

Asiloé J. Mora,^{a*}
Gerzon E. Delgado,^a
Gavin B. M. Vaughan,^b
Patrick Martin,^c Tomás Visbal^d
and Alfredo Usubillaga^d

^aLaboratorio de Cristalografía, Facultad de Ciencias, Departamento de Química, Universidad de Los Andes, Mérida 5101, Venezuela, ^bEuropean Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France, ^cLaboratoire de la Barrière Hémato-Encéphalique, Université d'Artois, F-62307 Lens, France, and ^dInstituto de Investigaciones, Facultad de Farmacia, Universidad de Los Andes, Mérida 5101, Venezuela

Correspondence e-mail: asiloe@ula.ve

Key indicators

Single-crystal synchrotron study
 $T = 173\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.046
 wR factor = 0.125
Data-to-parameter ratio = 5.8

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

A peracetylated glucosyl ester of kaurenic acid

The crystal structure of a peracetylated glucosyl ester of kaurenic acid, (4 α)-kaur-16-en-18-carbonyl 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranoside, $\text{C}_{34}\text{H}_{48}\text{O}_{11}$, is reported. The synchrotron X-ray diffraction experiment showed that the glucosyl moiety adopts an α -perpendicular orientation with respect to the plane of the kaurenic acid. This conformation would allow the sugar hydroxyl groups, one unprotected, to interact with solvent or with biological membranes, enhancing its *in vitro* activity against murine melanoma in mice.

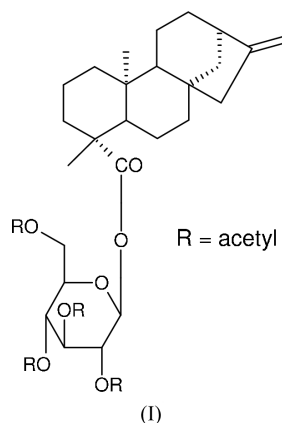
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Comment

Espeletiinae (Asteraceae) are resinous plants, popularly known as frailejon, that grow in cold regions of the tropical high Andean paramos, subparamos, and Andean forests of Venezuela, Colombia and Ecuador between 2500 and 4500 m above sea level. *Espeletia semiglobulata* is one of the 85 species of frailejon endemic to the Venezuelan Andean mountains. This plant, which grows above 3000 m, is rich in kaurenic acid, a diterpene that has the opposite stereochemistry to that of steroids. This compound has shown moderate antimicrobial activity against *Tripnozoma cruzi* (Alves *et al.*, 1995), inhibits growth of certain phytophagous insects (Elliger *et al.*, 1976) and has molluscicidal properties (Tomassini & Matos, 1979). Also, it has shown activity *in vivo* against certain cancer cells (Ryu *et al.*, 1996); in particular, it has been reported to slow the growth of murine melanoma in mice (Sosa-Sequera *et al.*, 1998), but its application has been limited because of its low solubility in water. To increase solubility, carbohydrate esters of kaurenic acid have been prepared. We report here the structure of a peracetylated glucosyl ester derivative, (I).



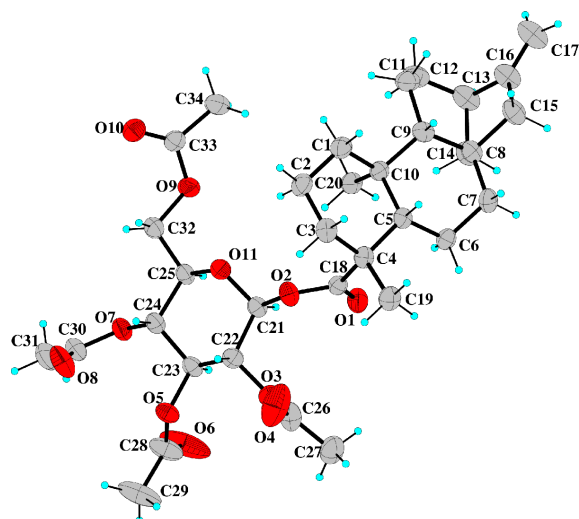


Figure 1
View of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The atom-numbering scheme and molecular conformation of the protected glucosyl ester of kaurenic acid are presented in Fig. 1. The Cremer & Pople (1975) puckering parameters [$Q = 0.597(2) \text{ \AA}$, $\theta = 2.7(2)^\circ$ and $\varphi = 325(5)^\circ$] and asymmetry parameters [$\Delta C_s(O11)_{\min} = 1.0(2)^\circ$, $\Delta C_s(C21)_{\max} = 7.7(2)^\circ$, $\Delta C_2(C22-C23)_{\min} = 4.5(2)^\circ$ and $\Delta C_2(C21-C22)_{\max} = 9.8(2)^\circ$] indicate that the carboxylate moiety adopts a 4C_1 chair conformation in the solid state (Griffin *et al.*, 1984). Distances and angles around atom O2, which links the carbohydrate with the carboxyl group of the kaurenic acid, are within expected ranges (see Table 1) (Cambridge Structural Database, Version 5.24; Allen, 2002).

