 (20)
C(1′)-C(2′)	1·364 (18)	C(4′)-O(33)	1·342 (18)
C(1′)-C(6′)	1·368 (19)	C(5′)-C(6′)	1·414 (19)
C(2′)-C(3′)	1·347 (19)	O(33)-C(34)	1·382 (21)
C(3′)-C(4′)	1·432 (21)	C(34)-O(35)	1·193 (20)
C(3′)-Br(2)	1·832 (17)	C(34)-C(36)	1·526 (24)

Description of the structure

The molecular formula and structure of 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin are shown in Figs. 1 and 2. Since the mono- and dibromo derivatives differ only in the atomic occupancy of the site bonded to the 3′ carbon atom, the structure will be described in terms of the dibromo derivative. The molecule consists of a glucosyl ring attached to the 8 carbon position of a flavone nucleus by a C–C bond. The bond lengths and bond angles are given in Tables 5 and 6. The six molecules per unit cell are related by a 6_5 screw axis along *z* and are shown in the stereo packing diagram in Fig. 3.

The sugar moiety is a tetra-*O*-acetylated derivative of a β-D-glucosyl ring. The average C–O bond length in the glucosyl ring is 1·44 Å and the average C–C bond is 1·54 Å. The distances compare favorably with the C–O bond of 1·43 Å and the C–C length of 1·52 Å found in β-D-glucose (Chu & Jeffrey, 1968). In the two benzene rings, the average C–C bond is 1·37 Å.

In the *β*-D-glucosyl ring, the C(2″), C(3″), C(5″), O(7″) seat of the expected chair conformation forms an angle of 86·5° with the benzene plane of the flavone nucleus. The dihedral angles of 54·8° between the C(3″)–C(4″)–C(5″) plane and the seat indicate little distortion in the chair geometry. The 2″-, 3″- and 4″-acetyl groups are bonded equatorially, forming an average dihedral angle of 88·0° between the C–O–C acetyl plane and the C–C–C ring plane of attachment. The 2″-acetyl group lies within a range of 4·8 to 7·0 Å of the benzopyrone ring atoms and is located midway between the 7-acetyl group and the phenyl ring. Torsional angles within the *β*-D-glucosyl ring and pertinent dihedral angles within the molecule are given in Table 7. Interatomic distances involving the acetyl groups are given in Table 8.

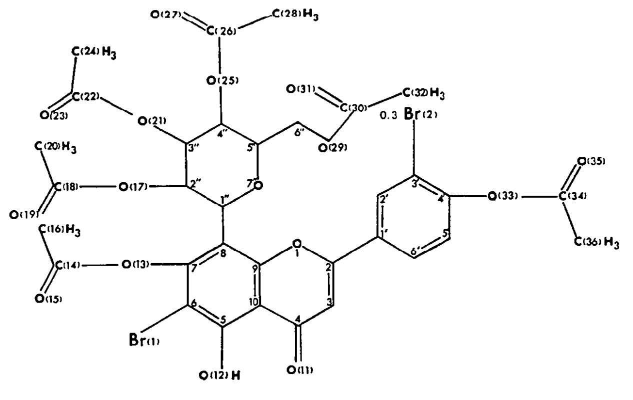

Fig. 1. The molecular formula illustrated for 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin.

Discussion

There is general geometric agreement between the flavone system in this crystal and in 3′,5,5′,6-tetramethylflavone (Ting, Watson & Domínguez, 1972). The benzene-ring plane forms angles of 5·7° with the O(1)–

Table 6. *Bond angles* (°) *in* 5-*hydroxy*-3′,6-*dibromo*-2″, 3″,4′,4″,6″,7-*hexaacetylvitexin*

