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(1*R*,2*R*)-2-(4-Methylenecyclohex-2-enyl)propyl (1*R*,4*S*)-camphanate

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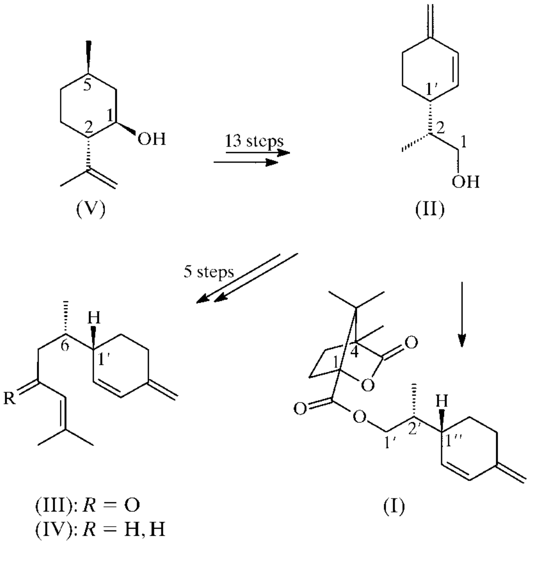
Esterification of a single diastereomer of 2-(4-methylenecyclohex-2-enyl)propanol, (II), with (1*R*,4*S*)-(+)-camphanic acid [(1*R*,4*S*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylic acid] leads to the crystalline title compound, $C_{20}H_{28}O_4$. The relative configuration of the camphanate was determined by X-ray diffraction analysis. The outcome clarifies the relative and absolute stereochemistry of the naturally occurring bisabolane sesquiterpenes β-turmerone and β-sesquiphellandrene, since we have converted (II) into both natural products *via* a stereospecific route.

Comment

During the course of our investigation on the stereospecific synthesis (Kreiser & Körner, 1999*a*) of β-turmerone, (III) [isolated from *Curcuma longa* by Golding *et al.* (1982) and Golding & Pombo (1992)], and β-sesquiphellandrene, (IV) (Kreiser & Körner, 1999*b*) [isolated from *Zingiber officinale* by Connell & Sutherland (1966)], we tried hard to get hold of a crystalline synthetic intermediate because the natural compounds, like all known natural bisabolane-sesquiterpenes, are provided in an oily state. In our view X-ray diffraction analysis of a crystal appeared to be the only reliable proof for the relative configuration of the vicinal centres of chirality, which remain untouched until the final stage of the synthesis, since the interpretation of NMR data had already led to contradictory assignments of (III). Compound (II) was prepared in a 13-step procedure from (−)-isopulegol, (V), and esterified with both (−)- and (+)-camphanic acid, originally with the aim to determine its enantiopurity by means of NMR and high-pressure liquid chromatography techniques. We were able to crystallize the title compound, (I), from 2-propanol and the result of the subsequent X-ray diffraction analysis is presented in Fig. 1.



Based on the fact enantiomerically pure (1*R*,4*S*)-(+)-camphanic acid is involved and that the stereogenic centre C1″ is derived from (1*R*,2*S*,5*R*)-(−)-isopulegol, (V), the absolute configuration of (I) could be assigned. In the solid state the cyclohexenyl ring of (I) adopts a half-chair conformation, being characterized by the almost planar arrangement of the four C*sp*^{2} atoms along with the low C2″—C3″—C4″—C4*A*″ torsion angle of −172.2 (3)°. The substituted isopropyl group bound to the cyclohexane ring is found in a quasi-equatorial position. On the other hand the bicyclic part of the molecule does not display any surprising structural features, according to its conformational rigidity. To us the most valuable piece of information that can be deduced from Fig. 1 is the *R* configuration at C2′ and the *R* configuration at C1″ of (I). The atoms C1′ and C2 during further transformation of (II) become C1′ and C6 in β-turmerone, (III), and β-sesquiphellandrene, (IV), respectively, and thus allow unambiguous assignment for the latter compounds.

