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Methyl *ent*-16β,17-epoxykauran-19-oate

Ronan Batista,[a]* Pablo A. García,[b] María A. Castro,[b] José M. Miguel del Corral,[b] Francisca Sanz,[c] Nivaldo L. Speziali[d] and Alaíde B. de Oliveira[e]

[a]Departamento de Estudos Básicos e Instrumentais, UESB, Brazil, [b]Departamento de Química Farmacéutica, Facultad de Farmacia, Universidad de Salamanca, Salamanca, Spain, [c]Servicio de Difracción de Rayos X, Universidad de Salamanca, Salamanca, Spain, [d]Departamento de Física, ICEx, UFMG, Brazil, and [e]Departamento de Produtos Farmacêuticos, Faculdade de Farmácia, UFMG, Brazil

Correspondence e-mail: ronbatis2004@gmail.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.082
Data-to-parameter ratio = 7.4

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

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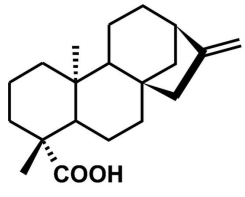
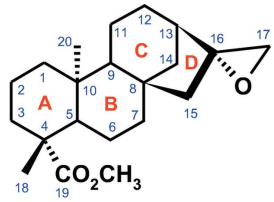
The title compound, $C_{21}H_{32}O_3$, was prepared by standard epoxidation of kaurenoic acid methyl ester. Its crystal structure confirms unequivocally the *ent*-16β epoxide configuration.

Comment

Kauranes represent an important class of naturally occurring diterpenes with a rigid tetracyclic skeleton. They show many interesting biological activities, such as plant-growth regulation, antitumour, anti-HIV, antiparasitic and antimicrobial properties (Ghisalberti, 1997; Hanson, 2002; Batista *et al.*, 1999, 2007). Kaurenoic acid [*ent*-kaur-16-en-19-oic acid, (I)], an intermediate in the biosynthesis of gibberelins and other secondary metabolites from plants and fungi, is found abundantly in some Brazilian species, such as *Wedelia paludosa* D. C. (Asteraceae), and *Xylopia frutescens* and *Annona glabra* (Annonaceae) (Batista *et al.*, 1999; Batista, Braga & Oliveira, 2005). Although, in the last few years, this abundant bioactive kaurane has been reported more and more in the literature as a starting material for synthetic purposes (Castellaro *et al.*, 1990; Costa *et al.*, 1996; Vieira *et al.*, 2002; Boeck *et al.*, 2005; Batista, García *et al.*, 2005; Batista *et al.*, 2007), it is certainly still far from being completely exploited by the current interest in the chemistry of natural products. Following our special interest in novel kaurane derivatives, and continuing our previous work on chemical transformations of naturally occurring diterpenoids isolated from *W. paludosa* D. C. (Batista *et al.*, 1999; Batista, Braga & Oliveira, 2005) into oxidized derivatives (Batista, García *et al.*, 2005), we have prepared the title epoxide, (II), and its crystal structure is reported here. Epoxide (II) constitutes a key intermediate for the preparation of oxidized *ent*-kaurane derivatives from kaurenoic acid, (I).



(I)



(II)

Compound (II) was obtained by standard *m*-CPBA epoxidation of kaurenoic acid methyl ester, according to the procedure of Miguel del Corral *et al.* (1998). Epoxide (II) has already been reported (Bohlman *et al.*, 1981) as a colourless gum and, at that time, it was identified by comparison of its ^{1}H NMR spectrum with those of other known kaurane

epoxides. The present crystal structure of (II) confirms unequivocally the *ent*-16β epoxide configuration.

There is a close similarity between the crystal structure of (II) and that of kaurenoic acid, (I), reported by Brassy *et al.* (1988), and the crystal structure of methyl *ent*-15α-hydroxy-16β-kauran-19-oate, reported previously by us (Batista, García *et al.*, 2005). The *ent*-16β epoxide configuration of (II) agrees with that expected from the stereoselective epoxidation of the double bond taking place at the less hindered face. Rings *A*, *B* and *C* are in chair conformations, as can be seen in Fig. 1. All the endocyclic torsion angles of ring *D* of (II) are very close to those observed for ring *D* of *ent*-16β-kaurane-2,12-dione (Yamaguchi *et al.*, 1994) and methyl *ent*-15α-hydroxy-16β-kauran-19-oate (Batista, García *et al.*, 2005).

Experimental

The title diterpene, (II), was obtained by epoxidation of (I), according to the methodology described by Miguel del Corral *et al.* (1998). Well shaped colourless single crystals were obtained by recrystallization from *n*-hexane.

Crystal data

$C_{21}H_{32}O_3$
M_r = 332.47
Orthorhombic, $P2_12_12_1$
a = 6.7100 (13) Å
b = 9.7380 (19) Å
c = 28.383 (6) Å
V = 1854.6 (6) Å^3
Z = 4
D_x = 1.191 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.61 mm^{-1}
T = 293 (2) K
Prism, colourless
0.2 × 0.2 × 0.2 mm

Data collection

Seifert 3003 SC diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1614 measured reflections
1614 independent reflections
1274 reflections with $I > 2\sigma(I)$
θ_{max} = 60.0°
2 standard reflections
every 700 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.082
S = 1.06
1614 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0065 (5)

Most of the H atoms were observed in Fourier difference syntheses, but they were all subsequently positioned geometrically, with C—H = 0.96–0.98 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(parent atom) for methyl H atoms or 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*.

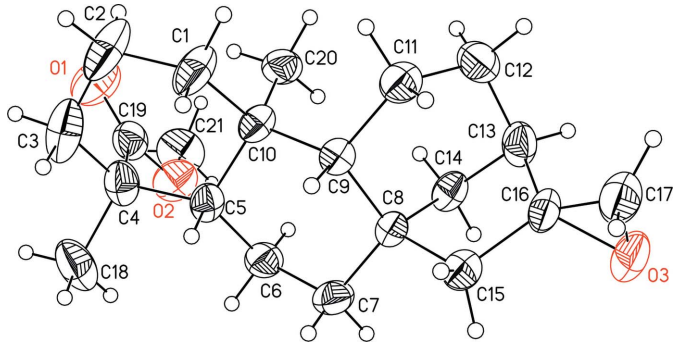


Figure 1
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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