Refinement

Refinement on F
$R = 0.067$
$wR = 0.057$
$S = 1.58$
1941 reflections
206 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F) + 0.0003F^2]$

$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-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* $(Å^2)$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.7960 (2)	0.8109 (2)	0.7747 (1)	0.064 (1)
C(2)	0.6957 (4)	0.9153 (3)	0.7439 (2)	0.056 (1)
C(3)	0.4657 (4)	0.8623 (3)	0.7239 (2)	0.050 (1)
N(4)	0.3689 (3)	0.6942 (2)	0.7397 (1)	0.047 (1)
C(5)	0.4747 (4)	0.6086 (3)	0.7731 (2)	0.044 (1)
C(6)	0.7004 (4)	0.6564 (3)	0.8023 (2)	0.049 (1)
O(2)	0.7968 (3)	1.0483 (2)	0.7317 (1)	0.089 (1)
C(31)	0.3859 (4)	0.9994 (3)	0.7819 (2)	0.069 (1)
O(5)	0.3907 (3)	0.4502 (2)	0.7867 (1)	0.055 (1)
C(51)	0.1792 (4)	0.3774 (3)	0.7530 (2)	0.066 (1)
C(61)	0.7673 (4)	0.6789 (3)	0.9021 (2)	0.055 (1)
C(62)	0.6516 (5)	0.7914 (4)	0.9551 (2)	0.083 (1)
C(63)	0.9962 (4)	0.7644 (4)	0.9226 (2)	0.078 (1)
C(64)	0.7302 (5)	0.5020 (4)	0.9269 (2)	0.082 (1)
C(1')	0.4108 (3)	0.8588 (3)	0.6247 (2)	0.049 (1)
C(2')	0.5015 (4)	0.7292 (3)	0.5680 (2)	0.058 (1)
C(3')	0.4483 (4)	0.7120 (3)	0.4711 (2)	0.059 (1)
O(3')	0.5752 (3)	0.7141 (3)	0.4213 (1)	0.085 (1)
C(4')	0.2298 (4)	0.6912 (4)	0.4397 (2)	0.075 (1)
C(5')	0.1394 (4)	0.8192 (4)	0.4968 (2)	0.074 (1)
C(6')	0.1836 (4)	0.8210 (3)	0.5941 (2)	0.063 (1)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(2)	1.336 (3)	O(1)—C(6)	1.439 (3)
C(2)—C(3)	1.513 (3)	C(3)—N(4)	1.455 (3)
N(4)—C(5)	1.256 (3)	C(5)—C(6)	1.502 (3)
C(2)—O(1)—C(6)	124.5 (2)	O(1)—C(2)—C(3)	120.2 (2)
C(2)—C(3)—N(4)	115.4 (2)	C(3)—N(4)—C(5)	120.0 (2)
N(4)—C(5)—C(6)	128.5 (2)	O(1)—C(6)—C(5)	110.3 (2)
C(6)—O(1)—C(2)—C(3)	−8.7 (3)	C(2)—O(1)—C(6)—C(5)	12.6 (3)
O(1)—C(2)—C(3)—N(4)	−0.5 (3)	C(2)—C(3)—N(4)—C(5)	4.3 (3)
C(3)—N(4)—C(5)—C(6)	0.8 (3)	N(4)—C(5)—C(6)—O(1)	−8.9 (3)

Six low-angle reflections suffered from extinction and were thus omitted. The methyl groups were refined as rigid groups in order to allow for internal rotation.

Data collection: profile fitting (Clegg, 1981). Cell refinement: program in Clegg (1981). Data reduction: *SHELXTL* (Sheldrick, 1983). Program(s) used to solve structure: *SHELXTL* using direct methods. Program(s) used to refine structure: *SHELXTL* using blocked-cascade least squares. Molecular graphics: *XP* (*SHELXTL*). Software used to prepare material for publication: *SHELXTL*.

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A Fully Cyclo-Substituted Cyclohexane

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Abstract

$1r,9t,16t$-Trioxahexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane, $C_{18}H_{24}O_3$, is mirror-symmetric with alternating three- and four-membered rings. Its structure agrees well with that of the parent hydrocarbon. Notable features are the strongly alternating bond angles within the cyclohexane ring and the differing bond lengths within the cyclobutane rings.

Comment

The structure and dynamics of cyclohexane derivatives depend on the number and the size of the substituents. Some highly substituted compounds show unusually high barriers of ring inversion (Fitjer *et al.*, 1988). For example, hexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane, a fully cycloalkylated cyclohexane with alternating three- and four-membered rings, adopts a chair conformation in the crystal but shows considerable populations of twist-boat conformations in solution (Fitjer *et al.*, 1984). We have determined the structure of a derivative, (I), in which a methylene group is replaced by an O atom in each of the three-membered rings.

