Crystal structure of *ent*-(16*R*,17*R*)-17-hydroxy-17-methoxykauran-19-oic acid, $C_{21}H_{34}O_4$

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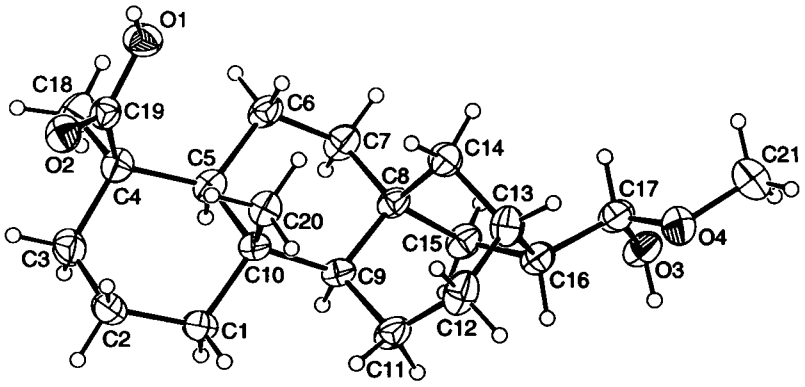

Abstract

$C_{21}H_{34}O_4$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.4324(2) Å, b = 10.7639(2) Å, c = 21.1593(6) Å, V = 1920.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.125, T = 293 K.

Source of material

Crystals of the hemiacetal *ent*-(16*R*,17*R*)-17-hydroxy-17-methoxykauran-19-oic acid were obtained in MeOH at room temperature from *ent*-(16*R*)-kauran-17-al-19-oic acid ($C_{20}H_{30}O_3$) isolated from unripe fruits of *Annona cacans Warm.* (Annonaceae).

Experimental details

H atoms were located from stereochemical reasons, except those of the hydroxyl groups, and were refined riding on a carrier atom with an isotropic displacement parameter of 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the attached atom. Those of the hydroxyl groups were found in a Fourier difference map and refined freely.

Discussion

Annona cacans Warm. is a native tree of the south and southeast of Brazil. Its fruits are reported to be laxative by natives. The tetracyclic *ent*-kaurane diterpenoid is regarded as an intermediate in the biogenesis of the gibberellin plant growth hormones. The biological activity of medicinal plant, such as exhibiting anti-microbial, anti-inflammatory, cardiovascular, diuretic, anti-HIV, and cytotoxic effects, can sometimes be attributed in plant to the presence of *ent*-kaurane diterpenoid constituents [1]. The anti-platelet aggregation [1], anti-HIV [1-3], antifeedant activity [4,5] and anticancer effects [6] have been reported for diterpenes. Several of the last compounds have been isolated from genus *Annona* [1,2].

In the title compound, all the single C–C bond distances are normal with a mean value of 1.543 Å. Both cyclohexane rings are in a pure-chair conformation as indicated by the Cremer & Pople puckering parameters [7] being q_2 = 0.11 Å, q_3 = –0.547 Å, θ = 178.8°, φ = 82.0°, Q = 0.547 Å, and q_2 = 0.11 Å, q_3 = –0.55 Å, θ = 169.0°, φ = 218.0°, Q = 0.56 Å, respectively. For the hemiacetal and carboxylic acid groups, the bond lengths are compatible with the values found in the literature. The molecules in the packing interact by two typical hydrogen bonds: O3–H3O···O2^i, where d(O3—H) = 0.86(3) Å, d(H···O2^i) = 1.94(3) Å, d(O3···O2^i) = 2.794(2) Å, ∠O3–H···O2^i = 177(3)°, (i: $-x-\frac{1}{2},-y+1,z-\frac{1}{2}$), and O1–H1O···O3^{ii}, where d(O1—H) = 0.92(4) Å, d(H···O3^{ii}) = 1.75(4) Å, d(O1···O3^{ii}) = 2.666(2) Å, ∠O1–H···O3^{ii} = 174(3)°, (ii: $-x, y-\frac{1}{2},-z+\frac{1}{2}$). An inspection of the literature disclosed that this structure was solved in monoclinic system using a crystal obtained from MeOH: H_2O [8]. In this case the hemiacetal group is involved in hydrogen bonds with the water molecules, while that in the present case of the anhydrous form, the hydrogen bond occurs between oxygen atoms of the hemiacetal group and oxygen atoms of carboxylic acid groups of the molecules related by symmetry operation, implying in different arrangements of the molecules in the packing.

