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Structure of 8-(2,6-Dideoxy-β-*ribo*-hexopyranosyl)-5-hydroxy-2-(4-hydroxyphenyl)-7-methoxy-4*H*-1-benzopyran-4-one Sesquihydrate, Aciculatin

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Abstract. $C_{22}H_{22}O_8.1{\cdot}5H_2O$, $M_r = 441{\cdot}4$, monoclinic, *I*2, $a = 21{\cdot}037$ (7), $b = 7{\cdot}371$ (2), $c = 27{\cdot}512$ (4) Å, $\beta = 100{\cdot}34$ (2)°, $V = 4196{\cdot}8$ (8) Å^3, $Z = 8$, $D_x = 1{\cdot}397$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 1{\cdot}029$ cm^{-1}, $F(000) = 1864$, $T = 295$ K, final R (on F) = 0·058 for 2113 observed reflections with $I \geq 2\sigma(I)$. Aciculatin crystallizes as a sesquihydrate with two independent molecules per asymmetric unit. The 2,6-dideoxy-β-*ribo*-hexopyranosyl ring is linked to C8 of the flavone through a β-*C*-glycosidic bond. Intramolecular hydrogen bonding occurs between the hydroxyl and ketonic O atoms of the flavone ring system.

Introduction. Flavonoids are a naturally occurring class of plant pigments which frequently occur as glycosides containing either a glucose or rhamnose sugar moiety (Mayer & Cook, 1943). These pigments display a variety of therapeutic properties including anti-carcinogenic, anti-inflammatory, antioxidant and anti-allergenic activities (Glusker & Rossi, 1986).

The present crystallographic study was carried out to confirm the molecular structure of aciculatin, a flavonoid isolated from the plant *Chrysopogon aciculatis* (Carte, DeBrosse, Offen, Carr, Hemling, Berry, Mackenzie-LoCastro & Westley, 1991).

Experimental. Yellow plates were obtained from slow evaporation of an aqueous ethanol solution at room temperature. A suitable crystal of approximate dimensions 0·3 × 0·3 × 0·05 mm was mounted on the tip of a glass fiber with epoxy resin and used in the diffraction study.

Intensity data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters obtained by least-squares refinement of angular settings from 25 reflections in 2θ range 24–30°. Intensity data (5603 reflections) collected using variable speed ω–2θ scans with $2 \leq 2\theta \leq 56°$ ($0 \leq h \leq 27$, $0 \leq k \leq 9$, $-36 \leq l \leq 36$). Three standard reflections ($\bar{3}$,3,$\bar{10}$, 4,$\bar{3}$,11, 9$\bar{3}\bar{6}$) monitored every 3 h of X-ray exposure time showed intensity changes of −5·6%; a correction for deterioration was made (correction: min. 1·000, max. 1·0290). Symmetry-equivalent data were averged, $R_{int} = 4{\cdot}7\%$ (on I); the 5460 unique reflections were corrected for Lorentz and polarization effects.

The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1985). The y coordinate of atom O*W*1 was held fixed to define the origin. Non-H atoms were refined with isotropic temperature factors, then with anisotropic displacement parameters. Most of the H-atom positions were located from difference Fourier maps; those not located were calculated at C—H = 1·00 Å. H-atom coordinates were held fixed at the located or calculated positions along with fixed isotropic temperature factors ($1{\cdot}3 \times B_{eq}$ of the adjacent atom). The positions of H*W*42 and hydroxyl hydrogen, H2*A*, were not determined. The final refinement converged (max. $\Delta/\sigma = 0{\cdot}02$) to values of the standard crystallographic agreement factors of $R = 0{\cdot}058$, $wR = 0{\cdot}065$ and $S = 1{\cdot}179$ for 2113 reflections with $I \geq 2\sigma(I)$ and 569 parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Weights were assigned to the data as $w = 4F_o^2/\sigma^2(I)$ where $\sigma(I) = [\sigma(I)^2 + (0{\cdot}07F_o)^2]^{1/2}$. An extinction coefficient of the form proposed by Zachariasen (1963) was applied and refined: $g = 1{\cdot}80\,(1) \times 10^{-7}$. O*W*1 and O*W*2 were located on special crystallographic positions with occupancies of 0·5. Neutral atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) except for H atoms (Stewart, Davidson & Simpson, 1965). The effects of anomalous dispersion for non-H were included. A final difference Fourier map showed max. excursions of $(\Delta\rho)_{max} = 0{\cdot}253$ to $(\Delta\rho)_{min} = -0{\cdot}238$ e Å^{-3}. The atomic coordinates and equivalent isotropic thermal parameters are collected in Table 1.* All programs

