

Fig. 2. Molecular packing of the title compound viewed along the *b* axis.

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Structure of *ent*-(12*R*)-Methyl-15,16-epoxy-9,10-friedolabda-5(10),13(16),14-trien-19-oate 20,12-Lactone (Penduliflaworosin)

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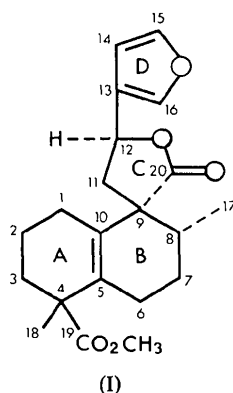
Abstract. Systematic name: 5-(3-furanyl)-3',4,4',5,5',-6',7',8'-octahydro-2',5'-dimethyl-2-oxospiro[furan-3(2*H*),1'(2'*H*)-naphthalene]-5'-carboxylic acid methyl ester, $C_{21}H_{26}O_5$, $M_r = 358.4$, orthorhombic, $P2_12_12_1$, $a = 6.2780$ (5), $b = 12.3069$ (10), $c = 25.1047$ (22) Å, $V = 1939.66$ Å³, $Z = 4$, $D_x = 1.227$ Mg m⁻³. Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1.54178$ Å), $\mu(\text{Cu } K\alpha) = 0.67$ mm⁻¹, $F(000) = 768$, $T = 290$ K. Final $R = 0.044$, $wR = 0.045$ for 1914 'observed' reflections and 313 variables. The two six-membered rings *A* and *B* adopt half-chair and intermediate half-chair/envelope conformations, respec-

tively, while the lactone ring is close to a half-chair (C_2 form). Methyl groups C(18) and C(17) are pseudo-axial and bisectonal respectively. The conformation of the methoxycarbonyl group is synperiplanar.

Introduction. The title compound, isolated from *Croton penduliflorus* Hutch (Euphorbiaceae), an important medicinal plant used by the Yorubas of Nigeria as a remedy for stomach complaints, was reported to have the structure (I) (Adesogan, 1981). In the structure (I), proposed on spectroscopic (NMR, IR, UV) and chemical evidence, the stereochemistry was inferred on biogenetic grounds. Penduliflaworosin is of interest in view of the current emphasis and importance which the Nigerian government places on local medicinal plants

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as a source for developing local drugs. The X-ray analysis was undertaken in order to resolve the stereochemistry of the title compound.



Experimental. Suitable single crystals were obtained by recrystallization from methanol. A light yellow crystal approximately $0.10 \times 0.15 \times 0.06$ mm was used during the measurements. The unit-cell dimensions were determined from the angular settings of 25 reflections in the range $22 < \theta < 29^\circ$. The space group was inferred from systematic absences ($h00$ with $h = 2n + 1$, $0k0$ with $k = 2n + 1$, $00l$ with $l = 2n + 1$). The intensity data of 8090 reflections up to $\theta = 70^\circ$ in the range $-7 \leq h \leq 0$, $-15 \leq k \leq 15$, $-30 \leq l \leq 30$ were measured, using the $\omega-2\theta$ scan-technique with a scan angle of 1.00° and a variable scan rate with a maximum scan time of 20 s per reflection. Throughout the experiment Cu $K\alpha$ radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 single-crystal diffractometer ($\lambda = 1.54178 \text{ \AA}$). The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 minutes. The final drift correction factors were between 1.00 and 1.04. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); an empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0.88 to 1.00). Symmetry-equivalent reflections were averaged, $R_{\text{int}} = 0.045$, resulting in 3671 unique reflections of which 1914 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values.

The structure was solved with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The positions of all non-hydrogen atoms were obtained. Isotropic least-squares refinement with *SHELX* (Sheldrick, 1976) converged at $R = 0.116$. At this stage an additional empirical absorption correction was applied (Walker & Stuart, 1983), leading to a further reduction of R to 0.074. All the hydrogen atoms were located from a difference Fourier calculation.