(I)
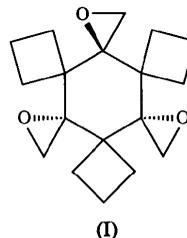
The structure exhibits exact mirror symmetry with two opposite substituent rings in the mirror plane. The cyclohexane ring, which adopts a chair conformation, shows alternating bond angles, the larger ones being centred at the atoms that form part of a three-membered ring. The bond lengths within the four-membered rings are quite different, those to the spiro C atoms being considerably longer. One cyclobutane ring is slightly puckered while the other is forced to be planar by the crystallographic symmetry. All these properties agree well with the crystal structure of the parent hydrocarbon (Fitjer *et al.*, 1984).
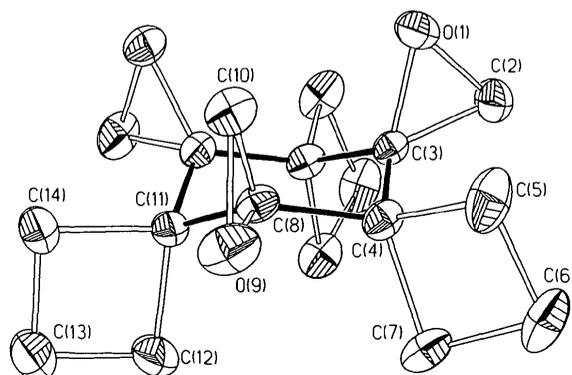
Fig. 1. Molecular structure of (I) showing 30% probability displacement ellipsoids (H atoms omitted).

Experimental

The compound was provided by Professor L. Fitjer (University of Göttingen, Germany) and recrystallized from acetone.

Crystal data

$C_{18}H_{24}O_3$
$M_r = 288.4$
Orthorhombic
$Pmn2_1$
$a = 13.734\,(2)$ Å
$b = 8.281\,(1)$ Å
$c = 6.530\,(1)$ Å
$V = 742.7$ Å^3
$Z = 2$
$D_x = 1.290$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 10$–$12.5°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Block
$0.5 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Stoe–Siemens four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1465 measured reflections
746 independent reflections
645 observed reflections
  $[F > 3\sigma(F)]$

$R_{int} = 0.027$
$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -7 \rightarrow 7$
3 standard reflections
  monitored every 100 reflections
  intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.056$
$S = 1.21$
645 reflections
105 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-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 (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	1/2	0.7320 (4)	0.6081	0.052 (1)
C(2)	1/2	0.5824 (6)	0.5002 (11)	0.051 (2)
C(3)	1/2	0.7342 (5)	0.3851 (10)	0.032 (2)
C(4)	0.4050 (2)	0.7987 (4)	0.2969 (8)	0.037 (1)
C(5)	0.3113 (3)	0.7288 (5)	0.3978 (11)	0.060 (2)
C(6)	0.2983 (3)	0.6160 (5)	0.2130 (10)	0.065 (2)
C(7)	0.3721 (3)	0.7173 (5)	0.0918 (9)	0.052 (1)
C(8)	0.4125 (2)	0.9828 (4)	0.2956 (9)	0.034 (1)
O(9)	0.3221 (2)	1.0671 (3)	0.2649 (8)	0.055 (1)
C(10)	0.3675 (3)	1.0724 (4)	0.4635 (9)	0.045 (1)
C(11)	1/2	1.0526 (5)	0.1873 (10)	0.036 (2)
C(12)	1/2	1.0400 (7)	-0.0509 (11)	0.059 (2)
C(13)	1/2	1.2190 (7)	-0.0673 (13)	0.073 (3)
C(14)	1/2	1.2406 (6)	0.1605 (11)	0.053 (2)

Table 2. *Selected geometric parameters (Å, °)*

C(3)—C(4)	1.523 (5)	C(4)—C(5)	1.558 (6)
C(4)—C(7)	1.566 (7)	C(4)—C(8)	1.528 (5)
C(5)—C(6)	1.536 (8)	C(6)—C(7)	1.536 (7)
C(8)—C(11)	1.509 (5)	C(11)—C(12)	1.56 (1)
C(11)—C(14)	1.567 (7)	C(13)—C(14)	1.50 (1)
C(12)—C(13)	1.486 (9)		

C(4)—C(3)—C(4^i)	117.9 (5)	C(5)—C(4)—C(7)	87.9 (3)
C(3)—C(4)—C(8)	107.1 (3)	C(4)—C(8)—C(11)	116.0 (3)
C(12)—C(11)—C(14)	87.4 (4)	C(8)—C(11)—C(8^i)	105.5 (5)

C(4^i)—C(3)—C(4)—C(8)	-49.6 (7)
C(4)—C(5)—C(6)—C(7)	-14.8 (3)
C(3)—C(4)—C(8)—C(11)	54.4 (6)
C(4)—C(8)—C(11)—C(8^i)	-58.8 (7)

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

Reflection pairs h,k,l and $h,k,\bar{l}$ were merged. The structure solution in the correct space group failed so the symmetry was temporarily reduced to Pn. No evidence for (CH_2/O) disorder within the three-membered rings was observed.