* Lists of anisotropic displacement parameters, selected torsion angles, least-squares planes, H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54288 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B (Å²)
O1A	0·2695 (2)	0·8396 (9)	−0·1610 (2)	3·2 (1)
O3″A	0·1033 (2)	0·6017 (9)	−0·0495 (2)	3·7 (1)
O4A	0·4627 (2)	0·837 (1)	−0·1602 (2)	6·2 (2)
O4′A	0·0913 (3)	0·878 (1)	−0·3664 (2)	7·3 (2)
O4″A	0·0129 (2)	0·832 (1)	−0·1005 (2)	3·5 (1)
O5A	0·4830 (2)	0·803 (1)	−0·0678 (2)	6·8 (2)
O7A	0·2994 (2)	0·796 (1)	0·0113 (2)	4·1 (2)
O7″A	0·1812 (2)	0·9665 (8)	−0·0952 (2)	2·9 (1)
C1′A	0·2407 (4)	0·864 (1)	−0·2467 (3)	3·0 (2)
C1″A	0·2111 (3)	0·801 (1)	−0·0750 (3)	2·6 (2)
C2A	0·2930 (3)	0·857 (1)	−0·2037 (3)	2·7 (2)
C2′A	0·1769 (4)	0·892 (1)	−0·2405 (5)	3·9 (2)
C2″A	0·1774 (3)	0·642 (1)	−0·1039 (3)	2·8 (2)
C3A	0·3560 (4)	0·864 (2)	−0·2043 (3)	4·3 (3)
C3′A	0·1281 (4)	0·900 (2)	−0·2812 (3)	4·5 (3)
C3″A	0·1061 (3)	0·644 (1)	−0·0995 (3)	2·3 (2)
C4A	0·4021 (4)	0·843 (2)	−0·1600 (3)	4·7 (3)
C4′A	0·1412 (4)	0·872 (2)	−0·3270 (3)	4·7 (3)
C4″A	0·0759 (3)	0·827 (1)	−0·1143 (3)	2·6 (2)
C5A	0·4184 (4)	0·808 (2)	−0·0692 (3)	4·5 (2)
C5′A	0·2044 (4)	0·844 (2)	−0·3345 (3)	4·2 (2)
C5″A	0·1147 (4)	0·980 (1)	−0·0869 (3)	3·5 (2)
C6A	0·3934 (4)	0·795 (2)	−0·0261 (3)	4·3 (2)
C6′A	0·2533 (4)	0·839 (2)	−0·2936 (3)	4·1 (2)
C6″A	0·0900 (4)	1·164 (1)	−0·1063 (4)	4·8 (3)
C7A	0·3266 (3)	0·802 (1)	−0·0303 (3)	3·2 (2)
C8A	0·2834 (3)	0·812 (1)	−0·0750 (3)	3·1 (2)
C9A	0·3103 (3)	0·829 (1)	−0·1170 (3)	2·8 (2)
C10A	0·3778 (3)	0·827 (2)	−0·1143 (3)	3·7 (2)
C11A	0·3420 (4)	0·787 (2)	0·0585 (3)	6·0 (3)
O1B	0·2703 (2)	0·2042 (9)	0·2072 (2)	3·0 (1)
O3″B	0·1945 (2)	0·4285 (8)	0·0224 (2)	2·9 (1)
O4B	0·4239 (2)	0·194 (1)	0·3198 (2)	4·5 (2)
O4′B	−0·0039 (2)	0·213 (1)	0·2567 (2)	6·5 (2)
O4″B	0·0892 (2)	0·2142 (9)	0·0248 (2)	3·4 (1)
O5B	0·4994 (2)	0·208 (1)	0·2543 (2)	5·5 (2)
O7B	0·3975 (2)	0·256 (1)	0·0858 (2)	5·1 (2)
O7″B	0·2382 (2)	0·0709 (8)	0·1076 (2)	2·6 (1)
C1′B	0·1920 (3)	0·202 (1)	0·2561 (3)	2·9 (2)
C1″B	0·2747 (3)	0·231 (1)	0·1051 (2)	2·5 (2)
C2B	0·2610 (4)	0·202 (1)	0·2542 (3)	3·0 (2)
C2′B	0·1474 (4)	0·159 (1)	0·2144 (3)	3·2 (2)
C2″B	0·2319 (4)	0·399 (1)	0·1087 (3)	3·1 (2)
C3B	0·3116 (4)	0·198 (1)	0·2925 (3)	3·3 (2)
C3′B	0·0819 (4)	0·162 (1)	0·2148 (3)	3·9 (2)
C3″B	0·1719 (4)	0·393 (1)	0·0679 (3)	2·8 (2)
C4B	0·3772 (4)	0·198 (1)	0·2836 (3)	3·7 (2)
C4′B	0·0609 (4)	0·215 (2)	0·2583 (3)	4·2 (2)
C4″B	0·1392 (3)	0·210 (1)	0·0661 (3)	2·7 (2)
C5B	0·4457 (3)	0·216 (2)	0·2196 (3)	3·6 (2)
C5′B	0·1050 (4)	0·254 (2)	0·3006 (3)	4·5 (3)
C5″B	0·1864 (3)	0·056 (1)	0·0657 (3)	2·3 (2)
C6B	0·4516 (4)	0·231 (2)	0·1704 (3)	4·5 (2)
C6′B	0·1703 (4)	0·247 (1)	0·2990 (3)	3·3 (2)
C6″B	0·1569 (4)	−0·127 (1)	0·0696 (3)	3·2 (2)
C7B	0·3955 (3)	0·241 (1)	0·1342 (3)	3·2 (2)
C8B	0·3340 (3)	0·224 (1)	0·1462 (3)	2·8 (2)
C9B	0·3305 (3)	0·209 (1)	0·1952 (3)	2·7 (2)
C10B	0·3852 (3)	0·210 (1)	0·2330 (3)	2·8 (2)
C11B	0·4590 (4)	0·282 (2)	0·0709 (3)	7·8 (4)
OW1	0·000	0·500	0·000	3·8 (2)
OW2	0·500	0·436 (1)	0·500	3·6 (2)
OW3	0·2616 (3)	1·252 (1)	−0·0418 (2)	5·9 (2)
OW4	0·3835 (3)	1·302 (2)	−0·0466 (2)	12·5 (4)

