The acetyl derivative of humirianthol

Robert A. Burrow,[a]* **Ademir F. Morel,**[a]† **Ilmar B. Graebner,**[b] **David H. Farrar**[c] **and Alan J. Lough**[c]

[a]Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, Rio Grande do Sul 97119-900, Brazil, [b]Departamento da Ciência da Natureza, Universidade Federal de Acre, Acre, Brazil, and [c]Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1H6

† Contact author with regard to extraction and identification; e-mail: afmorel@base.ufsm.br.

Correspondence e-mail: rburrow@ewald.base.ufsm.br

The title compound, 15α-acetato-3β,20:14β,16-diepoxy-3α-hydroxy-9-epi-7-pimaren-19,6β-olide, $C_{22}H_{28}O_7$, formed from the acetylation of humirianthol, isolated from the tubers of *Humirianthera ampla*, crystallizes in the chiral space group $P2_12_12_1$. The absolute configuration was set using the absolute configuration of C15, as determined by the Horeau method. The structure comprises a pimarane ring system with a methylene ether bridge over ring *A*, a double bond in ring *B*, and two five-membered furanyl rings, one fused to rings *A* and *B* and the other to ring *C*.

Comment

The crystal structure of the title compound, (I), was undertaken to confirm the stereochemistry of the parent natural compound, humirianthol, which was extracted from the tuber of *Humeririanthol ampla* collected from Rio Branco, Acre, Brazil. The structure of humirianthol has been determined by multidimensional NMR techniques, including the absolute configuration of one chiral centre by the Horeau method (Graebner *et al.*, 2000). Since pure humirianthol yielded only fibrous crystals, unsuitable for X-ray diffraction, the acetyl derivative of the natural compound was synthesized and crystallized for this study.

(I)
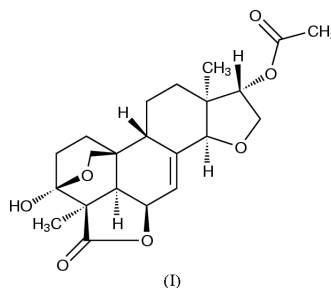
Compound (I) crystallizes as a chiral compound with one molecule in the asymmetric unit. Based on the previously determined (*S*) absolute configuration of C15 of the parent compound, the absolute structure of (I) can be determined. The following chiral centres were established: C3 (*S*), C4 (*R*), C5 (*R*), C6 (*R*), C10 (*S*), C13 (*R*), C14 (*S*). An atomic displacement ellipsoid plot of (I), showing the absolute stereochemistry, atomic labelling scheme and ring designations, is given in Fig. 1.

The core of (I), a pimarane skeleton, comprises two saturated six-membered rings and one six-membered ring with one double bond on the outside. Ring *A* has a 1,4-bridging methylene ether moiety which forces the ring into a boat conformation. The Cremer & Pope (1975) puckering para-
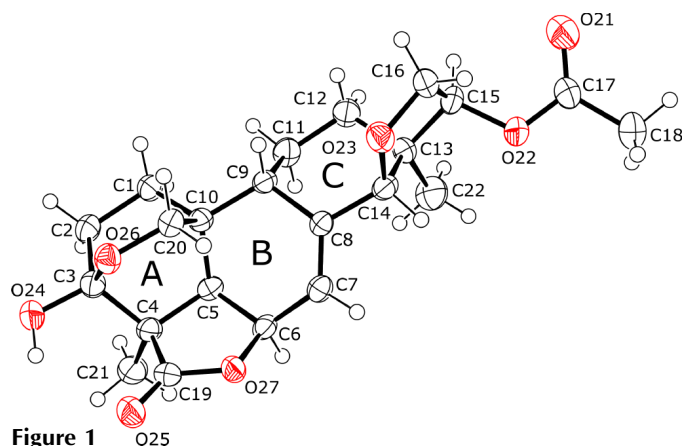
Figure 1
A displacement ellipsoid plot of the title compound drawn at the 50% probability level, with the atomic labelling scheme.