Experimental

(I) was prepared by addition of (+)-camphanoyl chloride (572 mg, 2.64 mmol) in tetrahydrofuran (THF) (2 ml) to a solution of (II) (200 mg, 1.32 mmol), 4-(dimethylamino)pyridine (40 mg, 0.33 mmol) and pyridine (2 ml) in THF (3 ml). After stirring at room temperature for 3 h, Et_2O (100 ml) was added, the solution was washed with saturated $NaHCO_3$ solution, H_2O and brine, dried (Na_2SO_4) and evaporated. The crude material was purified by column chromatography (cyclohexane:ethyl acetate = 10:1, R_f = 0.30). The pure ester (360 mg) was dissolved in 2-propanol (6.0 ml) at 313 K. The solution was cooled to 273 K within 1 h and crystals of (I) (m.p. 351–352 K) were grown by standing at this temperature for 24 h. The mother

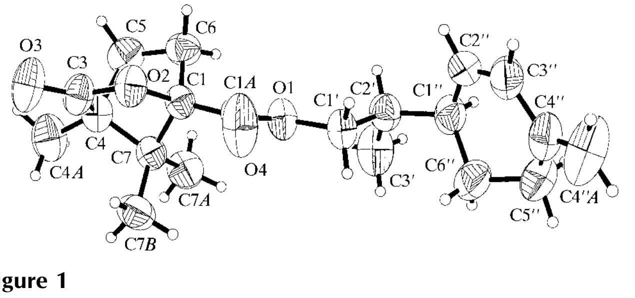


Figure 1
View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of an arbitrary radius.

liquor was decanted, the crystals were washed with 2-propanol (1.0 ml) at 273 K and dried *in vacuo*.

Crystal data

$C_{20}H_{28}O_4$
$M_r = 332.42$
Monoclinic, $P2_1$
$a = 6.2171$ (6) Å
$b = 12.5197$ (9) Å
$c = 12.2224$ (9) Å
$\beta = 97.225$ (5)°
$V = 943.79$ (13) Å^3
$Z = 2$
$D_x = 1.170$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12305 reflections
$\theta = 3.66$–25.36°
$\mu = 0.080$ mm^{-1}
$T = 291$ (1) K
Needle, colourless
0.30 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Four sets at different κ-angles with 386 frames *via* φ-rotation ($\Delta\varphi$ = 1°) and 2 × 90 s per frame
Absorption correction: none
12 305 measured reflections
1810 independent reflections
1391 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 25.36°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 15$
$l = -14 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.086$
$S = 0.997$
1810 reflections
222 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.048 (11)

Data collection: *KappaCCD Reference Manual* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

Table 1
Selected geometric parameters (Å, °).

C1″—C2″	1.502 (4)	C4″—C4″*A*	1.337 (5)
C1″—C6″	1.525 (4)	C4″—C5″	1.486 (5)
C2″—C3″	1.315 (4)	C5″—C6″	1.522 (4)
C3″—C4″	1.434 (4)		
C1″—C2″—C3″—C4″	2.3 (5)	C3″—C4″—C5″—C6″	−38.4 (4)
C2″—C3″—C4″—C4″*A*	−172.2 (3)	C4″—C5″—C6″—C1″	57.9 (3)
C2″—C3″—C4″—C5″	8.7 (4)	C2″—C1″—C6″—C5″	−45.5 (3)
C4″*A*—C4″—C5″—C6″	142.5 (3)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1308). Services for accessing these data are described at the back of the journal.

References

Connell, D. W. & Sutherland, M. D. (1966). *Aust. J. Chem.* **19**, 283–288.
Golding, B. T. & Pombo, E. (1992). *J. Chem. Soc. Perkin Trans.* pp. 1519–1524.
Golding, B. T., Pombo, E. & Samuel, C. J. (1982). *J. Chem. Soc. Chem. Commun.* pp. 363–364.
Kreiser, W. & Körner, F. (1999*a*). *Helv. Chim. Acta*, **82**, 1610–1629.
Kreiser, W. & Körner, F. (1999*b*). *Helv. Chim. Acta*, **82**, 1427–1433.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Nonius (1998). *KappaCCD Reference Manual.* Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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