Data collection: profile fitting (Clegg, 1981). Cell refinement: program in Clegg (1981). Data reduction: *SHELXTL* (Sheldrick, 1983). Program(s) used to solve structure: *SHELXTL* using direct methods. Program(s) used to refine structure: *SHELXTL* using blocked-cascade least squares. Molecular graphics: *XP (SHELXTL)*. Software used to prepare material for publication: *SHELXTL*.

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(1)

(2)

2-(6-Methoxy-7-methyl-1,2,3,4-tetrahydro-1-naphthyl)ethyl 4,7,7-Trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate

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Abstract

The determination of the crystal structure of the title compound, $C_{24}H_{32}O_5$, allowed indirect elucidation of the absolute configuration of 7-methoxy-1-demethylcalamenene (calamenene: 1,2,3,4-tetrahydro-4-isopropyl-1,6-dimethylnaphthalene), a natural norsesquiterpene of the calamenene group, which was synthesized by an enantioselective silane-terminated Heck reaction.

Comment

The norsesquiterpene 7-methoxy-1-demethylcalamenene, (1), was isolated, together with several other calamenene and cadinene derivatives, from species of the North American genus *Heterotheca grandiflora* (Bohlmann, Zdero, Robinson & King, 1979; for review see Nath, Bordoloi, Shukla & Sharma, 1989). The absolute configurations of (1) and similar compounds have not, so far, been determined (for the X-ray structure of calamenene see Croft, Ghisalberti, Hocart, Jeffries, Raston & White, 1978).

The first total synthesis of enantiopure (1) (Tietze & Raschke, 1995) was accomplished *via* a silane-terminated intramolecular asymmetric Heck reaction (Tietze & Schimpf, 1994) to give a vinyldecaline derivative, which was converted into compound (1) by
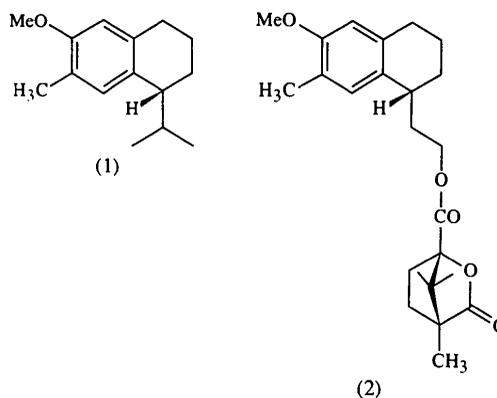
a three-step sequence. The Heck product can also be transformed by hydroboration into a primary alcohol, which can then be acylated with (−)-(1S,4R)-camphanic acid chloride to give the title crystalline ester (2). The X-ray crystallographic analysis of compound (2) (Fig. 1) allowed us to determine the relative configuration of the stereogenic centers. Since the stereochemistry of the camphanic acid moiety is known, the absolute configuration of the decaline moiety and hence that of 7-methoxy-1-demethylcalamenene could be deduced. This is the first example of the structure determination of a compound of the 1-demethyl series.
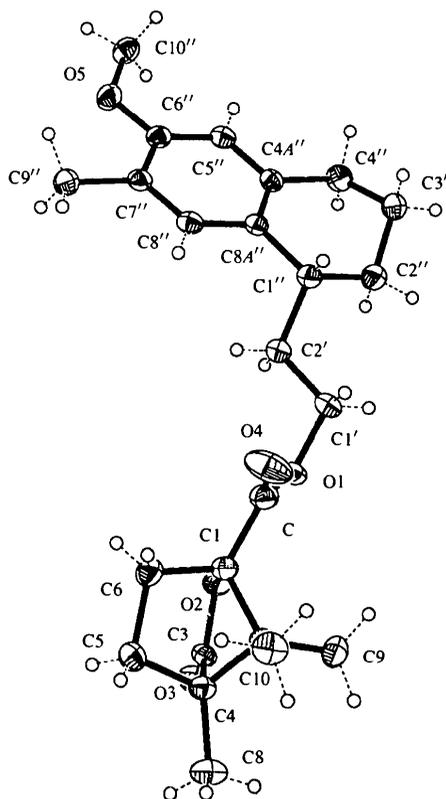
Fig. 1. The structure of compound (2) showing 50% probability displacement ellipsoids.