

Refinement

Refinement on *F**R* = 0.037*wR* = 0.042*S* = 1.34

1263 reflections

138 parameters

All H-atom parameters refined

w = 1 for $|F_o| < 30$ and*w* = 30/ $|F_o|$ for $|F_o| \geq 30$ $(\Delta/\sigma)_{\max} = 0.02$ $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
S(1)	0.32808 (3)	0.16666 (7)	0.58959 (3)	3.06 (1)
C(2)	0.17734 (11)	0.3144 (2)	0.54967 (9)	2.54 (3)
N(2)	0.14971 (10)	0.4988 (2)	0.60255 (8)	3.36 (3)
N(3)	0.09820 (9)	0.2257 (2)	0.46822 (8)	2.46 (2)
C(4)	0.10550 (11)	-0.1133 (2)	0.34737 (9)	2.62 (3)
C(5)	0.17726 (14)	-0.3044 (3)	0.32142 (10)	3.26 (4)
C(6)	0.30004 (14)	-0.3546 (3)	0.37847 (11)	3.44 (4)
C(7)	0.35356 (12)	-0.2166 (3)	0.46304 (10)	3.07 (3)
C(8)	0.28241 (12)	-0.0288 (3)	0.48793 (9)	2.67 (3)
C(9)	0.15492 (11)	0.0325 (2)	0.43211 (9)	2.33 (3)
N(4)	-0.02310 (10)	-0.0702 (2)	0.28228 (8)	2.90 (3)
O(1)	-0.09683 (9)	0.0703 (2)	0.30805 (8)	4.11 (3)
O(2)	-0.05270 (10)	-0.1783 (2)	0.20156 (7)	4.37 (3)

Table 2. Selected geometric parameters (\AA , °)

S(1)—C(2)	1.754 (1)	C(5)—C(6)	1.371 (2)
S(1)—C(8)	1.726 (1)	C(6)—C(7)	1.381 (2)
C(2)—N(2)	1.315 (2)	C(7)—C(8)	1.366 (2)
C(2)—N(3)	1.312 (2)	C(8)—C(9)	1.420 (2)
N(3)—C(9)	1.367 (2)	C(4)—N(4)	1.453 (2)
C(4)—C(9)	1.398 (2)	N(4)—O(1)	1.210 (2)
C(4)—C(5)	1.389 (2)	N(4)—O(2)	1.224 (2)
C(2)—S(1)—C(8)	88.91 (6)	C(6)—C(7)—C(8)	118.77 (13)
S(1)—C(2)—N(2)	119.42 (10)	C(7)—C(8)—S(1)	127.12 (10)
S(1)—C(2)—N(3)	115.95 (9)	C(7)—C(8)—C(9)	123.72 (12)
N(2)—C(2)—N(3)	124.60 (12)	S(1)—C(8)—C(9)	109.16 (9)
C(2)—N(3)—C(9)	110.25 (10)	C(8)—C(9)—N(3)	115.72 (11)
C(5)—C(4)—C(9)	121.57 (12)	C(8)—C(9)—C(4)	115.10 (11)
C(5)—C(4)—N(4)	117.13 (11)	N(3)—C(9)—C(4)	129.18 (11)
C(9)—C(4)—N(4)	121.30 (11)	C(4)—N(4)—O(1)	120.08 (11)
C(4)—C(5)—C(6)	120.57 (13)	C(4)—N(4)—O(2)	117.91 (11)
C(5)—C(6)—C(7)	120.27 (13)	O(1)—N(4)—O(2)	122.00 (12)

Table 3. Hydrogen-bonding geometry (\AA , °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N(2)—H1N2...O(1 ¹)	0.85 (2)	2.40 (2)	2.774 (2)	107 (1)
N(2)—H2N2...O(1 ¹)	0.84 (2)	2.49 (2)	2.774 (2)	100 (1)
N(2)—H1N2...N(3 ¹)	0.85 (2)	2.12 (2)	2.978 (2)	178 (2)

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

Data collection: Syntex P2₁ software. Cell refinement: Syntex P2₁ software. Data reduction: XP21 (Pavelčík, 1987). Program(s) used to solve structure: MULTAN80 (Main *et al.*, 1980). Program(s) used to refine structure: NRC Crystallographic Programs (Ahmed & Singh, 1973). Molecular graphics: ORTEPII (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: CF1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tarapacol 15-Acetate, a New Diterpenoid from *Grindelia tarapacana* Phil.

