organic papers

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.010 Å
R factor = 0.043
wR factor = 0.138
Data-to-parameter ratio = 10.2

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

Longipilin acetate

Longipilin acetate, $C_{23}H_{28}O_9$, is a compound isolated from *Espeletia killipii*, a Colombian native plant. The molecule contains two non-planar rings, a ten-membered ring and a five-membered lactone. Various substituents around the ten-membered ring provide very weak intramolecular hydrogen-bonding interactions that determine the molecular folding.

Comment

Sesquiterpene lactones are characterized by the presence of carbocyclic skeletons and classified according to the type of nucleus (Torrenegra *et al.*, 1994). Among the natural sesquiterpene lactones, germacranolides represent one of the most abundant groups. Owing to their prominent and diverse physiological activity, there is a wide interest in the elucidation of the conformational properties of germacranolide compounds (Wong & Brown, 2002). The conformational studies reported for these ten-membered lactones are based mainly on NMR spectroscopy (Milosavljevic *et al.*, 2003). Moreover, the inhibition activity (Fischer, 1991) and cytotoxicity (Siedle *et al.*, 2003) of these molecules have been studied in order to examine structure—activity relationships.


(I)
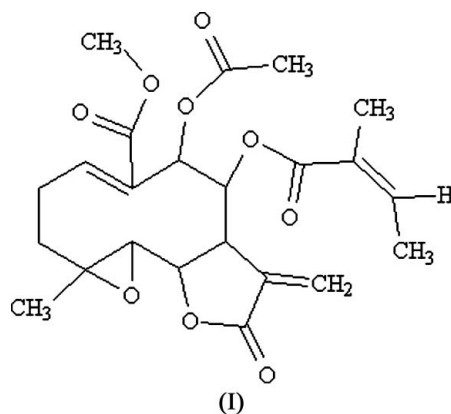
Longipilin acetate, (I), was extracted from Frailejón, a Colombian native plant that belongs to the *Espeletia* species, *Espeletia killipii*, of the family asteraceae \\rm. It grows between 2600 and 3300 m above sea level, and previous work has attributed a variety of medicinal properties to it (Torrenegra & Téllez, 1996). The aim of the present work was to provide experimental information about the conformation of (I), a member of the germacranolide family. We report here its X-ray crystal structure (Fig. 1 and Table 1).

The molecule has a ten-membered ring and a five-membered lactone ring, both of which deviate significantly from planarity. The ring-puckering parameters are $Q_T =$

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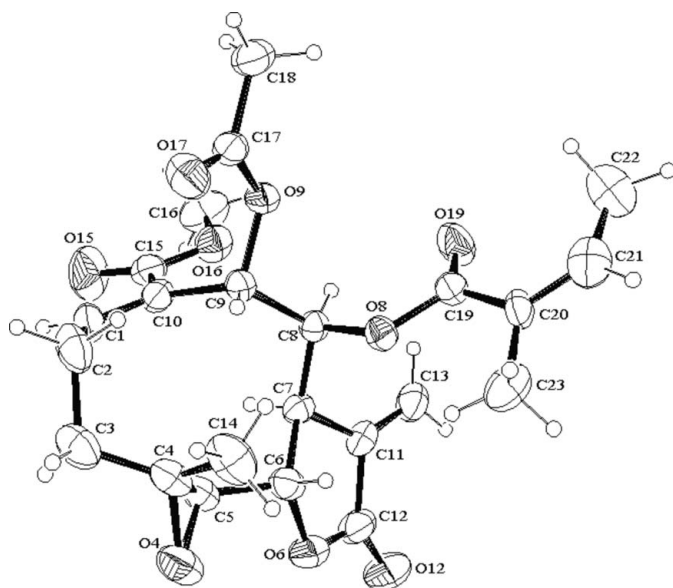
Figure 1
View of (I), showing the numbering scheme and displacement ellipsoids drawn at the 30% probability level.
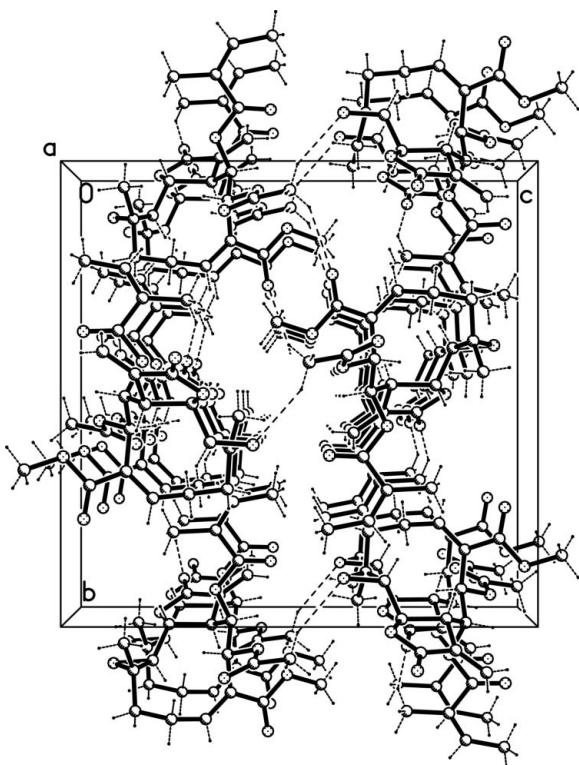
Figure 2
Packing diagram with hydrogen bonds represented as dashed lines.

