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*Acta Cryst.* (1996). C**52**, 2256–2258

# 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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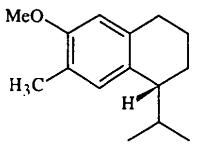
## Abstract

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.

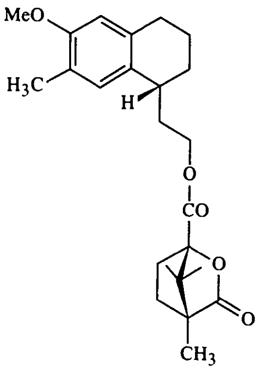
## Comment

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 (−)-(1*S*,4*R*)-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.



(1)



(2)

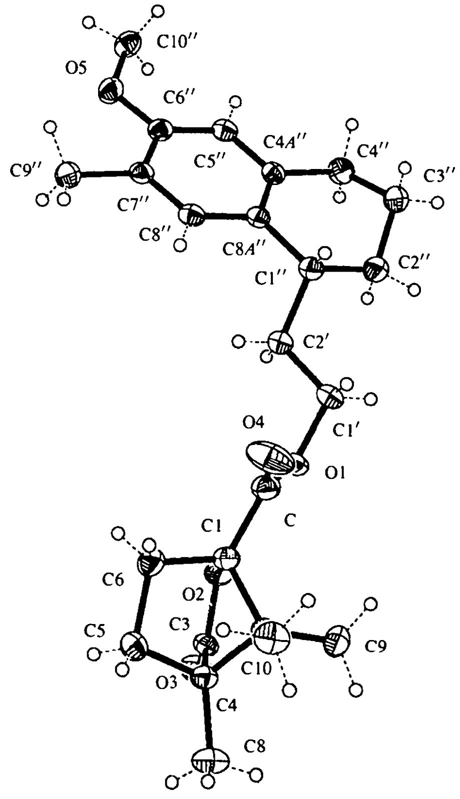


Fig. 1. The structure of compound (2) showing 50% probability displacement ellipsoids.

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## Experimental

The title compound was crystallized from an *n*-hexane/dichloromethane/diethyl ether solution at 279 K. Data were collected by the real-time learnt-profile method (Clegg, 1981).

### *Crystal data*

$C_{24}H_{32}O_5$
$M_r = 400.50$
Orthorhombic
$P2_12_12_1$
$a = 6.4190\,(10)$ Å
$b = 13.340\,(2)$ Å
$c = 24.701\,(2)$ Å
$V = 2115.1\,(5)$ Å$^3$
$Z = 4$
$D_x = 1.258$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 10$–$12.5°$
$\mu = 0.087$ mm$^{-1}$
$T = 153\,(2)$ K
Block
0.80 × 0.80 × 0.70 mm
Colorless

### *Data collection*

Stoe AED-2 four-circle diffractometer
Profile fitted $2\theta$-$\omega$ scans
Absorption correction: none
4299 measured reflections
2151 independent reflections
2003 observed reflections $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0326$
$\theta_{\max} = 24.94°$
$h = -7 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 29$
3 standard reflections frequency: 90 min intensity decay: none

### *Refinement*

Refinement on $F^2$
$R(F) = 0.0320$
$wR(F^2) = 0.0818$
$S = 1.066$
2150 reflections
267 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.47P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.213$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.153$ e Å$^{-3}$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −1.2 (13); consequently the absolute structure was assigned according to that of the camphane group