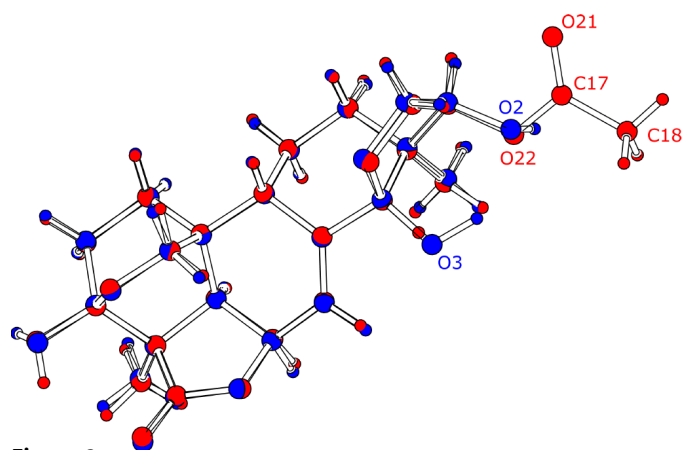**Figure 2**
Superposition of (I) (red) on icacinol (blue).

meters are $\theta = 87.5\ (3)°$, $\varphi = 292.1\ (4)°$ and puckering amplitude $Q = 0.856\ (4)$ Å. Ring *B*, which has a double bond, is also conformationally limited by being fused to four other ring systems. It adopts an envelope conformation [$\theta = 55.6\ (8)°$, $\varphi = 311.2\ (9)°$ and $Q = 0.406\ (5)$ Å]. Ring *C*, which is fused to ring *B* and a furan ring, is in a chair conformation [$\theta = 7.9\ (5)°$, $\varphi = 21\ (4)°$ and $Q = 0.559\ (5)$ Å]. The structure of (I) is very similar to that of icacinol, isolated from the roots of *Icacina claessensis* (On'okoko *et al.*, 1985). Icacinol differs from humirianthol by the addition of a hydroxyl group on C14. The conformations of the pimarane skeleton in (I) and icacinol are identical. Fig. 2 shows a plot of the superposition of the two molecules, determined by the quaternion transformation method (MacKay, 1984), using *MOLFIT* in *PLATON* (Spek, 2002); the root-mean-square difference of the fit between the 14 C atoms of the cores of the two structures is 0.027 Å.

Atom H24 participates in an intramolecular and an intermolecular hydrogen-bonding interaction (Table 2). The latter gives rise to head-to-tail interactions between neighbouring molecules of (I) related by unit-cell translations along *a* and *b*.

Experimental

Previously isolated and purified humirianthol (0.5 mmol; Graebner *et al.*, 2000), was stirred for 3 h in a mixture of 3 ml of pyridine and 3 ml

of acetic anhydride, then the solvent was removed *in vacuo*. The residue was dissolved in chloroform and washed with 2 *M* aqueous hydrochloric acid. Removal of solvent gave pure acetylated humirianthol. Crystals were obtained from the slow evaporation of a solution in chloroform with a small quantity of added methanol.

Table 1
Selected geometric parameters (Å, °).

C3—O24	1.386 (6)	C15—O22	1.466 (5)
C3—O26	1.440 (6)	C16—O23	1.449 (6)
C4—C21	1.533 (7)	C17—O21	1.228 (6)
C6—C7	1.478 (6)	C17—O22	1.292 (6)
C6—O27	1.485 (6)	C17—C18	1.514 (7)
C7—C8	1.327 (6)	C19—O25	1.197 (6)
C13—C15	1.523 (7)	C19—O27	1.347 (6)
C13—C22	1.525 (7)	C20—O26	1.443 (6)
C14—O23	1.427 (6)		
C8—C7—C6	123.3 (4)	O21—C17—C18	124.9 (5)
C7—C8—C14	120.3 (4)	O22—C17—C18	112.4 (5)
O22—C15—C13	107.8 (4)	O25—C19—O27	122.0 (5)
O21—C17—O22	122.2 (5)	C17—O22—C15	116.8 (4)
C18—C17—O22—C15	179.9 (5)	O25—C19—O27—C6	173.1 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O24—H24$\cdots$O21^i	0.78 (6)	2.25 (6)	2.871 (6)	138 (6)
O24—H24$\cdots$O25	0.78 (6)	2.48 (6)	3.071 (5)	134 (6)

Symmetry code: (i) $1 + x, y - 1, z$.

The intensities of the data were, in general, weak, leading to the high value of R_{int}. The H atoms of the methyl groups were refined as riding atoms, with ideal tetrahedral geometry, allowed to rotate to fit the electron density; the isotropic displacement parameters were fixed to be 50% larger than those of the atoms to which the H atoms

were bonded. H24 was allowed to refine freely with its isotropic displacement parameter set to 50% larger than the parent O24. The other H atoms were constrained to ideal geometric positions (tetrahedral for methylene groups or trigonal planar for aromatic groups) with C—H distances fixed to default values. Their isotropic displacement parameters were set to be 20% larger than the those of the atoms to which the H atoms were bonded.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-*3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

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