used were from the locally modified Enraf–Nonius (1979) *Structure Determination Package*.

Discussion. Aciculatin crystallizes as a sesquihydrate with two independent molecules per asymmetric unit. The molecular structure of molecule *B* is presented in Fig. 1. Selected bond distances and bond angles are listed in Table 2. Intermolecular hydrogen bonding interactions are collected in Table 3.

The flavone distances and angles are comparable to those in 4′-bromo-5-hydroxyflavone or 4′-bromo-3-hydroxyflavone (Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974), hymenoxin (Watson, Kashyap, Gao & Mabry, 1991), glabratephrin (Vleggaar, Kruger, Smalberger & van den Berg, 1978), 3-chloroflavanone (Tomlin & Cantrell, 1990), 3-hydroxyflavone (Etter, Urbanczyk-Lipkowska, Baer & Barbara, 1986) or 5-hydroxyflavone (Shoja, 1990), 5-hydroxy-7-methoxyflavone (Shoja, 1989), 5,4′-dihydroxy-3,6,7,8-tetramethoxyflavone (Vijayalakshmi, Rajan, Srinivasan & Ramachandran Nair, 1986), 3′,5,5′,6-tetramethoxyflavone (Ting, Watson & Dominguez, 1972), 4′,5,7-trihydroxyisoflavone (Breton, Precigoux, Courseille & Hospital, 1975), 5,7,4′-trimethoxyflavanone (Mariezcurrena, 1978), and 5-hydroxy-6-bromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin or 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin (Jurnak & Templeton, 1975).

The benzopyran is virtually planar; the dihedral angle between planar ring halves is 1 (2)° for molecule *A* and 3·1 (6)° for molecule *B*. The phenolic substituent is planar, but is not coplanar to the benzopyran in either molecule as evidenced by the C3—C2—C1′—C6′ torsion angles of 14 (2) and 18 (2)° for molecules *A* and *B*, respectively. The twisting of the phenolic ring is a result of steric and electronic effects. Theoretical calculations (Glusker & Rossi, 1986; Rossi, Cantrell, Farber, Dyott, Carrell & Glusker, 1980) suggest that for flavones with an H atom at position 3 a torsion angle of 22·8° results in a minimum-energy conformation.

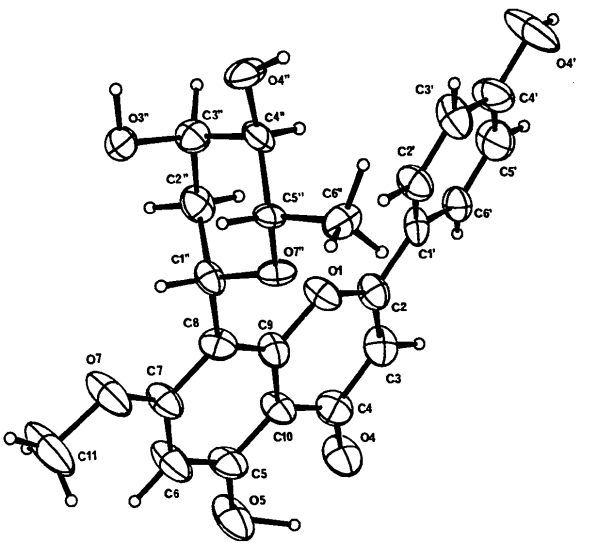

Fig. 1. Molecular structure of aciculatin (molecule *B*) showing labelling scheme. Non-H atoms are drawn with ellipsoids of 50% probability, H atoms are represented as spheres of arbitrary size.

