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Glycoric Acid, a New Degraded Carotenoid from *Glycosmis arborea*

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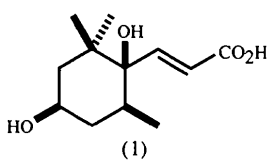
Abstract

The title compound, (7*E*)-3β,6β-dihydroxy-10-normegastigm-7-en-9-oic acid, (1) [(*E*)-3-(1,4-dihydroxy-2,2,6-trimethyl-1-cyclohexyl)acrylic acid, $C_{12}H_{20}O_4$], which is a kind of degraded carotenoid, was isolated from the hepatoprotective *n*-butanol-soluble fraction of the methanol extract of *Glycosmis arborea*. From NMR and other spectral analyses, (1) was inferred to possess a new 10-normegastigmane skeleton and its molecular formula was determined by high-resolution mass spectrometry. We describe herein the conformation of the ring system and the configuration of the substituents based on X-ray diffraction analysis. The crystal structure is stabilized by intermolecular O—H···O hydrogen bonds.

Comment

Glycosmis arborea (Roxb.) DC (Rutaceae) is a plant native to India and is used locally to treat fever, liver complaints and some other diseases (Sastri, 1956). The *n*-butanol-soluble fraction of the methanol extract of the overground part of the plant was found to possess significant hepatoprotective activity against CCl_4-induced liver toxicity in experimental animals (Gomes, unpublished results). The chemical investigation of this fraction resulted in the isolation of the title compound, (1), which was found to be (7*E*)-3β,6β-dihydroxy-10-normegastigm-7-en-9-oic acid, possessing to a new 10-normegastigmane skeleton, based on one-dimensional (^{1}H and ^{13}C) and two-dimensional NMR, and other spectral analyses (Chakravarty, Das, Masuda & Ageta, 1996).



(1)

As can be seen from the torsion angles in Table 2, the six-membered ring adopts a chair configuration. Atoms C6, C7, C8, C9, O3 and O4, which include the carboxyl group, are coplanar, the mean deviation from the least-squares plane being 0.063 (2) Å.

The crystal structure of (1) is stabilized by intermolecular O—H···O hydrogen bonds between hydroxyl and carboxyl groups, and between hydroxyl groups, which results in the structure being in the rare $P6_5$ space group. Hydrogen-bonding parameters are as follows: O1···O2^{i} 2.756 (2) Å and O1—H18···O2^{i} 159 (3)°; O2···O3^{ii} 2.791 (2) Å and O2—H19···O3^{ii} 160 (3)°; O4···O1^{iii} 2.644 (2) Å and O4—H20···O1^{iii} 176 (3)° [symmetry codes: (i) $y+1$, $y-x+1$, $z+\frac{1}{6}$; (ii) $x+1$, y, z; (iii) $x-y-1$, $x-1$, $z-\frac{1}{6}$].

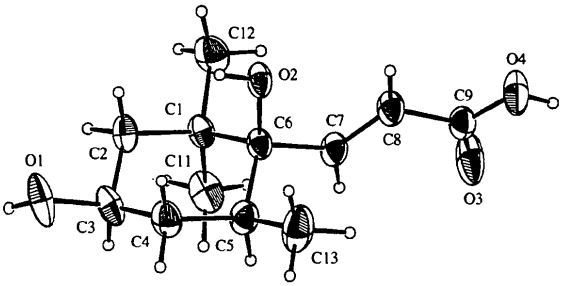


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of (1) with all H atoms shown. Displacement ellipsoids are drawn at the 50% probability level.

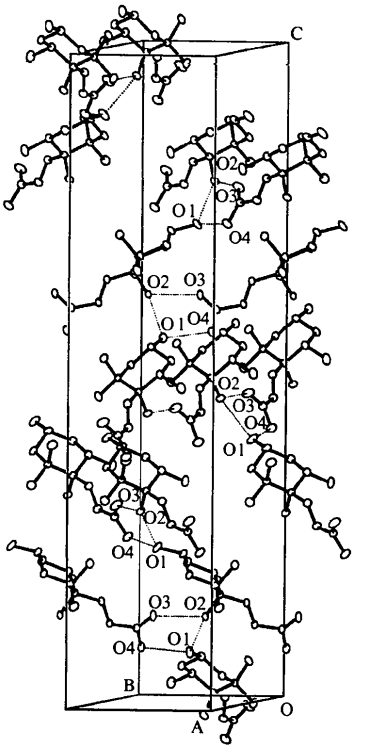


Fig. 2. An *ORTEP*II (Johnson, 1976) packing diagram of (1). The hydrogen bonds are shown by dashed lines. Displacement ellipsoids are drawn at the 25% probability level.

Experimental

Single crystals of the title compound were obtained by recrystallization from methanol solution.