The C21–O2 bond and the normal to the average glucosyl plane make an angle of $65.56(4)^\circ$, indicating that atom O2 is equatorial to the ring, a characteristic of all β anomers. Evaluation of the torsion angles about the C21–O2 bond places the O2–C18 bond *gauche* with respect to both C21–C22 and C21–O11. In this conformation, there are no short interactions between the carboxylate and kaurenic acid portions of the same molecule, or with neighbouring molecules, 2.584 \AA being the shortest contact for H17B...H31A related by the translation $(1+x, y, 1+z)$. Furthermore, packing in the solid state is dominated by very weak C–H...O hydrogen bonds [$\geq 3.348(4) \text{ \AA}$] and van der Waals interactions (see Table 2).

Experimental

Pure kaurenic acid was obtained after processing, extraction, and purification from leaves of *Espeletia semiglobulata* Cuatrecasas collected at Paramo of Piedras Blancas, Venezuelan Andes. Kaurenic acid was then transformed into its sodium salt and subsequently treated with silver nitrate to obtain the silver salt. The silver kaurenate was dried, ground and kept in the dark. Reaction of silver kaurenate with the bromide of peracetylated glucose yielded the protected carbohydrate ester of kaurenic acid.

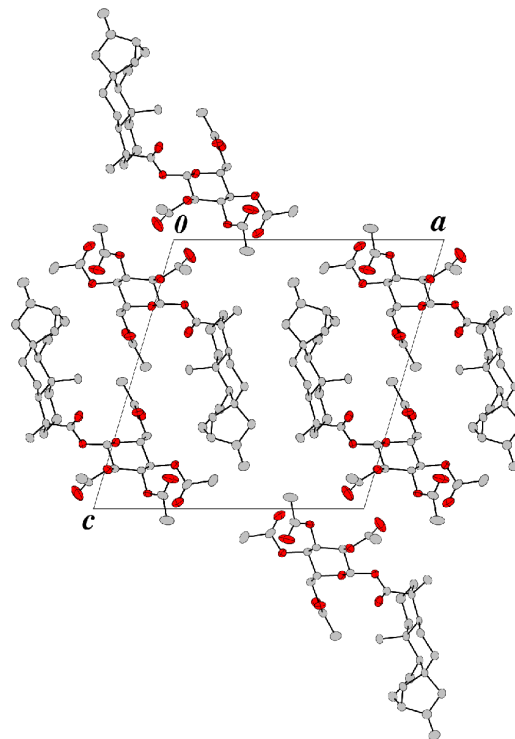


Figure 2
Packing diagram of (I), viewed down the *c* axis.

Crystal data

$C_{34}H_{48}O_{11}$	$D_x = 1.236 \text{ Mg m}^{-3}$
$M_r = 632.72$	Synchrotron radiation, $\lambda = 0.5338 \text{ \AA}$
Monoclinic, $P2_1$	Cell parameters from 1024 reflections
$a = 15.3738(8) \text{ \AA}$	$\theta = 2.4\text{--}19.3^\circ$
$b = 7.2254(2) \text{ \AA}$	$\mu = 0.06 \text{ mm}^{-1}$
$c = 15.9661(9) \text{ \AA}$	$T = 173(2) \text{ K}$
$\beta = 106.578(2)^\circ$	Needle, colourless
$V = 1699.82(14) \text{ \AA}^3$	$0.15 \times 0.03 \times 0.03 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART CCD area-detector diffractometer	2240 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.057$
Absorption correction: none	$\theta_{\text{max}} = 18.1^\circ$
8193 measured reflections	$h = -17 \rightarrow 17$
2336 independent reflections	$k = -7 \rightarrow 8$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 0.2167P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
2336 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
406 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (\AA).

O1–C18	1.195(4)	O11–C21	1.402(5)
O2–C18	1.348(4)	C4–C18	1.528(4)
O2–C21	1.407(4)	C4–C19	1.536(5)
O3–C22	1.427(5)	C21–C22	1.533(4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13A \cdots O6 ⁱ	1.00	2.54	3.348 (5)	138
C21—H21A \cdots O10 ⁱⁱ	1.00	2.38	3.281 (4)	150
C27—H27C \cdots O4 ⁱⁱⁱ	0.98	2.59	3.361 (8)	135

Symmetry codes: (i) $-x, y - \frac{1}{2}, 1 - z$; (ii) $x, 1 + y, z$; (iii) $-x, \frac{1}{2} + y, -z$.

X-ray data were collected on Beam Line ID11 at the European Synchrotron Radiation Facility using an undulator source and a double-bounce sagittally focusing Si(111) monochromator. Data were collected at 173 K, as the compound was observed to undergo a first-order irreversible phase transition below that temperature. All H atoms were placed in geometrically calculated positions ($C-H = 0.95-1.00$ Å) and refined using a riding model, with $U_{iso} = 1.2$ (1.5 times for methyl groups) U_{eq} of the parent atoms. Friedel pairs were merged, in the absence of anomalous scattering effects.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2000).

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