87 (1)°. The ethoxy side chain exhibits an extended conformation with a C(14)C(13)O(12)C(2) torsion angle of 178·4 (8)°.

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rel-(2*S*,3*S*)-3-Hydroxy-7-methoxy-3′,4′-methylenedioxyflavan

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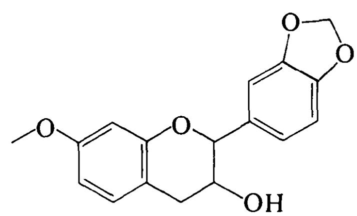
Abstract. $C_{17}H_{16}O_5$, M_r = 300·33, monoclinic, $P2_1$, a = 12·634 (2), b = 11·491 (3), c = 4·881 (1) Å, β = 99·64 (1)°, V = 698·6 (3) Å^3, Z = 2, d_c = 1·427, d_o = 1·42 Mg m^{-3}, μ = 0·828 mm^{-1}. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1082 reflexions led to a final R of 0·045. The two ring systems exhibit an interplanar angle of 19·2 (7)°. An intermolecular hydrogen bond is formed between the hydroxyl H and the methoxy O atom of adjacent molecules.

Introduction. Extracts of the bulbs of *Hippeastrum añañuca* (Amaryllidaceae) exhibited cytotoxic activity in the *in vitro* KB cell assay (Pacheco, Silva, Steglich & Watson, 1978). The alkaloids lycorine (Gopalakrishna, Watson, Pacheco & Silva, 1976), 17-epihomolycorine (Gopalakrishna, Watson, Silva & Pacheco, 1978), maritidine (Zabel, Watson, Pacheco & Silva, 1979) and hippeastidine (Watson, Taira, Silva & Pacheco, 1977) were isolated and identified by spectroscopic and single-crystal X-ray diffraction techniques. A white crystalline nonalkaloidal compound, m.p. 411–412 K, was also isolated and proved to be the new procyanidin 3-hydroxy-7-methoxy-3′,4′-methylenedioxyflavan (I). Procyanidins occur in many fruit-bearing plants as oligomers where the yield is highly dependent upon the state of fruit maturity. The occurrence of procyanidins in the bulbs of Amaryllidaceae has not been reported previously.



(I)

A crystal of dimensions 0·15 × 0·25 × 0·35 mm was used to collect intensity data on a Syntex $P2_1$ diffractometer system by the θ:2θ scanning technique using a variable scan speed with Cu $K\alpha$ radiation (λ = 1·54178 Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 medium-angle reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group $P2_1$. 1102 independent reflexions were measured for $2\theta < 120°$ and 1082 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were applied, but no

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Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$)

	x	y	z
O(1)	9046 (2)	0877*	1312 (6)
C(2)	8419 (3)	1460 (4)	−1027 (8)
C(3)	8418 (3)	2781 (4)	−0609 (8)
C(4)	9561 (4)	3211 (4)	−0232 (9)
C(4a)	10257 (3)	2536 (4)	2073 (8)
C(5)	1119 (3)	2973 (4)	3603 (9)
C(6)	11829 (3)	2340 (4)	5660 (9)
C(7)	11496 (3)	1222 (4)	6201 (8)
C(8)	10567 (3)	0761 (4)	4692 (9)
C(8a)	9964 (3)	1408 (4)	2624 (8)
O(9)	7925 (2)	2993 (3)	1776 (6)
O(10)	12052 (3)	0500 (3)	8173 (7)
C(11)	12920 (5)	0980 (6)	10064 (12)
C(1′)	7328 (3)	0891 (5)	−1521 (8)
C(2′)	7083 (4)	−0021 (5)	0081 (14)
C(3′)	6104 (4)	−0528 (4)	−0556 (12)
C(4′)	5356 (4)	−0189 (6)	−2721 (11)
C(5′)	5560 (6)	0718 (12)	−4331 (16)
C(6′)	6579 (5)	1245 (9)	−3744 (12)
O(7′)	5699 (4)	−1462 (5)	0789 (17)
C(8′)	4637 (5)	−1642 (6)	−0568 (24)
O(9′)	4447 (3)	−0858 (5)	−2914 (10)
H(2)	873 (3)	139 (5)	−274 (9)
H(3)	793 (4)	315 (5)	−230 (10)
H(4α)	977 (4)	307 (5)	−226 (9)
H(4β)	965 (3)	406 (5)	040 (8)
H(5)	1151 (5)	372 (8)	339 (12)
H(6)	1254 (5)	261 (6)	677 (10)
H(8)	1042 (4)	012 (6)	511 (10)
H(9)	804 (6)	389 (8)	237 (12)
H(11α)	1315 (5)	048 (7)	1202 (13)
H(11β)	1277 (7)	179 (9)	1115 (16)
H(11γ)	1347 (5)	112 (5)	916 (10)
H(2′)	749 (6)	−029 (7)	128 (13)
H(5′)	496 (7)	128 (8)	−581 (15)
H(6′)	681 (7)	189 (9)	−503 (15)
H(8α′)	444 (6)	−245 (10)	−092 (15)
H(8β′)	391 (5)	−138 (7)	065 (12)

* Fixed during the refinement.