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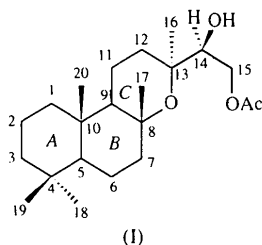
Abstract

In the title compound, 15-acetoxy-14(*S*)-hydroxy-13-*epi*-manoyl oxide {IUPAC systematic name: 2-(dodecahydro-3,4a,7,7,10a-pentamethyl-1*H*-naphtho[2,1-*b*]pyran-3-yl)-2-hydroxyethyl acetate}, C₂₂H₃₈O₄, rings *A* and *B* have chair conformations. Ring *C* adopts a boat con-

formation with the 16-methyl group in an axial position and the bulky glycol monoacetate group in an equatorial position. Ring systems *A/B* and *B/C* (conventional IUPAC labdane diterpenoid nomenclature) are *trans* fused about the C(5)—C(10) and C(8)—C(9) bonds, respectively. The present study establishes the relative stereochemistry at the C(14) position.

Comment

Seven new diterpenoids, namely tarapacanol *A* and *B*, tarapacanone, tarapacol and their acetate derivatives, as well as two diterpenes, 13-*epi*-manoyl oxide and 12 α -hydroxy-13-*epi*-manoyl oxide, have been isolated from *Grindelia tarapacana* Phil. (Asteraceae), and their structural characterizations have been carried out by means of spectroscopic data and chemical correlations (Zhou, Fuentes, Hoffmann & Timmermann, 1995). These compounds are a group of 13-*epi*-manoyl oxides with oxygen functions at the C(14) and C(15) positions. Optical-rotation studies favored the 14(*S*) configuration for these compounds. In order to confirm the structure of this group of compounds and to establish the relative stereochemistry at the C(14) position, X-ray analysis of tarapacol 15-acetate (1) was undertaken.



As in normal diterpenes, the junction between the two six-membered carbon rings is *trans*; the junction for the third ring is also *trans*. The six-membered rings *A* and *B* possess slightly flattened chair conformations. The tetrahydropyran ring is in the form of a slightly twisted boat. Since the deacetyl derivative of (1) showed positive optical rotation, the final atomic coordinates of (1) were chosen in accordance with the absolute

configuration of 13-*epi*-manoyl oxide (Bower & Rowe, 1967; Demetzos, Harvala & Philianos, 1990; Zdero, Bohlmann & Niemeyer, 1991). Position 14 has the *S* configuration. The large value of B_{eq} for O(4), together with the less pronounced anisotropy of the other atoms of the group, may indicate disorder of the acetoxy moiety. The molecules form chains parallel to the *b* axis due to hydrogen bonds between O(1) and the H atom on O(2) of a molecule related by the 2_1 axis. This intermolecular O(1)···O(2) distance is 2.878 (3) Å. Atoms O(3) and O(4) of the acetyl group do not participate in the hydrogen-bonding network.

Experimental

Suitable crystals of (1) (m.p. 385–387 K) were grown from acetone by slow evaporation. Specific optical rotation: -15° ($c = 3.00$, chloroform). The IR, MS and NMR data were consistent with the derived structure. The density D_m was measured by flotation in KBr.

Crystal data

$\text{C}_{22}\text{H}_{38}\text{O}_4$
 $M_r = 366.55$
 Monoclinic
 $P2_1$
 $a = 9.720$ (4) Å
 $b = 7.657$ (2) Å
 $c = 14.708$ (7) Å
 $\beta = 103.63$ (4) $^\circ$
 $V = 1063.9$ Å 3
 $Z = 2$
 $D_x = 1.14$ Mg m $^{-3}$
 $D_m = 1.13$ Mg m $^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10$ – 13°
 $\mu = 0.0715$ mm $^{-1}$
 $T = 298$ K
 Rectangular block
 $0.30 \times 0.15 \times 0.12$ mm
 Colorless, transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4310 measured reflections
 3739 independent reflections
 2455 observed reflections
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25^\circ$
 $h = -11 \rightarrow 0; 0 \rightarrow 11$
 $k = -9 \rightarrow 0; 0 \rightarrow 9$
 $l = -17 \rightarrow 17; -17 \rightarrow 17$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.060$
 $wR = 0.067$
 $S = 1.92$
 2455 reflections
 234 parameters
 H-atom parameters not refined
 $w = 4F_o^2/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{\text{max}} = 0.01$

$\Delta\rho_{\text{max}} = 0.40$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.35$ e Å $^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
 Absolute configuration: assigned to agree with that expected from the studies of optical rotation

