We wish to thank M. Simard for assistance in collecting the X-ray data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles in the phosphine ligand and weighted least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71068 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1027]

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XIII. A Substituted 1-Methyltricyclo[7.4.0.$0^{2,6}$]-tridec-7-ene

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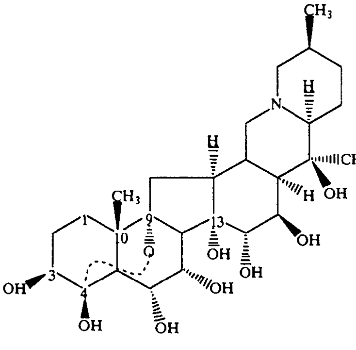
Abstract

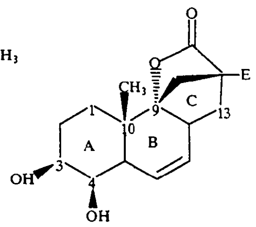
The structure of *rel*-(1*S*,2*R*,4*R*,6*S*,9*S*,10*R*,11*S*)-4-methoxycarbonyl-1-methyltricyclo[7.4.0.$0^{2,6}$]tridec-7-ene-10,11-diol-4,2-carbolactone monohydrate (methyl 7,8-dihydroxy-10a-methyl-2-oxo-3,10b-methano-3,4,4a,6a,7,8,9,10,10a,10b-decahydro-2*H*-benzo[*h*]chromene-3-carboxylate monohydrate) has been determined. The tricyclic compound has the same configuration at C3 (*S*), C9 (*R*) and C10 (*S*) (steriod numbering) as Veratrum alkaloids. The relative stereochemistry is *cis* for the *A*/*B* ring junction, *anti* between C10 methyl and C9 carbolactone and *cis* for the *B*/*C* ring junction.

Comment

The natural Veratrum alkaloids are well known for their important biological activity (Krayer & Acheson, 1946), in particular for their ability to lower blood pressure (Gerber & Nies, 1991; Krayer & Drill, 1958; Meilman & Krayer, 1950). The large number of asymmetric centers [17 in protoverine (1)] and the unusual presence of a tertiary hydroxyl group at position 9 (steroid numbering) present an ambitious goal for total synthesis. Intramolecular processes usually give excellent control on chemo-, regio- and stereoselectivity, such as transannular Diels–Alder cyclization of macrocyclic trienes to synthesize functionalized tricyclic *A*.*B*.*C*[6.6.5] compounds (Quimpère, Ruest & Deslongchamps, 1992*a*). These preliminary results were used to devise a synthetic strategy for the *A*.*B*.*C*[6.6.5] portion of the Veratrum skeleton by Quimpère, Ruest & Deslongchamps (1992*b*), where the introduction of the oxygen bridge between positions 9 and 4 was investigated. These authors supplied a sample of suitable crystalline material; this paper reports the crystallographic structure of (2) containing a 9-hydroxyl group lactonized with the adjacent methyl ester of the malonate moiety. The predicted stereochemistry (Quimpère, Ruest & Deslongchamps, 1992*a*) of all the asymmetric centers of the molecule is confirmed.



(1)



(2) $E = CO_2Me$

The crystal structure, anisotropic thermal ellipsoids and atomic numbering are shown in Fig. 1. As predicted, the C3 proton is α and axially oriented. Ring *A* has a chair conformation, ring *B* a half-chair [C5—C6—C7—C8 = −1.7 (5)°], and ring *C* is in a β-envelope conformation; C11 is 0.873 (4) Å from the plane defined by atoms C8, C9, C12 and C13. The *A*/*B* ring junction is *cis*; *B*/*C* is

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also *cis* and the C9 and C10 substituents are *anti* (*cis-anti-cis*). The H atom at C5 and the methyl group at C10 are β-oriented; the lactone bridge and the H atom at C8 are α-oriented. The relative configurations of C3 and C4 are *R* and *S*, respectively. Intra- and intermolecular geometry calculations (*PLATON*; Spek, 1990) show one intramolecular hydrogen bond and three hydrogen bonds involving the water molecule (Table 2). Fig. 2 shows a packing diagram with the hydrogen bonds indicated by dotted lines. The molecules are aligned head to head with their hydroxyl groups facing each other, trapping the water molecules in an infinite two-dimensional network of (100) and (010) base vectors. Similar hydrogen bonding is reported for the cevine molecule (Eeles, 1960). No abnormally short contacts were observed.

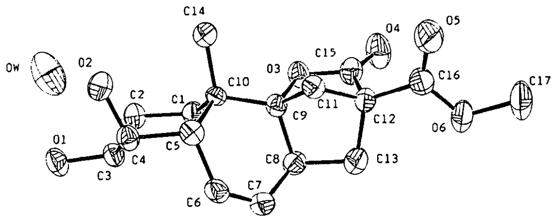

Fig. 1. *ORTEP*II perspective view of the title compound with crystallographic numbering. Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity.

