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(1*SR*,2*RS*,5*RS*,6*SR*,8*RS*)-7,7-Dimethyltricyclo[6.2.1.$0^{1,6}$]undecane-2,5,6-triol: a supramolecular framework built from O—H···O hydrogen bonds

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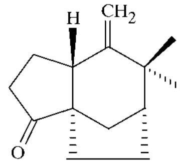
In the title compound, $C_{13}H_{22}O_3$, the asymmetric unit has two independent molecules linked by a strong O—H···O hydrogen bond. The cyclohexane ring is *trans* fused to the cyclopentane ring bridged through an ethyl moiety. The hydroxyl groups act as donors as well as acceptors, resulting in an extensive two-dimensional hydrogen-bonded network in the (011) plane. Intermolecular O—H···O bonds between centrosymmetrically related molecules form a four-membered supramolecular assembly, leading to infinite chains parallel to the [$01\overline{1}$] direction, crosslinked in the [100] direction.

Comment

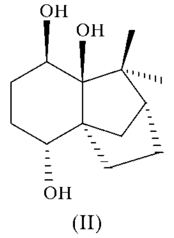
Khusimone, (I), a norsesquiterpene ketone containing a tricyclo[6.2.1.$0^{1,5}$]undecane skeleton, is one of the main olfactively important constituents of vetiver oil (Büchi *et al.*, 1977). In connection with our studies directed towards the synthesis and characterization of bridged ring systems related to tricyclic sesquiterpenes (Das *et al.*, 1996; Pati *et al.*, 2000), the title tricyclic triol, (II), has been synthesized. This triol possesses the requisite structural features for a potential intermediate in a total synthesis of khusimone. The structure determination of (II) was undertaken in order to establish the relative stereochemistries of the five asymmetric centres (C1, C2, C5, C6 and C8), and to devise the subsequent sequence of reactions leading to the total synthesis of (I).

Compound (II) consists of a cyclohexane ring *trans* fused to a cyclopentane ring bridged *via* an ethyl moiety. The asymmetric unit of (II) contains two crystallographically independent molecules, *A* and *B* (Fig. 1), with almost similar geometries. Equivalent bond distances and angles in the two molecules agree within experimental limits. In both molecules, the torsion angles (Table 1) about the C2*A*—C3*A*, C4*A*—C5*A*, C2*B*—C3*B* and C4*B*—C5*B* bonds indicate the equatorial orientations of the two hydroxyl groups at the C2 and C5 positions, while the axial orientation of the OH group at the ring-junction C atom (C6*A* and C6*B*) is evident from the torsion angles about the C5*A*—C6*A* and C5*B*—C6*B* bonds.

The two methyl groups at C7*A* and C7*B* are in almost synperiplanar and *gauche* orientations with respect to the C6*A*—O3*A* and C6*B*—O3*B* bonds [O3*A*—C6*A*—C7*A*—C12*A* −12.1 (3), O3*B*—C6*B*—C7*B*—C12*B* 14.5 (3), O3*A*—C6*A*—C7*A*—C13*A* −134.7 (3) and O3*B*—O6*B*—C7*B*—C13*B* 135.9 (2)°].



(I)



(II)

The C—C [1.515 (4)–1.596 (4) Å] and C—O [1.433 (3)–1.449 (3) Å] bond distances agree well with the corresponding values reported in the literature (Allen *et al.*, 1987). The lengthening of the $C_3C—CC_2O$ bond distances [C6*A*—C7*A* 1.596 (4) Å in molecule *A* and C6*B*—C7*B* 1.589 (4) Å in molecule *B*] compared with other C—C bond lengths (Table 1) is consistent with observations in related tricycloundecane structures (Pati *et al.*, 2002).

The C1–C6 cyclohexane ring displays a chair conformation, with puckering parameters (Cremer & Pople, 1975) Q = 0.586 (3) Å, q_2 = 0.051 (3) Å, q_3 = −0.584 (3) Å and θ = 175.1 (3)° for molecule *A*, and Q = 0.579 (3) Å, q_2 = 0.060 (3) Å, q_3 = 0.576 (3) Å and θ = 5.9 (3)° for molecule *B*. The cyclopentane ring (C1/C6/C7/C8/C11) adopts a near-envelope conformation, with atom C11 deviating by 0.877 (4) Å in both molecules *A* and *B* from the least-squares plane through the remaining endocyclic atoms.