1.555 (5) Å, $\varphi_2 = 8.9$ (3)° and $\theta_2 = 64.6$ (2)°, and $q_2 = 0.287$ (5) Å and $\varphi_2 = 21.6$ (12)° for the ten- and five-membered rings, respectively (Cremer & Pople, 1975). The five-membered lactone ring adopts an envelope conformation,

with C7 located 0.459 (5) Å from the C11/C12/O6/C6 mean plane.

The methyl ester group located at C10 is almost planar [the maximum deviation from the C15/O15/C16/O16 mean plane is 0.029 (8) Å for C15]. The acetoxy substituent at C9 is also planar [maximum deviation from the O9/C17/O17/C18 mean plane is 0.004 (8) Å for O17]. The C9—O9 bond is in an equatorial orientation with the H atom axial. The angeloyl group [OCOC(CH₃)=CHCH₃] located on atom C8 adopts an axial configuration with the corresponding H atom equatorial. This group is not planar, the O8—C19—C20—C23 torsion angle being −11.7 (7)°

Electrostatic interactions determine the way in which the molecule is folded. Atoms H8, C8, O8, C19 and O19 lie in a plane [maximum deviation from the mean plane is 0.031 (4) Å for C8] with a C8—O8—C19—O19 torsion angle of −0.2 (8)°. This favours interactions between H8 and O19, and between O8 and H6. Similar weak interactions between H9 and O17, H1 and O15, and H8 and O16 (Table 2) also determine the overall conformation. In the crystal structure, the packing is governed by very weak intermolecular hydrogen bonds involving H atoms from terminal methyl groups and carbonyl O atoms (Fig. 2 and Table 2).

Experimental

The compound was extracted and purified in the phytochemical section of Pontificia Javeriana University, and crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution in chloroform/ethanol (1:3 v/v) at room temperature. The crystals were very weakly diffracting, particularly at high 2θ values.

Crystal data

$C_{23}H_{28}O_9$	Mo $K\alpha$ radiation
$M_r = 448.45$	Cell parameters from 20
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.354$ (9) Å	$\theta = 20–25°$
$b = 16.39$ (7) Å	$\mu = 0.1$ mm^{-1}
$c = 16.78$ (1) Å	$T = 293$ (2) K
$V = 2297$ (9) Å^3	Prism, colourless
$Z = 4$	$0.6 \times 0.4 \times 0.3$ mm
$D_x = 1.297$ Mg m^{-3}	

Data collection

Rigaku AFC6 diffractometer	1032 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.105$
Absorption correction: ψ scan	$\theta_{max} = 27.5°$
(*MSC/AFC6S Diffractometer*	$h = -10 \rightarrow 10$
Control Software; Molecular	$k = -21 \rightarrow 0$
Structure Corporation, 1993)	$l = -21 \rightarrow 1$
$T_{min} = 0.95$, $T_{max} = 0.97$	3 standard reflections
5981 measured reflections	every 147 reflections
2990 independent reflections	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.92$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
2990 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
294 parameters	

Table 1
Selected bond lengths (Å).

C8—C7	1.524 (6)	C2—C3	1.544 (8)
C8—C9	1.543 (7)	C3—C4	1.517 (10)
C9—C10	1.524 (9)	C4—C5	1.473 (8)
C10—C1	1.327 (7)	C5—C6	1.478 (8)
C1—C2	1.485 (8)	C6—C7	1.569 (7)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C23—H23$B\cdots$O12[i]	0.96	2.57 (1)	3.39 (1)	144 (1)
C18—H18$B\cdots$O4[ii]	0.96	2.52 (1)	3.41 (1)	155 (1)
C18—H18$C\cdots$O15[iii]	0.96	2.49 (1)	3.31 (1)	144 (1)
C14—H14$A\cdots$O19[iv]	0.96	2.58 (1)	3.47 (1)	153 (1)
C8—H8$\cdots$O19	0.98	2.25 (1)	2.704 (9)	107 (1)
C6—H6$\cdots$O8	0.98	2.51 (1)	2.919 (7)	105 (1)
C9—H9$\cdots$O17	0.98	2.39 (1)	2.706 (7)	98 (1)
C1—H1$\cdots$O15	0.93	2.38 (1)	2.767 (8)	105 (1)
C8—H8$\cdots$O16	0.98	2.46 (1)	2.919 (8)	108 (1)

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (iv) $-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$.

All H atoms were refined using a riding model, with C—H = 0.93 Å for alkene, 0.98 Å for CH, 0.97 Å for CH$_2$ and 0.96 Å for CH$_3$ H atoms, and with U_{iso}(H) = 1.5U_{eq}(C) for CH$_3$ atoms and U_{iso}(H) = 1.2U_{eq}(C) for other H atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *MSC/AFC6S Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC6S Diffractometer Control Software*; data reduction: *MSC/AFC6S Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fischer, N. (1991) *Sesquiterpenoid Lactones in Methods in Plant Biochemistry*, series editors P. M. Dey & J. B. Harborne, Vol. 7, *Terpenoids*, pp. 187–212. London: Academic Press.
Milosavljevic, S., Juranic, I., Aljancic, I., Vajs, V. & Todorovic, N. (2003). *J. Serb. Chem. Soc.* **68**, 281–289.
Molecular Structure Corporation (1993). *MSC/AFC6S Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1997) *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Siedle, B., Gustavsson, L., Johansson, S., Murillo, R., Castro, V., Bohlin, L. & Merfort, I. (2003). *Biochem. Pharmacol.* **65**, 897–903.
Torrenegra, R. & Téllez, A. (1996). *Rev. Latinoam. Quim.* **24**, 2–6.
Torrenegra, R., Téllez, A. & García, G. (1994). *Rev. Colomb. Quim.* **23**, 29–35.
Wong, H. F. & Brown, D. (2002). *Phytochemistry*, **59**, 529–536.