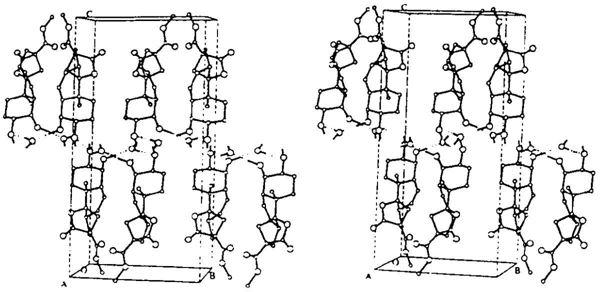

Fig. 2. *PLUTO* stereodiagram of the unit-cell contents along the *a* axis. H atoms are omitted for clarity.

Experimental

Crystal data

$C_{17}H_{22}O_6.H_2O$
M_r = 340.38
Monoclinic
$P2_1/A$
a = 7.3138 (5) Å
b = 10.6101 (6) Å
c = 21.2238 (11) Å
β = 94.443 (5)°
V = 1642.02 (17) Å^3
Z = 4

D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.70930 Å
Cell parameters from 24 reflections
θ = 30.00–35.00°
μ = 0.10 mm^{-1}
T = 293 K
Prism
0.20 × 0.20 × 0.30 mm
Colorless

Data collection

Nonius diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3365 measured reflections
2111 independent reflections
1409 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 44.9°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
Final R = 0.040
wR = 0.033
S = 1.62
1409 reflections
226 parameters
All H-atom parameters refined
Weights based on counting statistics
$(\Delta/\sigma)_{\rm max}$ = 0.036

$\Delta\rho_{\rm max}$ = 0.190 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.210 e Å^{-3}
Extinction correction: Zachariasen (1963); Larson (1967)
Extinction coefficient: 0.50 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: *DATCOL* in *NRCCAD* (Le Page, White & Gabe, 1986). Cell refinement: *TRUANG* in *NRCCAD*. Data reduction: *DATRD*2 in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *LSTSQ* in *NRCVAX*. Molecular graphics: *ORTEP*II (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *DISANG*, *REPORT*, *TABLES*, *TORSHN* in *NRCVAX*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O*w*	0.5354 (3)	0.1601 (2)	0.47781 (10)	0.0623 (10)
O1	0.2508 (3)	0.55353 (19)	0.45744 (9)	0.0443 (8)
O2	0.5412 (3)	0.39211 (19)	0.43312 (9)	0.0434 (8)
O3	0.7663 (3)	0.61701 (18)	0.21807 (8)	0.0378 (7)
O4	0.9232 (3)	0.6518 (2)	0.13278 (9)	0.0587 (9)
O5	0.9651 (3)	0.3304 (2)	0.10673 (10)	0.0687 (10)
O6	0.7560 (3)	0.4036 (2)	0.03515 (9)	0.0663 (9)
C1	0.5349 (4)	0.6490 (3)	0.32372 (13)	0.0354 (11)
C2	0.4703 (4)	0.6513 (3)	0.39057 (13)	0.0374 (11)
C3	0.3261 (4)	0.5503 (3)	0.39682 (13)	0.0356 (11)
C4	0.4012 (4)	0.4206 (3)	0.38424 (13)	0.0353 (11)
C5	0.4731 (4)	0.4149 (3)	0.31799 (13)	0.0320 (10)
C6	0.3120 (4)	0.4120 (3)	0.26908 (14)	0.0394 (11)
C7	0.3069 (4)	0.4647 (3)	0.21273 (14)	0.0434 (11)
C8	0.4627 (4)	0.5393 (3)	0.19020 (13)	0.0356 (11)
C9	0.6354 (4)	0.5171 (3)	0.23448 (13)	0.0302 (10)
C10	0.6132 (4)	0.5206 (3)	0.30538 (13)	0.0283 (10)
C11	0.7216 (4)	0.4014 (3)	0.20562 (13)	0.0322 (11)
C12	0.7291 (4)	0.4633 (3)	0.14062 (13)	0.0349 (11)
C13	0.5255 (4)	0.4984 (3)	0.12462 (13)	0.0433 (11)
C14	0.8002 (4)	0.4978 (3)	0.34160 (13)	0.0405 (11)
C15	0.8229 (4)	0.5869 (3)	0.16035 (13)	0.0402 (11)
C16	0.8307 (4)	0.3920 (3)	0.09300 (13)	0.0417 (11)
C17	0.8493 (6)	0.3371 (4)	−0.01373 (16)	0.0909 (18)
HO*wa*	0.596 (5)	0.095 (4)	0.4678 (17)	0.159 (17)
HO*wb*	0.439 (5)	0.134 (4)	0.5025 (17)	0.153 (17)
HO1	0.339 (5)	0.546 (3)	0.4911 (17)	0.112 (14)
HO2	0.545 (6)	0.296 (4)	0.4497 (17)	0.146 (17)