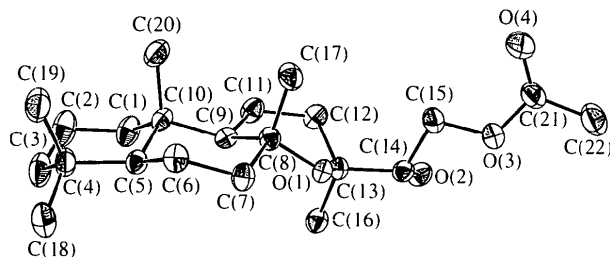


Fig. 1. ORTEP (Johnson, 1976) perspective view of the title compound with the crystallographic numbering scheme, showing 30% probability ellipsoids.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B _{eq}
O(1)	0.9917 (2)	0.967	0.6366 (2)	3.20 (5)
O(2)	1.1362 (3)	1.3556 (4)	0.5511 (2)	4.55 (6)
O(3)	1.3264 (3)	1.0818 (5)	0.5296 (2)	5.36 (7)
O(4)	1.5317 (4)	1.0452 (9)	0.6231 (3)	13.7 (2)
C(1)	0.7374 (5)	1.0876 (6)	0.8799 (3)	5.2 (1)
C(2)	0.6417 (5)	1.0214 (7)	0.9395 (3)	6.7 (1)
C(3)	0.5474 (5)	0.8771 (7)	0.8921 (3)	6.1 (1)
C(4)	0.6246 (4)	0.7205 (6)	0.8626 (3)	4.39 (9)
C(5)	0.7275 (4)	0.7932 (5)	0.8051 (2)	3.30 (8)
C(6)	0.8092 (4)	0.6553 (5)	0.7643 (3)	3.96 (9)
C(7)	0.8727 (4)	0.7350 (5)	0.6886 (3)	3.78 (8)
C(8)	0.9699 (4)	0.8872 (5)	0.7222 (3)	3.23 (8)
C(9)	0.8929 (4)	1.0187 (4)	0.7718 (2)	3.00 (8)
C(10)	0.8282 (4)	0.9429 (5)	0.8505 (2)	3.59 (8)
C(11)	0.9788 (5)	1.1864 (5)	0.7970 (3)	4.4 (1)
C(12)	1.0716 (4)	1.2278 (5)	0.7294 (3)	4.11 (9)
C(13)	1.0141 (4)	1.1556 (5)	0.6322 (3)	3.40 (8)
C(14)	1.1170 (4)	1.1748 (5)	0.5679 (3)	3.52 (8)
C(15)	1.2603 (4)	1.0984 (6)	0.6065 (3)	4.8 (1)
C(16)	0.8754 (4)	1.2423 (6)	0.5837 (3)	4.17 (9)
C(17)	1.1130 (4)	0.8210 (6)	0.7788 (3)	4.6 (1)
C(18)	0.5129 (5)	0.6067 (7)	0.8004 (3)	6.4 (1)
C(19)	0.6942 (5)	0.6104 (7)	0.9467 (3)	5.9 (1)
C(20)	0.9425 (5)	0.8834 (6)	0.9358 (3)	5.2 (1)
C(21)	1.4625 (4)	1.0532 (7)	0.5466 (3)	5.7 (1)
C(22)	1.5126 (5)	1.0373 (8)	0.4603 (3)	6.5 (1)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(8)	1.461 (5)	C(5)—C(10)	1.533 (6)
O(1)—C(13)	1.462 (5)	C(6)—C(7)	1.522 (6)
O(2)—C(14)	1.427 (5)	C(7)—C(8)	1.509 (6)
O(3)—C(15)	1.433 (5)	C(8)—C(9)	1.537 (5)
O(3)—C(21)	1.306 (6)	C(8)—C(17)	1.529 (6)
O(4)—C(21)	1.169 (7)	C(9)—C(10)	1.553 (6)
C(1)—C(2)	1.508 (7)	C(9)—C(11)	1.529 (6)
C(1)—C(10)	1.540 (6)	C(10)—C(20)	1.536 (6)
C(2)—C(3)	1.499 (8)	C(11)—C(12)	1.525 (6)
C(3)—C(4)	1.531 (7)	C(12)—C(13)	1.511 (6)
C(4)—C(5)	1.557 (6)	C(13)—C(14)	1.538 (5)
C(4)—C(18)	1.519 (7)	C(13)—C(16)	1.521 (6)
C(4)—C(19)	1.518 (7)	C(14)—C(15)	1.494 (6)
C(5)—C(6)	1.526 (6)	C(21)—C(22)	1.467 (7)
C(8)—O(1)—C(13)	120.4 (3)	C(8)—C(9)—C(11)	111.5 (3)
C(15)—O(3)—C(21)	119.1 (4)	C(10)—C(9)—C(11)	115.3 (3)
C(2)—C(1)—C(10)	113.2 (4)	C(1)—C(10)—C(5)	107.9 (4)
C(1)—C(2)—C(3)	111.8 (5)	C(1)—C(10)—C(9)	107.4 (3)
C(2)—C(3)—C(4)	115.0 (4)	C(1)—C(10)—C(20)	109.6 (4)
C(3)—C(4)—C(5)	107.2 (4)	C(5)—C(10)—C(9)	106.3 (3)
C(3)—C(4)—C(18)	107.0 (4)	C(5)—C(10)—C(20)	113.2 (4)
C(3)—C(4)—C(19)	111.0 (4)	C(9)—C(10)—C(20)	112.2 (3)
C(5)—C(4)—C(18)	109.7 (4)	C(9)—C(11)—C(12)	113.0 (4)
C(5)—C(4)—C(19)	114.9 (4)	C(11)—C(12)—C(13)	113.4 (4)
C(18)—C(4)—C(19)	106.9 (5)	O(1)—C(13)—C(12)	110.2 (3)
C(4)—C(5)—C(6)	115.3 (3)	O(1)—C(13)—C(14)	104.3 (3)
C(4)—C(5)—C(10)	116.8 (4)	O(1)—C(13)—C(16)	109.0 (3)
C(6)—C(5)—C(10)	110.3 (3)	C(12)—C(13)—C(14)	113.4 (3)
C(5)—C(6)—C(7)	110.4 (4)	C(12)—C(13)—C(16)	112.0 (4)
C(6)—C(7)—C(8)	113.6 (3)	C(14)—C(13)—C(16)	107.6 (3)
O(1)—C(8)—C(7)	104.4 (3)	O(2)—C(14)—C(13)	109.2 (3)
O(1)—C(8)—C(9)	108.7 (3)	O(2)—C(14)—C(15)	107.3 (4)
O(1)—C(8)—C(17)	108.0 (3)	C(13)—C(14)—C(15)	114.3 (4)
C(7)—C(8)—C(9)	108.9 (3)	O(3)—C(15)—C(14)	106.6 (4)
C(7)—C(8)—C(17)	109.9 (4)	O(3)—C(21)—O(4)	121.3 (5)
C(9)—C(8)—C(17)	116.2 (4)	O(3)—C(21)—C(22)	112.1 (5)
C(8)—C(9)—C(10)	115.9 (3)	O(4)—C(21)—C(22)	126.6 (5)
C(10)—C(1)—C(2)—C(3)	−55.86		
C(1)—C(2)—C(3)—C(4)	56.08		
C(2)—C(3)—C(4)—C(5)	−51.67		
C(3)—C(4)—C(5)—C(6)	−176.73		
C(3)—C(4)—C(5)—C(10)	51.38		