Table 1. Fractional positional and thermal parameters (with e.s.d.'s in parentheses)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} (\text{\AA}^2 \times 10^3)$
O(1)	-0.2084 (8)	0.3068 (4)	0.0525 (2)	11.4 (2)
O(2)	0.2653 (4)	0.2147 (2)	0.1809 (1)	4.5 (1)
O(3)	0.5565 (4)	0.2241 (2)	0.2301 (1)	4.6 (1)
O(4)	0.2558 (7)	0.4217 (3)	0.4812 (1)	9.6 (2)
O(5)	-0.0206 (6)	0.4381 (3)	0.4275 (1)	7.7 (1)
C(1)	0.0587 (7)	0.1908 (4)	0.3090 (2)	4.3 (1)
C(2)	0.0495 (9)	0.1331 (4)	0.3621 (2)	5.5 (2)
C(3)	0.0207 (8)	0.2171 (4)	0.4062 (2)	5.2 (2)
C(4)	0.2126 (6)	0.2931 (4)	0.4094 (1)	4.3 (1)
C(5)	0.2728 (6)	0.3362 (3)	0.3537 (2)	4.0 (1)
C(6)	0.4240 (8)	0.4324 (4)	0.3534 (2)	5.1 (2)
C(7)	0.5337 (7)	0.4456 (4)	0.3010 (2)	4.6 (1)
C(8)	0.3712 (6)	0.4472 (3)	0.2561 (2)	4.2 (1)
C(9)	0.2489 (6)	0.3375 (3)	0.2539 (1)	3.3 (1)
C(10)	0.1999 (5)	0.2908 (3)	0.3090 (1)	3.3 (1)
C(11)	0.0476 (7)	0.3498 (4)	0.2191 (2)	4.1 (1)
C(12)	0.0457 (6)	0.2555 (4)	0.1806 (2)	4.3 (1)
C(13)	-0.0149 (7)	0.2833 (4)	0.1256 (2)	5.3 (2)
C(14)	0.1083 (9)	0.3369 (5)	0.0863 (2)	7.5 (2)
C(15)	-0.0130 (2)	0.3486 (7)	0.0444 (2)	10.7 (3)
C(16)	-0.2060 (9)	0.2650 (6)	0.1032 (2)	8.1 (2)
C(17)	0.4716 (9)	0.4784 (4)	0.2028 (2)	5.2 (2)
C(18)	0.4036 (9)	0.2352 (5)	0.4345 (2)	6.8 (2)
C(19)	0.1566 (8)	0.3902 (4)	0.4440 (2)	5.8 (2)
C(20)	0.3761 (6)	0.2545 (3)	0.2223 (2)	3.7 (1)
C(21)	-0.0990 (1)	0.5295 (6)	0.4584 (3)	10.3 (3)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) (e.s.d.'s in parentheses)

O(1)–C(15)	1.347 (9)	C(5)–C(6)	1.518 (6)
O(1)–C(16)	1.373 (6)	C(5)–C(10)	1.334 (5)
O(2)–C(12)	1.467 (5)	C(6)–C(7)	1.495 (6)
O(2)–C(20)	1.344 (4)	C(7)–C(8)	1.520 (5)
O(3)–C(2)	1.209 (4)	C(8)–C(9)	1.554 (5)
O(4)–C(19)	1.188 (5)	C(8)–C(17)	1.529 (6)
O(5)–C(19)	1.325 (5)	C(9)–C(10)	1.529 (5)
O(5)–C(21)	1.453 (6)	C(9)–C(11)	1.545 (5)
C(1)–C(2)	1.511 (6)	C(9)–C(20)	1.520 (5)
C(1)–C(10)	1.517 (5)	C(11)–C(12)	1.510 (6)
C(2)–C(3)	1.526 (7)	C(12)–C(13)	1.472 (5)
C(3)–C(4)	1.528 (6)	C(13)–C(14)	1.416 (7)
C(4)–C(5)	1.542 (5)	C(13)–C(16)	1.344 (6)
C(4)–C(18)	1.531 (6)	C(14)–C(15)	1.307 (8)
C(4)–C(19)	1.519 (6)		
C(15)–O(1)–C(16)	105.9 (5)	C(8)–C(9)–C(20)	110.1 (3)
C(12)–O(2)–C(20)	111.4 (3)	C(10)–C(9)–C(20)	109.0 (3)
C(19)–O(5)–C(21)	117.6 (5)	C(11)–C(9)–C(20)	101.5 (3)
C(2)–C(1)–C(10)	113.8 (4)	C(1)–C(10)–C(5)	122.7 (4)
C(1)–C(2)–C(3)	109.1 (4)	C(1)–C(10)–C(9)	115.0 (3)
C(2)–C(3)–C(4)	111.0 (4)	C(5)–C(10)–C(9)	122.3 (3)
C(3)–C(4)–C(5)	110.9 (3)	C(9)–C(11)–C(12)	107.1 (3)
C(3)–C(4)–C(18)	110.7 (4)	O(2)–C(12)–C(11)	104.6 (3)
C(5)–C(4)–C(18)	110.0 (4)	O(2)–C(12)–C(13)	109.1 (3)
C(3)–C(4)–C(19)	109.2 (3)	C(11)–C(12)–C(13)	115.1 (4)
C(5)–C(4)–C(19)	107.7 (4)	C(12)–C(13)–C(14)	128.3 (4)
C(18)–C(4)–C(19)	108.2 (4)	C(12)–C(13)–C(16)	125.7 (5)
C(4)–C(5)–C(6)	115.2 (3)	C(14)–C(13)–C(16)	106.0 (4)
C(4)–C(5)–C(10)	122.3 (4)	C(13)–C(14)–C(15)	107.1 (6)
C(6)–C(5)–C(10)	122.5 (4)	O(1)–C(15)–C(14)	111.5 (6)
C(5)–C(6)–C(7)	112.2 (4)	O(1)–C(16)–C(13)	109.5 (5)
C(6)–C(7)–C(8)	110.1 (4)	O(4)–C(19)–O(5)	122.7 (5)
C(7)–C(8)–C(9)	110.3 (3)	O(4)–C(19)–C(4)	125.8 (5)
C(7)–C(8)–C(17)	112.0 (4)	O(5)–C(19)–C(4)	111.5 (4)
C(9)–C(8)–C(17)	113.0 (3)	O(2)–C(20)–O(3)	119.8 (4)
C(8)–C(9)–C(10)	113.2 (3)	O(2)–C(20)–C(9)	112.2 (3)
C(8)–C(9)–C(11)	109.8 (3)	O(3)–C(20)–C(9)	128.0 (4)
C(10)–C(9)–C(11)	112.6 (3)		