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s*

O1*A*	C2*A*	1·361 (9)	O1*B*	C2*B*	1·34 (1)
O1*A*	C9*A*	1·353 (9)	O1*B*	C9*B*	1·367 (9)
O3″*A*	C3″*A*	1·424 (9)	O3″*B*	C3″*B*	1·44 (1)
O4*A*	C4*A*	1·28 (1)	O4*B*	C4*B*	1·267 (9)
O4′*A*	C4′*A*	1·37 (1)	O4′*B*	C4′*B*	1·356 (9)
O4″*A*	C4″*A*	1·443 (9)	O4″*B*	C4″*B*	1·404 (9)
O5*A*	C5*A*	1·35 (1)	O5*B*	C5*B*	1·343 (9)
O7*A*	C7*A*	1·370 (9)	O7*B*	C7*B*	1·346 (9)
O7*A*	C11*A*	1·441 (9)	O7*B*	C11*B*	1·44 (1)
O7″*A*	C1″*A*	1·44 (1)	O7″*B*	C1″*B*	1·42 (1)
O7″*A*	C5″*A*	1·46 (1)	O7″*B*	C5″*B*	1·442 (9)
C1′*A*	C2*A*	1·46 (1)	C1′*B*	C2*B*	1·46 (1)
C1′*A*	C2′*A*	1·40 (1)	C1′*B*	C2′*B*	1·38 (1)
C1′*A*	C6′*A*	1·38 (1)	C1′*B*	C6′*B*	1·38 (1)
C1″*A*	C2″*A*	1·52 (1)	C1″*B*	C2″*B*	1·54 (1)
C1″*A*	C8*A*	1·52 (1)	C1″*B*	C8*B*	1·53 (1)
C2*A*	C3*A*	1·33 (1)	C2*B*	C3*B*	1·36 (1)
C2′*A*	C3′*A*	1·38 (1)	C2′*B*	C3′*B*	1·38 (1)
C2″*A*	C3″*A*	1·53 (1)	C2″*B*	C3″*B*	1·53 (1)
C3*A*	C4*A*	1·42 (1)	C3*B*	C4*B*	1·45 (1)
C3′*A*	C4′*A*	1·35 (1)	C3′*B*	C4′*B*	1·40 (1)
C3″*A*	C4″*A*	1·51 (1)	C3″*B*	C4″*B*	1·51 (1)
C4*A*	C10*A*	1·44 (1)	C4*B*	C10*B*	1·43 (1)
C4′*A*	C5′*A*	1·40 (1)	C4′*B*	C5′*B*	1·38 (1)
C4″*A*	C5″*A*	1·51 (1)	C4″*B*	C5″*B*	1·51 (1)
C5*A*	C6*A*	1·38 (1)	C5*B*	C6*B*	1·38 (1)
C5*A*	C10*A*	1·38 (1)	C5*B*	C10*B*	1·39 (1)
C5′*A*	C6′*A*	1·38 (1)	C5′*B*	C6′*B*	1·38 (1)
C5″*A*	C6″*A*	1·51 (1)	C5″*B*	C6″*B*	1·49 (1)
C6*A*	C7*A*	1·39 (1)	C6*B*	C7*B*	1·40 (1)
C7*A*	C8*A*	1·40 (1)	C7*B*	C8*B*	1·40 (1)
C8*A*	C9*A*	1·38 (1)	C8*B*	C9*B*	1·37 (1)
C9*A*	C10*A*	1·41 (1)	C9*B*	C10*B*	1·40 (1)