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

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

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$ |
|---|---|---|---|---|
| O1 | −0.1286 (2) | 0.00461 (11) | −0.68360 (6) | 0.0292 (4) |
| O2 | −0.1829 (2) | 0.13638 (11) | −0.75880 (5) | 0.0242 (3) |
| O3 | −0.1014 (3) | 0.20302 (12) | −0.83948 (6) | 0.0365 (4) |
| O4 | −0.4675 (3) | −0.0025 (2) | −0.65979 (8) | 0.0524 (5) |
| O5 | 0.3118 (3) | 0.24475 (11) | −0.38084 (6) | 0.0292 (4) |
| C1 | −0.3750 (3) | 0.0951 (2) | −0.73619 (8) | 0.0237 (5) |
| C3 | −0.2297 (4) | 0.1659 (2) | −0.81072 (8) | 0.0242 (5) |
| C4 | −0.4592 (3) | 0.1441 (2) | −0.81956 (8) | 0.0232 (5) |
| C5 | −0.5721 (4) | 0.2213 (2) | −0.78238 (9) | 0.0322 (5) |
| C6 | −0.5158 (4) | 0.1849 (2) | −0.72438 (9) | 0.0310 (5) |
| C7 | −0.4769 (4) | 0.0446 (2) | −0.78673 (8) | 0.0225 (5) |
| C8 | −0.5271 (4) | 0.1455 (2) | −0.87852 (8) | 0.0354 (6) |
| C9 | −0.3450 (4) | −0.0403 (2) | −0.81041 (9) | 0.0305 (5) |
| C1'' | 0.0766 (4) | −0.0450 (2) | −0.54053 (8) | 0.0232 (4) |
| C2'' | 0.2427 (4) | −0.1236 (2) | −0.55305 (8) | 0.0284 (5) |
| C3'' | 0.3543 (4) | −0.1602 (2) | −0.50274 (8) | 0.0300 (5) |
| C4'' | 0.4706 (4) | −0.0734 (2) | −0.47605 (9) | 0.0292 (5) |
| C4A'' | 0.3292 (3) | 0.01605 (15) | −0.46708 (8) | 0.0218 (4) |
| C5'' | 0.3857 (4) | 0.0870 (2) | −0.42784 (8) | 0.0241 (5) |
| C6'' | 0.2648 (4) | 0.1711 (2) | −0.41804 (8) | 0.0235 (5) |
| C7'' | 0.0788 (4) | 0.1861 (2) | −0.44678 (8) | 0.0237 (5) |
| C8'' | 0.0230 (3) | 0.11382 (15) | −0.48456 (8) | 0.0229 (4) |
| C8A'' | 0.1457 (3) | 0.02939 (14) | −0.49640 (8) | 0.0210 (4) |
| C10 | −0.6989 (4) | 0.0077 (2) | −0.77824 (10) | 0.0339 (6) |
| C10'' | 0.4897 (4) | 0.2300 (2) | −0.34738 (9) | 0.0296 (5) |
| C9'' | −0.0474 (4) | 0.2800 (2) | −0.43784 (9) | 0.0308 (5) |
| C | −0.3297 (4) | 0.0272 (2) | −0.68851 (9) | 0.0279 (5) |
| C1' | −0.0679 (4) | −0.0570 (2) | −0.63705 (8) | 0.0337 (6) |
| C2' | 0.0111 (4) | 0.0115 (2) | −0.59253 (8) | 0.0275 (5) |

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

| | | | |
|---|---|---|---|
| O1—C | 1.331 (3) | C7—C10 | 1.522 (3) |
| O1—C1' | 1.466 (2) | C7—C9 | 1.530 (3) |
| O2—C3 | 1.375 (2) | C1''—C2'' | 1.527 (3) |
| O2—C1 | 1.461 (3) | C1''—C8A'' | 1.539 (3) |
| O3—C3 | 1.195 (3) | C1''—C2' | 1.547 (3) |
| O4—C | 1.201 (3) | C2''—C3'' | 1.515 (3) |
| O5—C6'' | 1.379 (2) | C3''—C4'' | 1.527 (3) |
| O5—C10'' | 1.423 (3) | C4''—C4A'' | 1.516 (3) |
| C1—C | 1.514 (3) | C4A''—C8A'' | 1.394 (3) |
| C1—C6 | 1.528 (3) | C4A''—C5'' | 1.402 (3) |
| C1—C7 | 1.562 (3) | C5''—C6'' | 1.385 (3) |
| C3—C4 | 1.517 (3) | C6''—C7'' | 1.403 (3) |
| C4—C8 | 1.520 (3) | C7''—C8'' | 1.388 (3) |
| C4—C5 | 1.558 (3) | C7''—C9'' | 1.509 (3) |
| C4—C7 | 1.560 (3) | C8''—C8A'' | 1.405 (3) |
| C5—C6 | 1.555 (3) | C1'—C2' | 1.517 (3) |
| C—O1—C1' | 117.1 (2) | C2''—C1''—C8A'' | 112.6 (2) |
| C3—O2—C1 | 106.3 (2) | C2''—C1''—C2' | 110.8 (2) |
| C6''—O5—C10'' | 117.7 (2) | C8A''—C1''—C2' | 110.6 (2) |
| O2—C1—C | 111.2 (2) | C3''—C2''—C1'' | 112.7 (2) |
| O2—C1—C6 | 106.1 (2) | C2''—C3''—C4'' | 109.9 (2) |
| C—C1—C6 | 115.7 (2) | C4A''—C4''—C3'' | 111.6 (2) |
| O2—C1—C7 | 102.15 (15) | C8A''—C4A''—C5'' | 119.4 (2) |
| C—C1—C7 | 116.3 (2) | C8A''—C4A''—C4'' | 122.0 (2) |
| C6—C1—C7 | 104.0 (2) | C5''—C4A''—C4'' | 118.5 (2) |
| O3—C3—O2 | 121.5 (2) | C6''—C5''—C4A'' | 121.5 (2) |
| O3—C3—C4 | 131.5 (2) | O5—C6''—C5'' | 124.8 (2) |
| O2—C3—C4 | 107.0 (2) | O5—C6''—C7'' | 115.0 (2) |
| C3—C4—C8 | 114.5 (2) | C5''—C6''—C7'' | 120.2 (2) |
| C3—C4—C5 | 103.9 (2) | C8''—C7''—C6'' | 117.4 (2) |
| C8—C4—C5 | 115.0 (2) | C8''—C7''—C9'' | 122.5 (2) |
| C3—C4—C7 | 99.1 (2) | C6''—C7''—C9'' | 120.1 (2) |
| C8—C4—C7 | 119.2 (2) | C7''—C8''—C8A'' | 123.5 (2) |
| C5—C4—C7 | 102.8 (2) | C4A''—C8A''—C8'' | 117.9 (2) |
| C6—C5—C4 | 103.2 (2) | C4A''—C8A''—C1'' | 121.9 (2) |
| C1—C6—C5 | 101.9 (2) | C8''—C8A''—C1'' | 120.2 (2) |
| C10—C7—C9 | 109.4 (2) | O4—C—O1 | 125.9 (2) |
| C10—C7—C4 | 114.5 (2) | O4—C—C1 | 121.0 (2) |
| C9—C7—C4 | 113.0 (2) | O1—C—C1 | 113.1 (2) |
| C10—C7—C1 | 114.9 (2) | O1—C1'—C2' | 108.6 (2) |
| C9—C7—C1 | 113.1 (2) | C1'—C2'—C1'' | 113.5 (2) |
| C4—C7—C1 | 91.01 (15) | | |