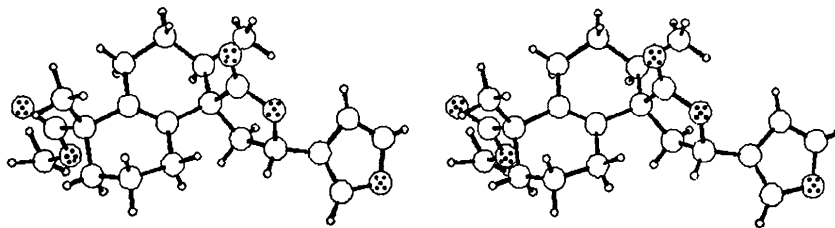


Fig. 1. Stereoview of the title compound. Oxygen atoms are shown dotted.

Full-matrix anisotropic least squares with *SHELX* (Sheldrick, 1976) on the positional parameters, but with temperature factors for the H atoms fixed at 0.060 \AA^2 , converged at $R = 0.044$ and $wR = 0.045$, $S = 1.081$ for the 1914 'observed' reflections and 313 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.00040F_o^2]$, $\sigma(F_o)$ from counting statistics. The maximum shift-to-e.s.d. ratios in the final full-matrix least-squares cycle were 0.03 and 0.09 for the non-hydrogen and the hydrogen atoms respectively, while the maximum noise level was 0.25 e \AA^{-3} . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Plots were made with *PLUTO* (Motherwell, 1976). After completion of the refinement, we tried to establish the absolute configuration of this natural product by calculating the average product of the calculated and observed Bijvoet difference as $+1.58 \pm 1.56$ on 811 Friedel pairs, which means that there is a probability of about 70% that the present parameters represent the absolute configuration of the structure.

Discussion. Final positional and thermal parameters are given in Table 1,* while molecular geometry data are collected in Table 2. A stereoview of the molecule showing the molecular configuration is given in Fig. 1. The crystallographic numbering scheme is given in Fig. 2. The C—H bond lengths in the molecule lie in the range $0.804\text{--}1.060 \text{ \AA}$, with an average of $0.961 (3) \text{ \AA}$. The six-membered ring *A* has a half-chair conformation, with a (pseudo-) twofold axis passing through the middle of C(2), C(3) while ring *B* has an intermediate half-chair/envelope form with C(7) out of the plane. In the notation introduced by Boeyens (1978) the rings approach forms denoted as 2H_3 and E_7 respectively. The lactone ring *C* is close to a half-chair (pseudo- C_2) form with a (pseudo-) twofold axis through C(20) and the centre of the C(11)—C(12). The

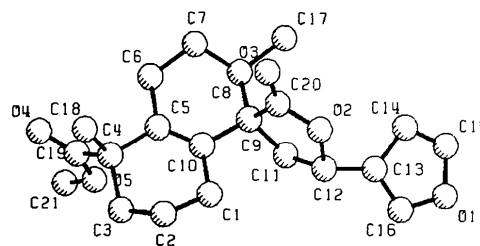


Fig. 2. Crystallographic atomic numbering scheme.