Crystal data

$C_{12}H_{20}O_4$
M_r = 228.29
Hexagonal
$P6_5$
a = 7.755 Å
c = 35.137 (2) Å
V = 1830.0 (1) Å^3
Z = 6
D_x = 1.24 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–19°
μ = 0.09 mm^{-1}
T = 296 K
Block
0.53 × 0.40 × 0.40 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.983, T_{max} = 0.999
1647 measured reflections
1262 independent reflections

1109 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.016
θ_{max} = 78°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = -42 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
R = 0.028
wR = 0.036
S = 1.31
1109 reflections
204 parameters
Only H-atom U's refined
$w = 4F_o^2/[\sigma^2(I) + (0.04F_o^2)^2]$

$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O1	1.0706 (2)	0.3864 (2)	0.56780 (5)	4.00 (3)
O2	0.6940 (2)	0.2994 (2)	0.462	2.45 (2)
O3	0.0444 (2)	0.2813 (2)	0.46196 (6)	4.60 (3)
O4	0.0458 (2)	0.1227 (2)	0.40978 (5)	3.63 (3)
C1	0.7353 (2)	0.5299 (2)	0.51369 (6)	2.19 (3)
C2	0.9260 (2)	0.5392 (2)	0.52924 (6)	2.51 (4)
C3	0.8854 (3)	0.3762 (3)	0.55753 (6)	2.85 (4)
C4	0.7523 (2)	0.1727 (3)	0.54045 (6)	2.77 (4)
C5	0.5592 (3)	0.1501 (3)	0.52402 (6)	2.57 (4)
C6	0.6004 (2)	0.3188 (2)	0.49541 (5)	2.04 (3)
C7	0.4045 (2)	0.2962 (2)	0.48295 (6)	2.45 (4)
C8	0.3254 (2)	0.2488 (3)	0.44868 (6)	2.65 (4)
C9	0.1250 (3)	0.2200 (3)	0.44137 (6)	2.53 (4)
C11	0.6302 (3)	0.5738 (3)	0.54606 (7)	3.29 (4)
C12	0.7959 (3)	0.6926 (3)	0.48334 (7)	3.42 (5)
C13	0.4357 (3)	−0.0558 (3)	0.50624 (8)	4.08 (6)

Table 2. *Selected geometric parameters (Å, °)*

O1—C3	1.444 (3)	C2—C3	1.512 (3)
O2—C6	1.433 (2)	C3—C4	1.513 (2)
O3—C9	1.199 (3)	C4—C5	1.531 (3)
O4—C9	1.310 (3)	C5—C6	1.551 (3)
C1—C2	1.544 (3)	C5—C13	1.526 (3)
C1—C6	1.574 (2)	C6—C7	1.504 (3)
C1—C11	1.534 (3)	C7—C8	1.318 (3)
C1—C12	1.535 (3)	C8—C9	1.478 (3)
C2—C1—C6	108.4 (2)	C6—C5—C13	112.0 (2)
C2—C1—C11	109.3 (2)	O2—C6—C1	109.7 (1)
C2—C1—C12	108.3 (1)	O2—C6—C5	110.3 (2)
C6—C1—C11	112.5 (1)	O2—C6—C7	106.4 (1)
C6—C1—C12	110.1 (2)	C1—C6—C5	111.3 (2)
C11—C1—C12	108.1 (2)	C1—C6—C7	110.3 (2)
C1—C2—C3	113.5 (1)	C5—C6—C7	108.7 (1)
O1—C3—C2	109.4 (1)	C6—C7—C8	126.9 (2)
O1—C3—C4	107.3 (2)	C7—C8—C9	120.6 (2)
C2—C3—C4	111.1 (2)	O3—C9—O4	123.6 (2)
C3—C4—C5	112.8 (2)	O3—C9—C8	123.5 (2)
C4—C5—C6	111.8 (1)	O4—C9—C8	112.9 (2)
C4—C5—C13	109.9 (2)		
C6 -C1 C2—C3	−56.5 (2)	C2—C3—C4—C5	−53.8 (2)
C11—C1—C2—C3	66.5 (2)	C3—C4—C5—C6	53.3 (2)
C12—C1—C2—C3	−175.9 (2)	C3—C4—C5—C13	178.3 (2)
C2—C1—C6—O2	−68.1 (2)	C4—C5—C6—O2	68.2 (2)
C2—C1—C6—C5	54.3 (2)	C4—C5—C6—C1	−53.8 (2)
C2—C1—C6—C7	175.0 (2)	C4—C5—C6—C7	−175.5 (2)
C11—C1—C6—O2	171.0 (2)	C13—C5—C6—O2	−55.6 (2)
C11—C1—C6—C5	−66.7 (2)	C13—C5—C6—C1	−177.6 (2)
C11—C1—C6—C7	54.0 (2)	C13—C5—C6—C7	60.7 (2)
C12—C1—C6—O2	50.3 (2)	O2—C6—C7—C8	6.0 (2)
C12—C1—C6—C5	172.6 (2)	C1—C6—C7—C8	124.9 (2)
C12—C1—C6—C7	−66.7 (2)	C5—C6—C7—C8	−112.8 (2)
C1—C2—C3—O1	174.9 (2)	C6—C7—C8—C9	176.2 (2)
C1—C2—C3—C4	56.6 (2)	C7—C8—C9—O3	18.3 (3)
O1—C3—C4—C5	−173.4 (2)	C7—C8—C9—O4	−162.4 (2)

Data collection: *CAD-4 Express* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OA1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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