The dihedral angle between the planar parts of the fused cyclohexane and cyclopentane rings is 16.3 (2)° in molecule *A* and 18.2 (1)° in molecule *B*. The other five-membered ring (C1/C10/C8/C9/C11), with ring puckering parameters q_2 = 0.606 (3) Å and φ = −43.4 (3)° for molecule *A*, and q_2 =

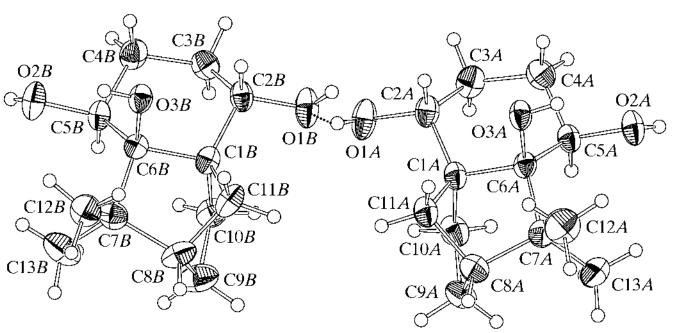


Figure 1
A view of the structure of (II), with displacement ellipsoids at the 50% probability level, showing the two independent molecules connected by O—H···O interactions. H atoms are drawn as small spheres of arbitrary radii.

0.613 (3) Å and φ = 136.4 (3)° for molecule *B*, also assumes a distorted envelope conformation, with atom C11 displaced from the ring plane by 0.884 (4) Å in molecule *A* and 0.887 (4) Å in molecule *B*. The molecule of (II) has five chiral centres (C1, C2, C5, C6 and C8) and, from the centrosymmetric space group, it follows that the crystal is a racemate.

Intramolecular O—H···O hydrogen bonds (Table 2) influence the conformation of the two independent molecules of (II), *A* and *B*. In addition, each hydroxyl group in the molecule acts as a potential donor as well as an acceptor in an extensive intermolecular hydrogen-bond network. The resulting hydrogen-bonded supramolecular structure is of considerable complexity. A similar supramolecular network, solely controlled by hydrogen bonds between hydroxyl groups, has been reported by Deák *et al.* (2001).

A simplified description of the supramolecular assembly in (II), in terms of tetramolecular motifs leading to parallel chains and the connections between such chains, can be visualized as follows. The two molecules in the asymmetric unit, *A* and *B*, are linked *via* a strong O1*A*—H1*A*···O1*B*(x, y, z) hydrogen bond (Table 2 and Fig. 1). The intermolecular O—H···O hydrogen bonds between the molecules in the asymmetric unit and their centrosymmetrically related counterparts, O2*B*—H2*B*1···O1*A*($1-x, 1-y, 1-z$), result in the formation of a four-membered A_2B_2 aggregate in the structure (Fig. 2). These supramolecular A_2B_2 units, connected through O2*A*—H2*A*1···O2*B*($x, y-1, 1+z$) hydrogen bonds, give rise to infinite ...*ABAB*... chains parallel to the $[01\overline{1}]$ direction (Fig. 3). These chains are interlinked by O3*A*—H3*A*···O2*A*($2-x, -y, 2-z$), O1*B*—H1*B*···O3*B*($2-x, 1-y, 1-z$) and O3*B*—H3*B*···O3*A*($2-x, 1-y, 1-z$) hydrogen bonds to complete the two-dimensional supramolecular network in the (011) plane.

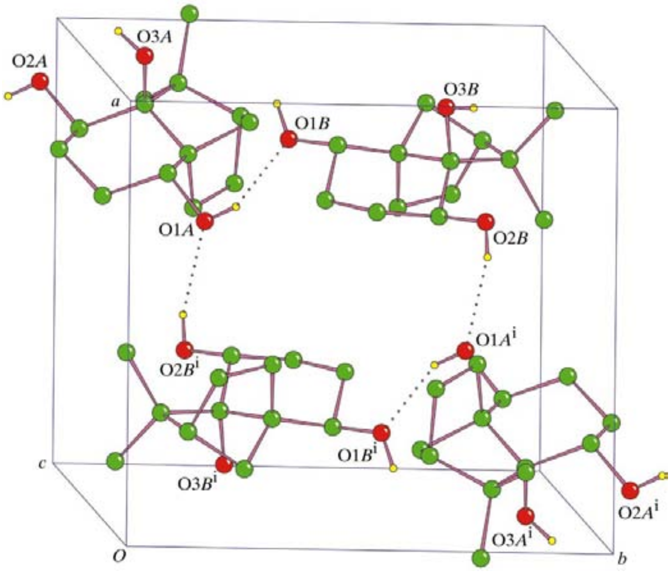


Figure 2
The four-membered supramolecular aggregates of (II) [symmetry code: (i) $1-x, 1-y, 1-z$]. H atoms bonded to C atoms have been omitted for the sake of clarity.