Benzopyrone ring			
C(2)—O(1)-C(9)	123·2 (1·4)	C(6)—C(7)—C(8)	123·1 (1·6)
O(1)—C(2)-C(3)	116·6 (1·2)	C(6)—C(7)—O(13)	119·9 (1·4)
O(1)—C(2)-C(1′)	114·5 (1·1)	C(8)—C(7)—O(13)	116·6 (1·3)
C(3)—C(2)-C(1′)	128·8 (1·5)	C(7)—C(8)—C(9)	116·0 (1·4)
C(2)—C(3)-C(4)	125·3 (1·5)	C(7)—C(8)—C(1″)	122·2 (1·4)
C(3)—C(4)-C(10)	113·2 (1·5)	C(9)—C(8)—C(1″)	121·7 (1·3)
C(3)—C(4)-O(11)	126·1 (1·6)	O(1)—C(9)—C(8)	117·3 (1·1)
C(10)-C(4)-O(11)	120·7 (1·6)	C(8)—C(9)—C(10)	120·8 (1·4)
C(6)—C(5)-C(10)	121·4 (1·7)	C(4)—C(10)-C(5)	120·8 (1·7)
C(6)—C(5)-O(12)	118·5 (1·5)	C(5)—C(10)-C(9)	120·1 (1·6)
C(10)-C(5)-O(12)	120·1 (1·4)	C(7)—O(13)-C(14)	117·4 (1·4)
C(5)—C(6)-C(7)	118·4 (1·6)	O(13)-C(14)-O(15)	123·9 (1·3)
C(5)—C(6)-Br(1)	122·0 (0·9)	O(13)-C(14)-C(16)	111·6 (1·3)
C(7)—C(6)-Br(1)	119·3 (0·8)	O(15)-C(14)-C(16)	124·5 (1·6)
β-D-Glucose ring			
		C(1″)-O(7″)-C(5″)	111·4 (1·2)
C(8)—C(1″)-C(2″)	114·7 (1·3)	C(2″)-O(17)-C(18)	115·1 (1·6)
C(8)—C(1″)-O(7″)	107·8 (1·2)	O(17)-C(18)-O(19)	125·0 (1·4)
C(2″)-C(1″)-O(7″)	110·1 (1·2)	O(17)-C(18)-C(20)	110·5 (1·4)
C(1″)-C(2″)-C(3″)	108·0 (1·2)	O(19)-C(18)-C(20)	124·3 (1·6)
C(1″)-C(2″)-O(17)	108·8 (1·2)	O(3″)-O(21)-C(22)	117·0 (1·6)
C(3″)-C(2″)-O(17)	138·1 (1·0)	O(21)-C(22)-O(23)	124·5 (1·7)
C(2″)-C(3″)-C(4″)	110·6 (1·3)	O(21)-C(22)-C(24)	109·4 (1·6)
C(2″)-C(3″)-O(21)	109·3 (1·3)	O(23)-C(22)-C(24)	125·4 (2·1)
C(4″)-C(3″)-O(21)	108·0 (1·3)	C(4″)-O(25)-C(26)	120·5 (1·8)
C(3″)-C(4″)-C(5″)	106·6 (1·2)	O(25)-C(26)-O(27)	117·1 (1·9)
C(3″)-C(4″)-O(25)	106·7 (1·2)	O(25)-C(26)-C(28)	114·5 (1·8)
C(5″)-C(4″)-O(25)	107·9 (1·2)	O(27)-C(26)-C(28)	127·8 (2·6)
C(4″)-C(5″)-C(6″)	110·6 (1·3)	C(6″)-O(29)-C(30)	119·9 (2·7)
C(4″)-C(5″)-O(7″)	109·0 (1·2)	O(29)-C(30)-O(31)	120·1 (3·2)
C(6″)-C(5″)-O(7″)	107·0 (1·3)	O(29)-C(30)-C(32)	107·1 (2·8)
C(5″)-C(6″)-O(29)	105·9 (1·3)	O(31)-C(30)-C(32)	131·0 (4·3)
Phenyl ring			
C(2)–C(1″)–C(2′)	116·3 (1·4)	C(3′)–C(4)′–O(33)	119·3 (1·5)
C(2)–C(1′)–C(6′)	120·7 (1·4)	C(5′)–C(4′)–O(33)	124·0 (1·5)
C(2′)–C(1′)–C(6′)	122·9 (1·6)	C(4′)–C(5′)–C(6′)	124·1 (1·7)
C(1′)–C(2′)–C(3′)	117·7 (1·5)	C(1′)–C(6′)–C(5′)	116·4 (1·5)
C(2′)–C(3′)–C(4′)	123·1 (1·6)	C(4′)–O(33)–C(34)	117·5 (1·7)
C(2′)–C(3′)–Br(2)	119·8 (0·9)	O(33)–C(34)–O(35)	122·4 (1·6)
C(4′)–C(3′)–Br(2)	116·9 (1·0)	O(33)–C(34)–C(36)	109·3 (1·4)
C(3′)–C(4′)–C(5′)	115·6 (1·6)	O(35)–C(34)–C(36)	128·0 (1·7)