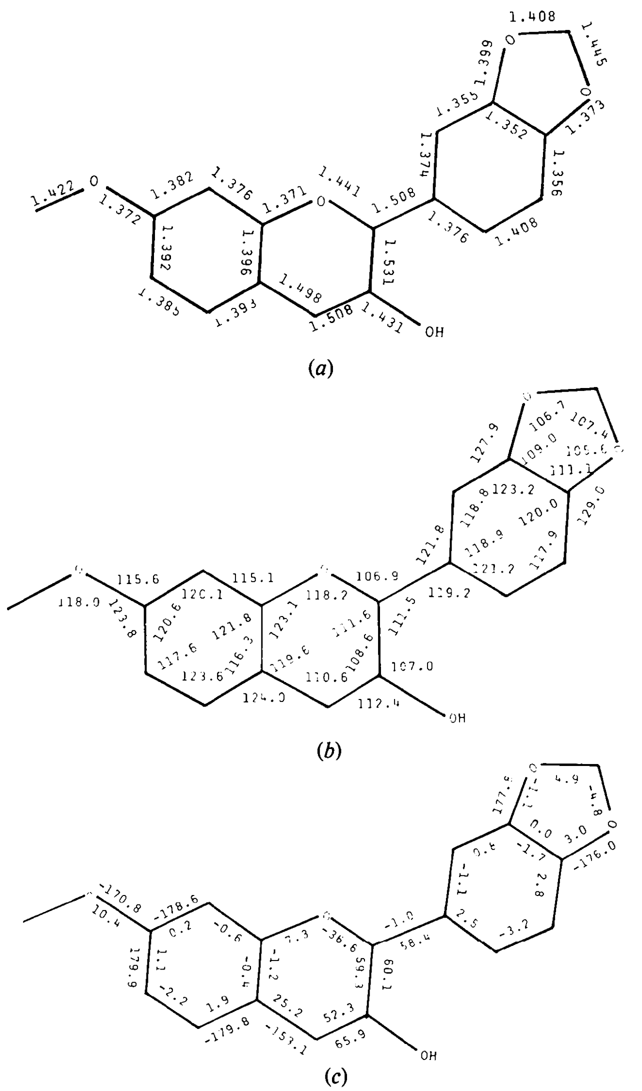

Fig. 1. (*a*) Interatomic distances (Å), (*b*) valence angles (°) and (*c*) torsion angles (°). Standard deviations in bond lengths range from 0·004 to 0·009 Å, in valence angles from 0·3 to 0·5° and in torsion angles from 0·5 to 1·1°.

absorption corrections were made. The direct methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300 $|E|$ values greater than 1·30. The phase set with the highest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of 16 atoms. Alternate least-squares refinements and difference Fourier calculations yielded the coordinates of the missing six C and 16 H atoms. Least-squares refinement yielded a final R of 0·045 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The R value using all 1102 reflexions was 0·049 while R_w was 0·075. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = [1/\sigma(F_o)]^2$ was determined from counting statistics.

A final difference map showed no peak larger than 0·18 e Å^{-3}, and all shifts in parameters were less than 0·5σ. The XRAY system (Stewart, 1976) was used in the final stages of refinement. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1 while interatomic distances, angles and torsion angles are presented in Fig. 1.* The C—H lengths average 1·01 (9) Å.

Discussion. Fig. 2 is an *ORTEP* drawing (Johnson, 1965) of the title compound. The two phenyl groups are planar and exhibit an interplanar angle of 19·2 (7)°.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34749 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

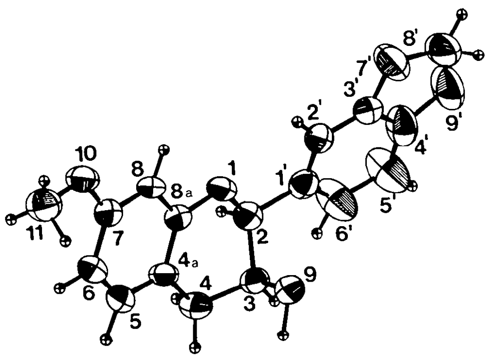

Fig. 2. *ORTEP* drawing of 3-hydroxy-7-methoxy-3′,4′-methylenedioxyflavan. Thermal ellipsoids are presented at the 50% probability level while H atoms are represented by spheres of arbitrary radius.

The methoxy methyl group bonded to C(7) is twisted slightly out of the plane as indicated by the C(6)C(7)-O(10)C(11) torsion angle of 10·4 (7)°. The five-membered ring is almost planar and a least-squares plane fitted to the atoms of the phenyl and methylenedioxy moieties shows a maximum deviation of 0·02 Å for O(7) and C(8). The conformation of the six-membered heterocyclic ring lies between the half-chair and 1,2-diplanar forms. The six C—C distances of the phenyl ring (4a–8a) average 1·387 (6) Å while the six C—C distances of the other phenyl ring average 1·370 (15) Å. The four $C(sp^2)$—$O(sp^3)$ distances average 1·378 (9) Å and the five $C(sp^3)$—$O(sp^3)$ distances 1·429 (11) Å. An intermolecular hydrogen bond is formed between the hydroxyl group bonded to C(3) and the O(10) methoxy O atom, O(9)···O(10) = 2·874 (5), O(9)—H(9) = 1·06 (9) and H(9)···O(10) = 1·87 (9) Å. The absolute configuration could not be assigned unambiguously from enantiomorph refinement and application of the Hamilton significance test.

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N,O-Diacetyl-4-hydroxynornantenine

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Abstract. $C_{23}H_{23}NO_7$, M_r = 425·15, tetragonal, $P4_12_12$, a = 14·996 (4), c = 17·960 (4) Å, V = 4039 (2) $Å^3$, Z = 8, d_c = 1·398 Mg m^{-3}, μ = 0·744 mm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1921 reflexions led to a final R of 0·045. 4-Hydroxynornantenine is a nor-aporphine-type alkaloid. The N and attached atoms form a reasonably planar system which implies sp^2 hybridization of the N atom and conjugation with the carbonyl of the *N*-acetyl function.

Introduction. *Laurelia phillipiana* Looser (Atherospermataceae) is a Chilean tree which has yielded several aporphines and 7-oxoaporphines (Urzua, Cassels, Comin & Sanchez, 1975). A further study of

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