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Methyl *ent*-15β-hydroxy-16α-kauran-19-oate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 6.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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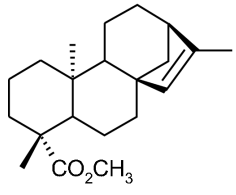
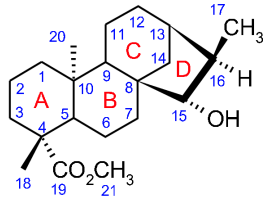
In the crystal structure of the title compound, $C_{21}H_{34}O_3$, molecules are linked to each other by intermolecular O—H···O hydrogen bonds, involving the ester carbonyl group and the hydroxyl group.

Comment

The kauranes are a very important class of naturally occurring diterpenes with a rigid tetracyclic skeleton. These compounds have attracted interest because of their structures and their wide spectrum of biological activities, as plant growth regulators, antitumor, anti-HIV and antimicrobial agents, among others (Ghisalberti, 1997; Batista *et al.*, 1999; Hanson, 2002). The biological effects of kaurane diterpenoids are very much influenced by the presence of oxygen substituents (Ghisalberti, 1997; Vieira *et al.*, 2000). This has motivated the synthesis of hydroxylated kaurane derivatives by chemical (Bruno *et al.*, 2001) and microbial (Silva *et al.*, 1999) transformations of naturally occurring non-polar kaurane compounds.



(1)



(2)

Methyl *ent*-15β-hydroxy-16α-kauran-19-oate, (2), was obtained by hydroboration–oxidation of methyl *ent*-kaur-15-en-19-oate, (1), which was isolated from an esterified *Wedelia paludosa D. C. (Asteraceae)* ethanol extract by column chromatography on silica gel. The unambiguous crystal structure of (2) is reported here for the first time.

The principal bond lengths and angles are given in Table 1; these are within normal ranges (Allen *et al.*, 1987). There is a close similarity to the crystal structure of the kaurenoic acid reported by Brassy *et al.* (1988), the differences being those related to the esterification of the carboxylic acid group and the absence of the C16═C17 double bond. All internal angles of ring *D* of (2) are very close to those observed for ring *D* of *ent*-16β-kauran-2,12-dione, a diterpene isolated from *Alisma orientale* (Yamaguchi *et al.*, 1994). The configurations at atoms C15 and C16 are those expected for the regio- and stereoselectivity of the hydroboration–oxidation reaction, with a *syn*-addition taking place at the less hindered face of the double bond (the *exo* side). Rings *A*, *B* and *C* are in chair conformations, as can be seen in Figs. 1 and 2.

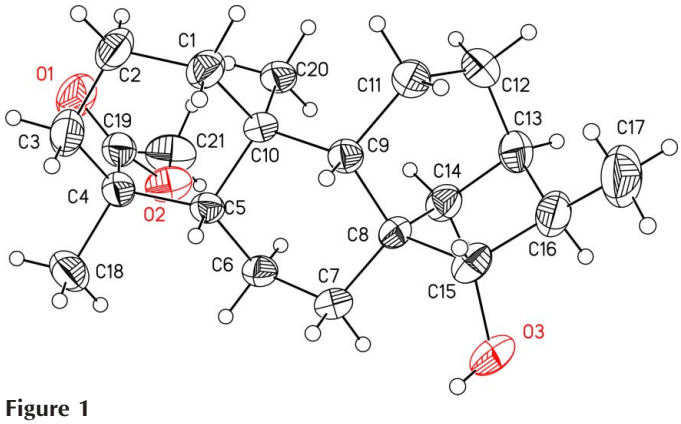


Figure 1
The molecular structure of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

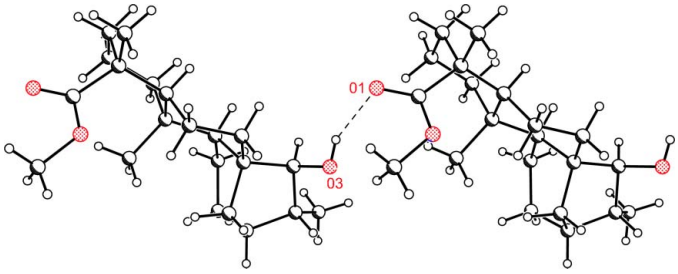


Figure 2
The intermolecular O—H···O hydrogen bond, shown as a dashed line.

In the crystal structure of the title compound, molecules are linked to each other by intermolecular O—H···O hydrogen bonds (Fig. 2 and Table 2). Weak intermolecular C—H···O interactions are also present.

Experimental

The diterpene (2) was prepared by hydroboration–oxidation of (1), according to the method of Castellaro *et al.* (1990). Well shaped colorless single crystals were obtained by recrystallization from hexane.

Crystal data

$C_{21}H_{34}O_3$
M_r = 334.48
Monoclinic, $P2_1$
a = 7.3470 (15) Å
b = 9.5010 (19) Å
c = 13.568 (3) Å
β = 97.81 (3)°
V = 938.3 (3) Å^3
Z = 2
D_x = 1.184 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 20 reflections
θ = 8–20°
μ = 0.60 mm^{-1}
T = 293 (2) K
Prism, colorless
0.2 × 0.2 × 0.2 mm

Data collection

Seifert XRD 3003 SC diffractometer
$\omega/2\theta$ scans
1491 measured reflections
1491 independent reflections
1434 reflections with $I > 2\sigma(I)$
θ_{max} = 60.0°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = -14 \rightarrow 14$
2 standard reflections
every 700 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.090
S = 1.03
1491 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.0837P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.042 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C19	1.205 (3)	C4—C19	1.522 (4)
O2—C19	1.337 (3)	C8—C15	1.562 (3)
O2—C21	1.445 (3)	C13—C12	1.522 (4)
O3—C15	1.430 (3)	C13—C16	1.536 (4)
C14—C8—C15	101.4 (2)	C17—C16—C13	117.3 (3)
C13—C14—C8	101.88 (19)	C17—C16—C15	115.9 (3)
C12—C13—C14	108.8 (2)	C13—C16—C15	104.8 (2)
C12—C13—C16	114.4 (2)	C16—C15—C8	106.2 (2)
C14—C13—C16	101.0 (2)	O1—C19—O2	122.0 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1^{i}	0.82	2.14	2.883 (3)	152
C1—H1B···O2^{ii}	0.97	2.59	3.432 (3)	145
C21—H21D···O3^{iii}	0.96	2.50	3.300 (4)	140

Symmetry codes: (i) $x, 1+y, z$; (ii) $x-1, y, z$; (iii) $x, y-1, z$.

Most of the H atoms were observed in Fourier difference syntheses, but subsequently they were all positioned geometrically, with C—H = 0.96–0.98 Å and O—H = 0.82 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(parent atom) for methyl H atoms and 1.2U_{eq}(parent atom) for all other H atoms.The data contain no Friedel pairs; the absolute configuration was assumed from the synthesis.

Data collection: *CRYSOM* (Martinez-Ripoll & Cano, 1996); cell refinement: *CRYSOM*; data reduction: *X-RAY80* (Stewart *et al.*, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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