Since Cu radiation was not available, the Flack parameter was not determined accurately and therefore the absolute configuration of compound (1) was inferred from that of compound (2) using chemical methods.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# A Fluorinated D-Homoestrone Derivative

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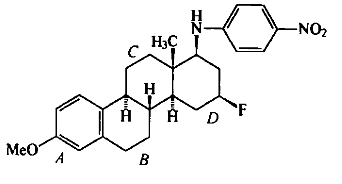
(*Received 11 January 1996; accepted 18 March 1996*)

## Abstract

The structure of 16β-fluoro-3-methoxy-17aβ-(4-nitroanilino)-17a-homoestra-1,3,5(10)-triene, $C_{26}H_{31}FN_2O_3$, is reported.

## Comment

The synthesis of the title compound, (I), *via* a cationic cyclization reaction of the corresponding D-secoestrone imine derivative will be published elsewhere (Wölfling, Schneider, Frank & Tietze, 1996). The product of this reaction has two new stereogenic centers at the C16 and C17*A* positions, and the assignment of the stereochemistry at these positions was the reason for the present study.



(I)

The *B*/*C* and *C*/*D* ring fusions are *trans*. Rings *C* and *D* adopt chair conformations, while ring *B* displays a twisted half-chair conformation. Both substituents of the *D* ring, the F atom at C16 and the 4-nitroanilino group at C17*A*, are equatorial, *i.e.* in the β position. For the crystal structure of a fluorinated estrone derivative see Neeman, Kartha, Go, Santodonato & Dodson-Simmons (1983) and for the structure of a D-homoestrone derivative see Antel, Sheldrick, Tietze & Wölfling (1988).

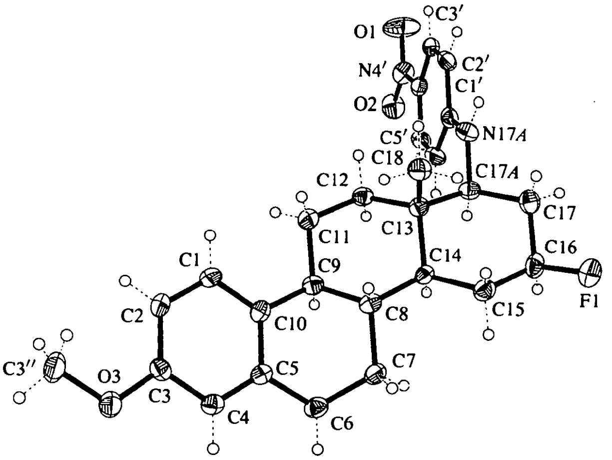


Fig. 1. View of the title compound with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

## Experimental

The title compound was crystallized from acetone. Data were collected by a real-time learnt-profile method (Clegg, 1981).

*Crystal data*

$C_{26}H_{31}FN_2O_3$
$M_r = 438.53$
Orthorhombic
$P2_12_12_1$
$a = 8.5500\,(10)$ Å
$b = 12.1890\,(10)$ Å
$c = 20.979\,(2)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 10.0–12.5°$
$\mu = 0.093\ \mathrm{mm^{-1}}$
$T = 153\,(2)$ K