Table 7. *Dihedral angles* (°)

Plane *A*	Plane *B*	Angle
C(2″), C(3″), C(5″), O(7″)	C(2″), C(1″), O(7″)	54·8
C(2″), C(3″), C(5″), O(7″)	C(3″), C(4″), C(5″)	54·0
Torsion angles		
C(1″), C(2″), C(3″)	C(2″), C(3″), C(4″)	55·7
C(2″), C(3″), C(4″)	C(3″), C(4″), C(5″)	57·4
C(3″), C(4″), C(5″)	C(4″), C(5″), O(7″)	61·5
C(4″), C(5″), O(7″)	C(5″), O(7″), C(1″)	66·3
C(5″), O(7″), C(1″)	O(7″), C(1″), C(2″)	64·2
O(7″), C(1″), C(2″)	C(1″), C(2″), C(3″)	57·0
Acetyl angles		
C(1″), C(2″), C(3″)	C(2″), O(17), C(18)	88·7
O(19), C(18), C(20)	C(2″), O(17), C(18)	9·4
C(2″), C(3″), C(4″)	C(3″), O(21), C(22)	88·1
O(23), C(22), C(24)	C(3″), O(21), C(22)	9·7
C(3″), C(4″), C(5″)	C(4″), O(25), C(26)	87·2
O(27), C(26), O(28)	C(4″), O(25), C(26)	9·4
C(4″), C(5″), O(7″)	C(5″), C(6″), O(29)	77·0
C(4″), C(5″), C(6″)	C(6″), O(29), C(30)	77·1
C(6″), C(5″), O(7″)	C(6″), O(29), C(30)	74·6
O(31), C(30), C(32)	C(6″), O(29), C(30)	15·1
C(5), C(6), C(7), C(8), C(9), C(10)	C(7), O(13), C(14)	81·2
C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	C(4′), O(33), C(34)	72·1
Flavone angles		
C(5), C(6), C(7), C(8), C(9), C(10)	O(1), C(2), C(3), C(4)	5·7
C(5), C(6), C(7), C(8), C(9), C(10)	C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	21·5
C(5), C(6), C(7), C(8), C(9), C(10)	C(2″), C(3″), C(5″), O(7″)	86·5

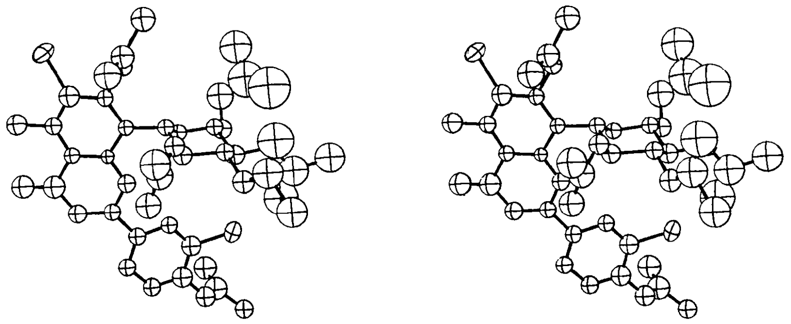

Fig. 2. A stereoscopic view of 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin. Only the bromine atoms are shown with anisotropic thermal ellipsoids. The shapes of all atoms represent 50% probability contours of the thermal motion.