C(4)—C(5)—C(6)—C(7)	164.04
C(10)—C(5)—C(6)—C(7)	−61.05
C(4)—C(5)—C(10)—C(1)	−52.41
C(4)—C(5)—C(10)—C(9)	−167.39
C(5)—C(6)—C(7)—C(8)	57.64
C(6)—C(7)—C(8)—O(1)	−167.29
C(6)—C(7)—C(8)—C(9)	−51.33
O(1)—C(8)—C(9)—C(10)	165.66
O(1)—C(8)—C(9)—C(11)	−59.80
C(7)—C(8)—C(9)—C(10)	52.47
C(7)—C(8)—C(9)—C(11)	−173.00
C(8)—C(9)—C(10)—C(1)	−171.32
C(8)—C(9)—C(10)—C(5)	−56.05
C(11)—C(9)—C(10)—C(1)	55.89
C(11)—C(9)—C(10)—C(5)	171.16
C(8)—C(9)—C(11)—C(12)	29.59
C(10)—C(9)—C(11)—C(12)	164.41
C(9)—C(11)—C(12)—C(13)	27.51
C(11)—C(12)—C(13)—O(1)	−55.55
C(8)—O(1)—C(13)—C(12)	24.04
C(13)—O(1)—C(8)—C(7)	148.20
C(13)—O(1)—C(8)—C(9)	32.07

Data collection and cell refinement were performed using *CAD-4 Software* (Enraf-Nonius, 1989). Space group *P2*₁ was determined from systematic absences: *0k0*, *k = 2n + 1*. Lorentz and polarization corrections were applied to the diffractometer data. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and succeeding difference Fourier syntheses. The positions of the H atoms were generated from assumed geometries, except for those of H15a, H16a, H17a, H18a, H19a, H20a, H22a and HO(2) which were found in succeeding difference electron density maps. Each H atom was included in the refinement but constrained to ride on the atom to which it is bonded. The structure was refined by full-matrix least-squares methods. The figure was prepared using *ORTEPII* (Johnson, 1976). All calculations were performed on a VAX computer using *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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