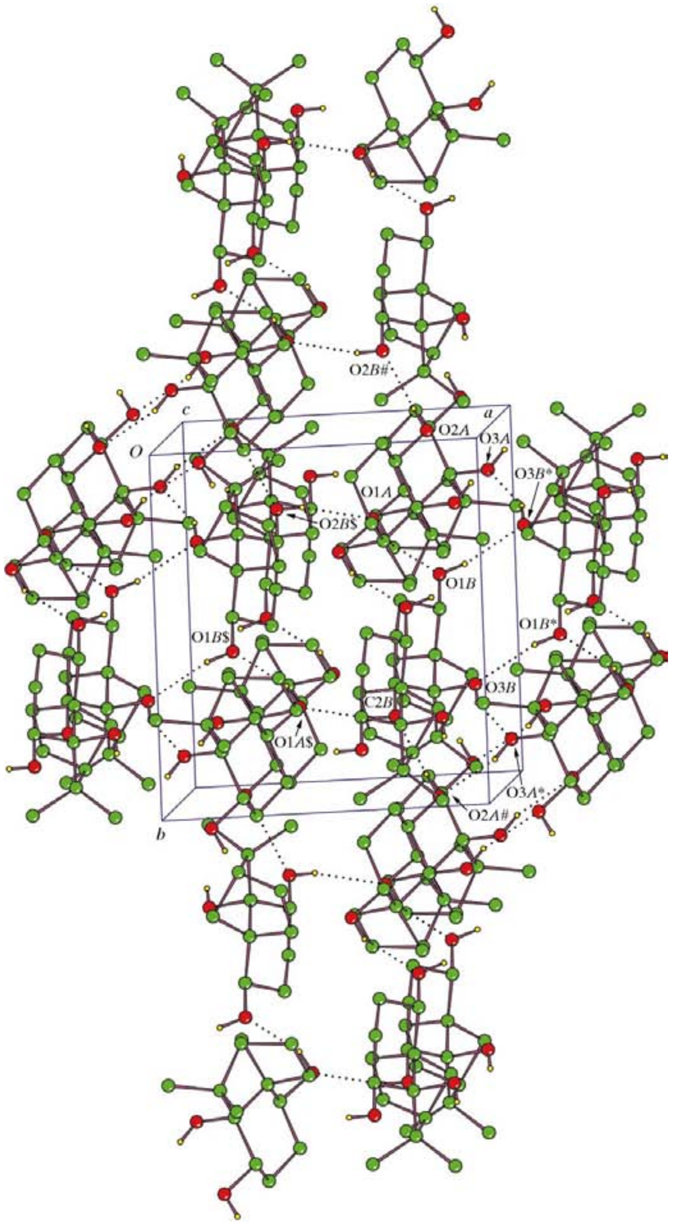


Figure 3
A packing diagram for (II), viewed down the *c* axis. Hydrogen bonds are indicated by dotted lines. Atoms marked with a dollar sign ($), hash (#) or asterisk (*) are at the symmetry positions ($1-x, 1-y, 1-z$), ($x, y-1, 1+z$) and ($2-x, 1-y, 1-z$), respectively. H atoms bonded to C atoms have been omitted for clarity.

Experimental

A solution of (1*RS*,2*RS*,8*RS*)-2-hydroxy-7,7-dimethyltricyclo-[6.2.1.0^{1,6}]undec-5-ene (0.31 g, 1.6 mmol) and OsO_4 (0.41 g, 1.6 mmol) in pyridine (6 ml) was stored at room temperature for 5 d. A saturated aqueous solution of sodium hydrogen sulfite (20 ml) was then added to the reaction mixture, and stirring was continued at room temperature for 3 h. Water (20 ml) was added and the product was extracted with ether. The ether extract was washed successively with dilute HCl and water, and then dried. The residue remaining upon evaporation of the solvent was crystallized from a mixture of ether and light petroleum (1:1) to furnish the title triol, (II) (0.3 g, 82%) (m.p. 451–453 K). Elemental analysis, calculated for $C_{13}H_{22}O_3$, requires: C 68.99, H 9.80%; found: C 68.85, H 9.92%.