Table 1. Data collection and handling.

Crystal:	colorless, irregular, size 0.2 × 0.25 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.20 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4312, 4312
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3502
$N(param)_{refined}$:	234
Programs:	SHELXS-97 [9], SHELXS-97 [10], ORTEP-3 [11], WinGX [12]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(9)	4*a*	−0.3512	0.6073	0.1793	0.051
H(20A)	4*a*	−0.1953	0.3410	0.2679	0.070
H(20B)	4*a*	−0.3372	0.2887	0.2281	0.070
H(20C)	4*a*	−0.3580	0.3125	0.3007	0.070
H(6A)	4*a*	−0.1229	0.6402	0.3452	0.063
H(6B)	4*a*	−0.0905	0.5096	0.3145	0.063
H(15A)	4*a*	−0.1708	0.6928	0.1136	0.062
H(15B)	4*a*	0.0042	0.7116	0.1378	0.062
H(16)	4*a*	−0.0916	0.5541	0.0432	0.061
H(7A)	4*a*	−0.1412	0.7308	0.2443	0.067
H(7B)	4*a*	0.0252	0.6680	0.2526	0.067
H(3A)	4*a*	−0.6460	0.5079	0.3921	0.071
H(3B)	4*a*	−0.6276	0.6160	0.3431	0.071
H(5)	4*a*	−0.3675	0.6453	0.2902	0.052
H(14A)	4*a*	0.1094	0.4947	0.1902	0.063
H(14B)	4*a*	−0.0235	0.3990	0.2103	0.063
H(1A)	4*a*	−0.5808	0.5536	0.2244	0.065
H(1B)	4*a*	−0.5742	0.4114	0.2091	0.065
H(13)	4*a*	0.0663	0.3757	0.0990	0.068
H(17)	4*a*	0.2184	0.5990	0.0904	0.067
H(11A)	4*a*	−0.4112	0.4020	0.1319	0.071
H(11B)	4*a*	−0.3376	0.5086	0.0912	0.071
H(18A)	4*a*	−0.4122	0.7227	0.3963	0.104
H(18B)	4*a*	−0.2725	0.6469	0.4263	0.104
H(18C)	4*a*	−0.4453	0.6314	0.4524	0.104
H(2A)	4*a*	−0.7505	0.4531	0.2933	0.073
H(2B)	4*a*	−0.6163	0.3609	0.3142	0.073
H(12A)	4*a*	−0.1819	0.2930	0.1337	0.080
H(12B)	4*a*	−0.1949	0.3398	0.0637	0.080
H(21A)	4*a*	0.3930	0.4451	−0.0318	0.147
H(21B)	4*a*	0.4304	0.5130	0.0321	0.147
H(21C)	4*a*	0.3748	0.5897	−0.0269	0.147
H(1O)	4*a*	−0.190(5)	0.342(4)	0.436(2)	0.11(1)
H(3O)	4*a*	0.082(4)	0.697(3)	−0.011(2)	0.076(9)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	4*a*	0.1414(2)	0.7074(2)	0.02181(8)	0.074(1)	0.065(1)	0.0446(9)	−0.0296(9)	−0.0072(8)	0.0051(8)
C(19)	4*a*	−0.3623(3)	0.4193(2)	0.40129(9)	0.050(1)	0.045(1)	0.040(1)	0.0061(9)	0.0028(9)	0.0047(8)
O(1)	4*a*	−0.2105(2)	0.4168(2)	0.41680(8)	0.0552(9)	0.063(1)	0.062(1)	0.0019(8)	−0.0078(8)	0.0167(8)
O(2)	4*a*	−0.4520(2)	0.3361(1)	0.41578(8)	0.062(1)	0.0513(8)	0.0568(9)	0.0000(8)	0.0049(8)	0.0133(7)