Table 2. *Geometric parameters* (Å, °)

O1—C3	1.439 (3)	C9—C10	1.526 (4)
O2—C4	1.432 (4)	C9—C11	1.530 (4)
O3—C9	1.488 (4)	C10—C14	1.535 (4)
O3—C15	1.361 (3)	C11—C12	1.533 (4)
O4—C15	1.192 (4)	C12—C13	1.547 (4)
O5—C16	1.197 (4)	C12—C15	1.524 (4)
O6—C16	1.310 (3)	C12—C16	1.504 (4)
O6—C17	1.466 (4)	O*w*—HO*wa*	0.86 (4)
C1—C2	1.530 (4)	O*w*—HO*wb*	0.95 (4)
C1—C10	1.539 (4)	O1—HO1	0.93 (4)
C2—C3	1.517 (4)	O2—HO2	1.08 (4)
C3—C4	1.513 (4)	O1—O2^{i}	2.738 (3)
C4—C5	1.540 (4)	O2—O*w*	2.640 (3)
C5—C6	1.509 (4)	O*w*—O1^{ii}	2.813 (3)
C5—C10	1.556 (4)	O*w*—O1^{iii}	2.827 (3)
C6—C7	1.318 (4)	HO1—O2^{i}	1.89 (4)
C7—C8	1.496 (4)	HO2—O*w*	1.56 (4)
C8—C9	1.533 (4)	HO*wa*—O1^{ii}	1.96 (4)
C8—C13	1.561 (4)	HO*wb*—O1^{iii}	1.89 (4)
C9—O3—C15	106.8 (2)	C1—C10—C5	109.4 (2)
C16—O6—C17	115.8 (3)	C1—C10—C9	109.9 (2)
C2—C1—C10	113.3 (2)	C1—C10—C14	110.3 (2)
C1—C2—C3	109.7 (2)	C5—C10—C9	105.9 (2)
O1—C3—C2	112.2 (2)	C5—C10—C14	111.9 (2)
O1—C3—C4	110.4 (2)	C9—C10—C14	109.3 (2)
C2—C3—C4	111.3 (2)	C9—C11—C12	93.5 (2)
O2—C4—C3	108.2 (2)	C11—C12—C13	101.5 (2)
O2—C4—C5	112.2 (2)	C11—C12—C15	99.7 (2)
C3—C4—C5	110.6 (2)	C11—C12—C16	116.3 (3)
C4—C5—C6	109.0 (2)	C13—C12—C15	105.0 (2)
C4—C5—C10	113.9 (2)	C13—C12—C16	119.4 (2)
C6—C5—C10	112.7 (2)	C15—C12—C16	112.5 (2)
C5—C6—C7	125.5 (3)	C8—C13—C12	102.5 (2)
C6—C7—C8	123.1 (3)	O3—C15—O4	123.2 (3)
C7—C8—C9	109.5 (2)	O3—C15—C12	106.7 (2)
C7—C8—C13	115.0 (3)	O4—C15—C12	130.0 (3)
C9—C8—C13	102.6 (2)	O5—C16—O6	123.6 (3)
O3—C9—C8	105.2 (2)	O5—C16—C12	123.4 (3)
O3—C9—C10	109.4 (2)	O6—C16—C12	113.0 (3)
O3—C9—C11	100.7 (2)	O1—HO1—O2^{i}	151 (3)
C8—C9—C10	117.1 (2)	O2—HO2—O*w*	175 (4)
C8—C9—C11	102.9 (2)	O*w*—HO*wa*—O1^{ii}	172 (3)
C10—C9—C11	119.5 (3)	O*w*—HO*wb*—O1^{iii}	169 (4)

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

The structure was solved by the application of direct methods and refined using full-matrix least squares on *F*. H-atom positional parameters were calculated for all C—H, and hydroxyl H atoms were located by difference Fourier map. Their positional and thermal parameters were refined except for the C17 H atoms for which positions were fixed; the thermal motion was very large at this position.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71119 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1039]

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Structures of *N*-Benzyl- and *N*-Cyclohexylmethyl-(4-diphenylacetoxy)piperidines

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Abstract

The crystal structures of *N*-benzyl-4-(diphenylacetoxy)piperidine methobromide (I) and hydrobromide (II) and *N*-(cyclohexylmethyl)-4-(diphenylacetoxy)piperidine hydrochloride (III) were determined. Cations of (I) [*N*-benzyl-4-(diphenylacetoxy)-*N*-methylpiperidinium] and (II) [*N*-benzyl-4-(diphenylacetoxy)piperidinium] adopt similar U-shaped conformations with the benzene ring of the benzyl moiety approaching the diphenylacetate group, while the cation of (III) [*N*-cyclohexylmethyl-4-(diphenylacetoxy)piperidinium] adopts a completely different (stretched) conformation. Compounds (I)–(III) are much less active at muscarinic M_2 receptors than at M_3 receptors but there is

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