C2*A*	O1*A*	C9*A*	120·5 (6)	C1″*A*	C8*A*	C9*A*	124·5 (7)
C7*A*	O7*A*	C11*A*	118·0 (6)	C7*A*	C8*A*	C9*A*	116·2 (7)
C1″*A*	O7″*A*	C5″*A*	111·2 (7)	O1*A*	C9*A*	C8*A*	117·5 (7)
C2*A*	C1′*A*	C2′*A*	120·4 (8)	O1*A*	C9*A*	C10*A*	121·3 (7)
C2*A*	C1′*A*	C6′*A*	120·6 (8)	C8*A*	C9*A*	C10*A*	121·0 (7)
C2′*A*	C1′*A*	C6′*A*	119·0 (8)	C4*A*	C10*A*	C5*A*	122·2 (8)
O7″*A*	C1″*A*	C2″*A*	108·7 (6)	C4*A*	C10*A*	C9*A*	117·6 (8)
O7″*A*	C1″*A*	C8*A*	108·9 (8)	C5*A*	C10*A*	C9*A*	120·2 (7)
C2″*A*	C1″*A*	C8*A*	114·3 (8)	C2*B*	O1*B*	C9*B*	122·3 (6)
O1*A*	C2*A*	C1′*A*	111·3 (7)	C4″*B*	C5*B*	C6″*B*	113·2 (7)
O1*A*	C2*A*	C3*A*	122·0 (8)	C5*B*	C6*B*	C7*B*	119·1 (8)
C1′*A*	C2*A*	C3*A*	126·6 (8)	C1′*B*	C6′*B*	C5′*B*	121·3 (9)
C1′*A*	C2′*A*	C3′*A*	119·9 (9)	O7*B*	C7*B*	C6*B*	122·4 (7)
C1″*A*	C2″*A*	C3″*A*	109·0 (7)	O7*B*	C7*B*	C8*B*	115·8 (7)
C2*A*	C3*A*	C4*A*	121·0 (8)	C6*B*	C7*B*	C8*B*	121·6 (8)
C2′*A*	C3′*A*	C4′*A*	120·3 (9)	C1″*B*	C8*B*	C7*B*	119·4 (7)
O3″*A*	C3″*A*	C2″*A*	106·7 (7)	C1″*B*	C8*B*	C9*B*	123·5 (7)
O3″*A*	C3″*A*	C4″*A*	111·3 (7)	C7*B*	O7*B*	C11*B*	118·8 (6)
C2″*A*	C3″*A*	C4″*A*	110·9 (7)	C1″*B*	O7″*B*	C5″*B*	111·3 (6)
O4*A*	C4*A*	C3*A*	121·9 (8)	C2*B*	C1′*B*	C2′*B*	120·1 (8)
O4*A*	C4*A*	C10*A*	120·7 (8)	C2*B*	C1′*B*	C6′*B*	120·9 (8)
C3*A*	C4*A*	C10*A*	117·4 (8)	C2′*B*	C1′*B*	C6′*B*	119·1 (8)
O4′*A*	C4′*A*	C3′*A*	118·6 (9)	O7″*B*	C1″*B*	C2″*B*	109·7 (6)
O4′*A*	C4′*A*	C5′*A*	120·2 (9)	O7″*B*	C1″*B*	C8*B*	108·2 (8)
C3′*A*	C4′*A*	C5′*A*	121·3 (9)	C2″*B*	C1″*B*	C8*B*	112·9 (8)