C(10)	4*a*	−0.3640(2)	0.4753(2)	0.24879(9)	0.0418(9)	0.0377(9)	0.0409(9)	−0.0018(8)	−0.0050(8)	0.0020(8)
C(9)	4*a*	−0.2907(2)	0.5310(2)	0.18675(9)	0.047(1)	0.0404(9)	0.039(1)	−0.0027(8)	−0.0087(9)	0.0038(8)
C(20)	4*a*	−0.3084(3)	0.3418(2)	0.2627(1)	0.057(1)	0.0354(9)	0.048(1)	−0.0041(9)	0.0028(9)	0.0023(8)
C(6)	4*a*	−0.1454(3)	0.5881(2)	0.3089(1)	0.061(1)	0.057(1)	0.038(1)	−0.019(1)	−0.006(1)	−0.0025(9)
C(8)	4*a*	−0.1165(2)	0.5742(2)	0.18961(9)	0.053(1)	0.0406(9)	0.0365(9)	−0.0089(9)	−0.0045(8)	0.0033(8)
C(15)	4*a*	−0.0769(3)	0.6502(2)	0.1288(1)	0.065(1)	0.045(1)	0.045(1)	−0.008(1)	−0.001(1)	0.0079(9)
C(4)	4*a*	−0.4126(3)	0.5382(2)	0.3675(1)	0.057(1)	0.040(1)	0.044(1)	0.0074(9)	0.0030(9)	0.0033(8)
C(16)	4*a*	−0.0168(3)	0.5564(2)	0.0787(1)	0.057(1)	0.054(1)	0.041(1)	−0.011(1)	−0.003(1)	0.0012(9)
C(7)	4*a*	−0.0875(3)	0.6516(2)	0.2488(1)	0.068(1)	0.055(1)	0.046(1)	−0.025(1)	−0.002(1)	−0.001(1)
C(3)	4*a*	−0.5914(3)	0.5331(2)	0.3538(1)	0.056(1)	0.065(1)	0.057(1)	0.018(1)	0.009(1)	0.013(1)
C(5)	4*a*	−0.3244(2)	0.5652(2)	0.30406(9)	0.056(1)	0.0348(9)	0.041(1)	0.0014(9)	−0.0004(9)	0.0019(8)
C(14)	4*a*	0.0018(3)	0.4672(2)	0.1821(1)	0.053(1)	0.054(1)	0.050(1)	−0.000(1)	0.001(1)	0.013(1)
C(1)	4*a*	−0.5469(2)	0.4735(2)	0.2405(1)	0.044(1)	0.067(1)	0.051(1)	−0.002(1)	−0.0058(9)	0.007(1)
C(13)	4*a*	−0.0199(3)	0.4299(2)	0.1134(1)	0.067(2)	0.047(1)	0.056(1)	−0.004(1)	0.012(1)	0.002(1)
C(17)	4*a*	0.1462(3)	0.5914(2)	0.0544(1)	0.059(1)	0.066(1)	0.042(1)	−0.013(1)	−0.005(1)	0.004(1)
C(11)	4*a*	−0.3169(3)	0.4523(2)	0.1260(1)	0.064(2)	0.073(2)	0.042(1)	−0.026(1)	−0.008(1)	−0.002(1)
C(18)	4*a*	−0.3828(4)	0.6450(2)	0.4152(1)	0.108(2)	0.050(1)	0.051(1)	0.006(1)	0.011(1)	−0.008(1)
C(2)	4*a*	−0.6376(3)	0.4457(3)	0.3012(1)	0.041(1)	0.081(2)	0.060(1)	0.001(1)	−0.001(1)	0.015(1)
C(12)	4*a*	−0.1802(4)	0.3664(2)	0.1071(1)	0.088(2)	0.058(1)	0.055(1)	−0.024(1)	0.013(1)	−0.012(1)
O(4)	4*a*	0.2019(2)	0.4977(2)	0.01458(8)	0.058(1)	0.080(1)	0.062(1)	−0.0046(9)	0.0079(8)	−0.0007(9)
C(21)	4*a*	0.3633(4)	0.5126(4)	−0.0046(2)	0.053(2)	0.152(3)	0.089(2)	0.000(2)	0.007(2)	0.000(2)

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