corresponding asymmetry parameters (Duax, Weeks & Rohrer, 1976) are: ring *A*: $\Delta C_2[C(2)\text{--}C(3)] = 2.8 (6)$; ring *B*: $\Delta C_2[C(7)\text{--}C(8)] = 13.4 (6)$, $\Delta C_3[C(7)] = 14.1 (6)$; ring *C*: $\Delta C_2[C(11)\text{--}C(12)] = 1.0 (6)^\circ$. The furan ring *D* is essentially planar, the maximum deviation of the atoms from the least-squares-fitted plane through C(13), C(14), C(15), O(1), C(16) being $0.009 (6) \text{ \AA}$. Methyl groups C(18) and C(17) are pseudo-axial and bisectonal, respectively. The C(4)—C(19) bond points into a pseudo-equatorial direction. The planar methoxycarbonyl group is almost perpendicular to the 'planes' of the two six-membered rings [dihedral angles are $92.9 (2)^\circ$ and $87.6 (2)^\circ$ respectively]. The conformation of the methoxycarbonyl group is synperiplanar [torsion angle C(21)—O(5)—C(19)—O(4) close to 0°], the same conformation as observed in free methyl acetate (Pyckhout, van Alsenoy & Geise, 1987). The least-squares planes through the atoms of rings *A* and *B* are at $169.7 (1)^\circ$ to one another. The deviations of H(12) and C(17) from the planes through the atoms O(2), C(12), C(11) and C(7), C(8), C(9) are $-2.72 (4)$ and $-1.14 (1) \text{ \AA}$ respectively, indicating the conformation of H(12) and C(17) to be α . Similarly the conformation of C(19) is β [deviation of C(19) from the plane through C(3), C(4), C(5) is $1.260 (5) \text{ \AA}$]. These results are in agreement with earlier results (Adesogan, 1981).

* Lists of structure factors, H-atom positions, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43438 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 3,4,5-Tri-*O*-acetyl-1-deoxy-1-[(2,2-dimethoxycarbonylvinyl)amino]- β -D-fructopyranose

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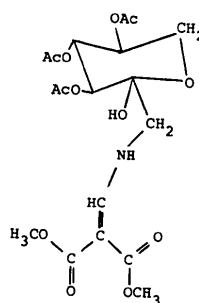
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Abstract. $C_{18}H_{25}NO_{12}$, $M_r = 447.4$, monoclinic, $P2_1$, $a = 8.879$ (2), $b = 7.375$ (3), $c = 16.990$ (2) Å, $\beta = 93.15$ (1)°, $V = 1110.9$ (5) Å³, $Z = 2$, $D_m = 1.32$, $D_x = 1.33$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.1065$ mm⁻¹, $F(000) = 472$, $T = 300$ K, final $R = 0.070$ for 2026 observed [$I \geq 2\sigma(I)$] independent reflections. Owing to the push–pull effect, the C=C bond distance is as long as 1.393 (8) Å and the twist angle around this bond is -174.2 (6)°. The sugar has a β -D configuration and the bond lengths and angles in the pyranose ring are normal. The two C–O glycosidic bond lengths are not equal [1.446 (9), 1.413 (7) Å], the shorter involving the anomeric carbon. The pyranose ring is in the chair conformation. The molecule has an intramolecular hydrogen bond between the NH and CO groups in the *Z* configuration, adopting the chelated form. The molecules are linked by van der Waals forces; additionally, one intermolecular hydrogen bond O–H...O through the OH group of the sugar and the carbonyl group in the configuration *E* is found.

Introduction. In the course of studying the behaviour of compounds with push–pull effects, and as a part of structural studies on enaminoesters and ketones ('enaminones'), the crystal structure of the title compound has been determined. A large number of substituted ethylenes are known where the C–C bond is significantly longer than in ethylene and the deviation from planarity is quite appreciable (Abrahamsson,

Rehnberg, Liljefors & Sandstrom, 1974; Ammon & Wheeler, 1975; Ammon, 1976; Adhikesavalu & Venkatesan, 1981, 1982; Diánez, López-Castro & Márquez, 1985). The two main factors which determine the geometry of the molecule are the conjugation push–pull effect and the steric strain in the planar state.

The compound of formula



has been obtained, as a subproduct, from 1-deoxy-1-[2,2-dimethoxycarbonylvinyl]amino]-D-fructose and acetic anhydride in pyridine (275–295 K).

In this communication we report our findings on the molecular geometry as observed in the crystal structure.

Experimental. D_m measured by flotation. Single crystal in form of colourless prism with approximate dimensions 0.30 × 0.31 × 0.43 mm used for intensity-data