O4″*B*	C4″*B*	C5″*B*	114·2 (8)	O1*B*	C2*B*	C1′*B*	110·6 (7)
C3″*B*	C4″*B*	C5″*B*	112·2 (6)	O1*B*	C2*B*	C3*B*	121·3 (8)
O5*B*	C5*B*	C6*B*	119·1 (7)	C1′*B*	C2*B*	C3*B*	128·1 (8)
O5*B*	C5*B*	C10*B*	120·3 (8)	C1′*B*	C2′*B*	C3′*B*	121·3 (8)
C6*B*	C5*B*	C10*B*	120·6 (8)	C1″*B*	C2″*B*	C3″*B*	110·2 (8)
C4′*B*	C5′*B*	C6′*B*	119·0 (9)	C2*B*	C3*B*	C4*B*	120·6 (8)
O7″*B*	C5″*B*	C4″*B*	109·8 (7)	C2′*B*	C3′*B*	C4′*B*	118·6 (8)
O7″*B*	C5″*B*	C6″*B*	106·1 (7)	O3″*B*	C3″*B*	C2″*B*	106·0 (7)
O4″*A*	C4″*A*	C3″*A*	108·3 (8)	O3″*B*	C3″*B*	C4″*B*	110·6 (7)
O4″*A*	C4″*A*	C5″*A*	106·8 (7)	C2″*B*	C3″*B*	C4″*B*	110·9 (8)
C3″*A*	C4″*A*	C5″*A*	111·6 (7)	O4*B*	C4*B*	C3*B*	119·7 (8)
O5*A*	C5*A*	C6*A*	120·6 (8)	O4*B*	C4*B*	C10*B*	123·7 (8)
O5*A*	C5*A*	C10*A*	118·9 (8)	C3*B*	C4*B*	C10*B*	116·5 (7)
C6*A*	C5*A*	C10*A*	120·6 (7)	O4′*B*	C4′*B*	C3′*B*	116·0 (9)
C4′*A*	C5′*A*	C6′*A*	118·2 (9)	O4′*B*	C4′*B*	C5′*B*	123·2 (9)
O7″*A*	C5″*A*	C4″*A*	108·6 (7)	C3′*B*	C4′*B*	C5′*B*	120·6 (8)
O7″*A*	C5″*A*	C6″*A*	106·3 (8)	O4″*B*	C4″*B*	C3″*B*	106·0 (7)
C4″*A*	C5″*A*	C6″*A*	111·9 (8)	C7*B*	C8*B*	C9*B*	117·1 (7)
C5*A*	C6*A*	C7*A*	117·5 (8)	O1*B*	C9*B*	C8*B*	117·2 (7)
C1′*A*	C6′*A*	C5′*A*	121·3 (8)	O1*B*	C9*B*	C10*B*	119·5 (7)
O7*A*	C7*A*	C6*A*	119·9 (7)	C8*B*	C9*B*	C10*B*	123·2 (8)
O7*A*	C7*A*	C8*A*	115·7 (7)	C4*B*	C10*B*	C5*B*	122·2 (7)
C6*A*	C7*A*	C8*A*	124·3 (8)	C4*B*	C10*B*	C9*B*	119·7 (7)
C1″*A*	C8*A*	C7*A*	119·3 (8)	C5*B*	C10*B*	C9*B*	118·1 (8)