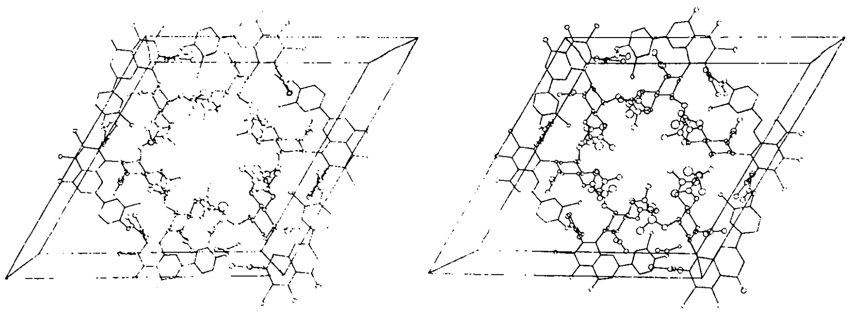

Fig. 3. A stereoscopic packing diagram of the vitexin derivative viewed down the 6_5 axis. For this drawing, the origin has been shifted by $\frac{1}{2},\frac{1}{2},0$ and the screw axis is in the center. The horizontal axis is the *y* direction.

Table 8. *Interatomic distances less than* 10 Å *between the acetyl groups and the aromatic rings*

Atoms in aromatic rings	C(20) in 2″-acetate	C(24) in 3″-acetate
O(1)	5·63	7·13
C(2)	6·52	7·87
C(3)	7·00	8·98
C(4)	6·92	9·59
C(5)	6·35	9·67
C(6)	6·01	9·38
C(7)	5·19	8·17
C(8)	4·86	7·21
C(9)	5·37	7·68
C(10)	6·08	8·91

C(2)–C(3)–C(4) heterocyclic ring and of 21·5° with the phenyl ring in the vitexin derivative and of 4 and 28°, respectively, in the tetramethylflavone compound.

The crystal structure confirms several structural predictions based on n.m.r. studies of vitexin and its derivatives. In accordance with Horowitz & Gentili (1964), the carbohydrate substituent is D-glycosyl with a β linkage of the sugar carbon to another carbon in the 8 position of the flavone nucleus. The overall conformation of the molecule is nearly identical to the major solution rotational isomer predicted by Eade, Hillis, Horn & Simes (1965). In both the solution and the crystal conformer, the plane of the pyranosyl ring is approximately perpendicular to the benzopyrone ring to minimize steric interactions with the acetyl substituents. In the n.m.r. studies of Hillis & Horn (1965), the 2″-acetyl proton signal is shifted upfield relative to the signals of the 3″- and 4″-acetyl groups. In the crystal structure, the 2″-acetyl group is situated over the aromatic heterocyclic ring, approximately midway between the 7-acetyl group and the phenyl ring. Interatomic distances indicate that the 2″ protons are within the calculated diamagnetic region of the heterocyclic π electrons (Johnson & Bovey, 1958). Although slight upfield shifting of the 6″-acetyl proton signal is observed, the 6″-acetyl group in the crystal structure is not located within the diamagnetic region of the phenyl ring. The 6″-acetyl group is oriented approximately 180° away from the phenyl plane. However, one must be careful about drawing such conclusions from the crystal data. The large anisotropic motion of the 6″-acetyl group atoms indicates that partial rotation about the C(5″)–C(6″) bond, and consequently other orientations of the 6″-acetyl group, may be possible. Another unexpected result is that the 7- and 2″-acetyl groups lie on the same side of the benzene plane. The 7-acetyl atoms exhibit small thermal motion, indicating that rotation of the group is probably restricted in solution by steric hindrance with neighboring substituents.

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