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Crystal data

$C_{13}H_{22}O_3$
M_r = 226.31
Triclinic, $P\overline{1}$
a = 9.812 (2) Å
b = 11.141 (1) Å
c = 11.443 (2) Å
α = 82.47 (1)°
β = 77.56 (1)°
γ = 89.46 (1)°
V = 1210.8 (3) Å^3
Z = 4
D_x = 1.241 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 reflections
θ = 6.9–8.1°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, colourless
0.5 × 0.4 × 0.3 mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
4499 measured reflections
4259 independent reflections
2972 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.015
$\theta_{\rm max}$ = 25°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: −1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.156
S = 1.10
4259 reflections
299 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.9623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.014
$\Delta\rho_{\rm max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1*A*—C2*A*	1.524 (4)	C1*B*—C2*B*	1.524 (4)
C2*A*—O1*A*	1.434 (3)	C2*B*—O1*B*	1.433 (3)
C5*A*—O2*A*	1.436 (3)	C5*B*—O2*B*	1.441 (3)
C6*A*—O3*A*	1.434 (3)	C6*B*—O3*B*	1.449 (3)
C6*A*—C7*A*	1.596 (4)	C6*B*—C7*B*	1.589 (4)
C7*A*—C8*A*	1.561 (4)	C7*B*—C8*B*	1.565 (4)
C2*A*—C1*A*—C6*A*	110.0 (2)	C2*B*—C1*B*—C6*B*	110.2 (2)
C11*A*—C1*A*—C6*A*	99.5 (2)	C11*B*—C1*B*—C6*B*	99.8 (2)
C11*A*—C1*A*—C10*A*	100.6 (2)	C11*B*—C1*B*—C10*B*	100.4 (2)
C1*A*—C6*A*—C7*A*	102.8 (2)	C1*B*—C6*B*—C7*B*	102.3 (2)
C8*A*—C7*A*—C6*A*	101.2 (2)	C8*B*—C7*B*—C6*B*	101.9 (2)
C6*A*—C1*A*—C2*A*—O1*A*	177.2 (2)	C6*B*—C1*B*—C2*B*—O1*B*	−178.8 (2)
O1*A*—C2*A*—C3*A*—C4*A*	−176.8 (2)	O1*B*—C2*B*—C3*B*—C4*B*	177.1 (2)
C3*A*—C4*A*—C5*A*—O2*A*	−175.2 (2)	C3*B*—C4*B*—C5*B*—O2*B*	174.6 (2)
O2*A*—C5*A*—C6*A*—O3*A*	63.7 (3)	O2*B*—C5*B*—C6*B*—O3*B*	−63.8 (3)
C4*A*—C5*A*—C6*A*—O3*A*	−57.2 (3)	C4*B*—C5*B*—C6*B*—O3*B*	58.4 (3)
O2*A*—C5*A*—C6*A*—C1*A*	179.1 (2)	O2*B*—C5*B*—C6*B*—C1*B*	−177.5 (2)
C2*A*—C1*A*—C6*A*—O3*A*	55.6 (3)	C2*B*—C1*B*—C6*B*—O3*B*	−55.9 (2)
C10*A*—C1*A*—C6*A*—O3*A*	−178.2 (2)	C10*B*—C1*B*—C6*B*—O3*B*	178.5 (2)
O3*A*—C6*A*—C7*A*—C12*A*	−12.1 (3)	O3*B*—C6*B*—C7*B*—C12*B*	14.5 (3)
O3*A*—C6*A*—C7*A*—C13*A*	−134.7 (3)	O3*B*—C6*B*—C7*B*—C13*B*	135.9 (2)
C1*A*—C6*A*—C7*A*—C8*A*	−9.0 (2)	C1*B*—C6*B*—C7*B*—C8*B*	8.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O1*B*	0.82	1.99	2.754 (3)	154
O3*A*—H3*A*···O2*A*	0.82	2.45	2.826 (2)	109
O3*B*—H3*B*···O2*B*	0.82	2.57	2.861 (3)	103
O2*B*—H2*B*1···O1*A*$^{\rm i}$	0.82	2.12	2.876 (3)	154
O2*A*—H2*A*1···O2*B*$^{\rm ii}$	0.82	2.09	2.908 (3)	177
O3*A*—H3*A*···O2*A*$^{\rm iii}$	0.82	1.99	2.733 (2)	151
O1*B*—H1*B*···O3*B*$^{\rm iv}$	0.82	2.17	2.971 (3)	166
O3*B*—H3*B*···O3*A*$^{\rm iv}$	0.82	2.17	2.940 (2)	155

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, y - 1, 1 + z$; (iii) $2 - x, -y, 2 - z$; (iv) $2 - x, 1 - y, 1 - z$.

H atoms were placed geometrically and were treated as riding. The hydroxyl H atoms were constrained using the *HFIX* 147 instruction, with the O—H distances fixed at 0.82 Å and the C—O—H angles tetrahedral. For the idealized methyl groups, the *HFIX* 137 instruction was used, with C—H = 0.96 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1554). Services for accessing these data are described at the back of the journal.

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