Table 3. *Intermolecular hydrogen-bonding interactions*

D—H···*A*	*D*···*A* (Å)	*D*—H···*A* (°)	Symmetry operation*
O4′*B*—H6*B*···O4*A*	2·67 (1)	179	(iii) 00 − 1
O4″*A*—H15*A*···O4*B*	2·81 (1)	150	(iii) − 10 − 1
O*W*3—H*W*31···O7″*A*	2·93 (1)	176	(i) 000
O*W*2—H*W*2···O4″*A*	2·928 (6)	145	(iii) − 10 − 1
O3″*B*—H13*B*···O3′*A*	2·80 (1)	150	(i) 000
O*W*3—H*W*32···O3″*B*	2·77 (1)	177	(i) 0 − 10
O4′*A*—H6*A*···O*W*4	2·60 (1)	163	(iv) 0 1 − 1
O*W*4—H*W*41···O*W*3	2·62 (1)	165	(i) 000
O4″*B*—H15*B*···O*W*2	2·78 (1)	174	(iii) − 1 − 1 − 1
O*W*1—H*W*1···O4″*B*	2·82 (1)	140	(i) 000
O3″*A*—H13*A*···O*W*1	2·863 (6)	143	(i) 000

* Translations are along *x*, *y* and *z*, respectively, with the symmetry operators defined as: (i) *x*, *y*, *z*; (ii) $-x$, *y*, $-z$; (iii) $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; (iv) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.

Intramolecular hydrogen bonding occurs between the hydroxyl and ketonic O atoms of the flavone ring system. In molecule *B*, the hydroxyl H atom, H2*B*, located directly from the difference Fourier map, shows hydrogen bonding to the ketonic O atom, O4*B* (O5*B*—H2*B* = 1·21, O5*B*···O4*B* = 2·61 (1), H2*B*···O4*B* = 1·76 Å and O5*B*—H2*B*···O4*B* = 122°). The related H atom was not located for molecule *A*; however, its presence is inferred from the distance of O5*A*···O4*A* = 2·514 (9) Å and the absence of other short contacts to O5*A*. The intramolecular hydrogen bonding of aciculatin is similar to that exhibited in the related hydroxyflavones, hymenoxin (Watson, Kashyap, Gao & Mabry, 1991), 3-hydroxyflavone (Etter, Urbanczyk-Lipkowska, Baer & Barbara, 1986) or 5-hydroxyflavone (Shoja, 1990), 5-hydroxy-7-methoxyflavone (Shoja, 1989), 5,4′-dihydroxy-3,6,7,8-tetramethoxyflavone (Vijayalakshmi, Rajan, Srinivasan & Ramachandran Nair, 1986) and 4′,5,7-trihydroxyisoflavone (Breton, Precigoux, Courseille & Hospital, 1975).

The 2,6-dideoxy-β-*ribo*-hexopyranosyl ring is linked to C8 of the flavone through a β-*C*-glycosidic bond. The hexopyranosyl ring adopts a chair conformation with C1″ and C4″ located on opposite sides of the plane generated by C2″—C3″—C5″—O7″. This is similar to both pyran rings in isokidamycin bis(*m*-bromobenzoate) (Furukawa & Iitaka, 1974, 1980) or one of the pyran rings (ring *E*) in triacetylmethoxykidamycin bis(trimethylammonium) iodide (Furukawa, Itai & Iitaka, 1973; Furukawa & Iitaka, 1974) and the β-D-glucosyl ring in 5-hydroxy-3′,6-dibromo-2″,3″,4′,4″,6″,7-hexaacetylvitexin (Jurnak & Templeton, 1975). The 4″-OH and 5″-CH_3 substituents adopt equatorial positions while the 3″-OH substituent adopts an axial position. As with the vitexin derivative, the plane of the hexopyranosyl ring is essentially perpendicular to the benzopyran ring [molecule *A* 91·4 (3), molecule *B* 88·9 (3)°] in order to minimize steric interactions.

The two independent molecules of aciculatin also differ in the magnitude of the torsion angles associated with the hydroxyl groups on the phenolic and

hexopyranosyl rings. The 4′-OH [C5′*A*—C4′*A*—O4′*A*—H6*A* = −8 (1) and C5′*B*—C4′*B*—O4′*B*—H6*B* = 30 (2)°] and 3″-OH (C4″*A*—C3″*A*—O3″*A*—H13*A* = 93·1 (8) and C4″*B*—C3″*B*—O3″*B*—H13*B* = 74·9 (7)°] torsion angles are moderately different. The largest difference in torsion angles occurs with the 4″-hydroxyls [C5″*A*—C4″*A*—O4″*A*—H15*A* = 128·4 (7) and C5″*B*—C4″*B*—O4″*B*—H15*B* = 64·6 (8)°].

Intermolecular hydrogen bonding (Table 3) occurs between O3″*A* and O3″*B* [O3″*B*···O3″*A* = 2·80 (1) Å and 150°] of the two independent molecules. In addition, hydrogen bonding occurs between the ketonic O atom O4*A* and the phenolic O atom O4′*B* [O4′*B*···O4*A* = 2·67 (1) Å and 179°] and between the ketonic O atom O4*B* and the hydroxyl O atom O4″*A* [O4″*A*···O4*B* = 2·81 (1) Å and 150°]. There is also a network of hydrogen-bonding interactions between the aciculatin molecules and the water molecules which stabilizes the crystal lattice.

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Structure of Cortivazol, 11β,17α,21-Trihydroxy-6,16α-dimethyl-2′-phenyl-2′*H*-pregna-2,4,6-trieno[3,2-*c*]pyrazol-20-one 21-Acetate

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Abstract. $C_{32}H_{38}N_2O_5$, $M_r = 530{\cdot}7$, monoclinic, *C*2, $a = 30{\cdot}625$ (5), $b = 6{\cdot}229$ (2), $c = 15{\cdot}289$ (2) Å, $\beta = 93{\cdot}86$ (2)°, $V = 2909{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}211$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}2$ cm^{-1}, $F(000) = 1136$, $T = 292$ K, final $R = 0{\cdot}047$ for 2415 reflections with $I > 2{\cdot}5\sigma(I)$. All bond lengths and angles are within normal limits. Ring *A* with two double bonds is not planar, but is in the 1α,10β half-chair conformation. Ring *B* is in a 9α,10β half-chair conformation distorted towards a 9α sofa. Ring *C* is in the expected chair conformation, whereas ring *D* is in the 13β envelope conformation. The C20, C26, C27 and N29 substituents are equatorial, O11, C18 and C19 are β axial, and O17 and C25 are α axial. Rings *C* and *D*

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