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Structure of 9-Acetyl-4,8,8-trimethyltricyclo[5.2.2.0^{1,5}]undecan-6-ol

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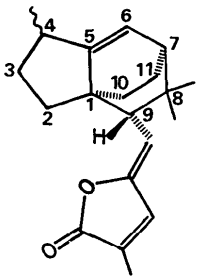
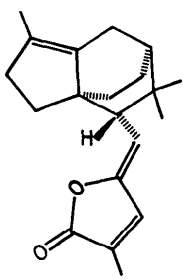
Abstract. $C_{16}H_{26}O_2$, $M_r = 250{\cdot}38$, monoclinic, $P2_1/a$, $a = 14{\cdot}607$ (4), $b = 9{\cdot}517$ (4), $c = 10{\cdot}423$ (4) Å, $\beta = 92{\cdot}27$ (3)°, $V = 1447{\cdot}8$ (9) Å^3, $Z = 4$, $D_m = 1{\cdot}10$, $D_x = 1{\cdot}15$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = $0{\cdot}40$ cm^{-1}, $F(000) = 552$, $T = 293$ K, $R = 0{\cdot}043$ for 1375 observed reflections. The title compound has a unique tricyclo[5.2.2.0^{1,5}]undecane skeleton in which the three six-membered rings adopt boat conformations. The molecules related by an **a** glide are linked by O—H···O hydrogen bonds.

Introduction. Eremolactone (1) was isolated from *Eremophila fraseri* and *E. freelingii* (Jefferies, Knox & Middleton, 1962; Birch, Grimshow & Turnbull, 1963; Pattenden, 1978). As (1) easily isomerizes to isoeremolactone (2), only the structure of (2) has been determined (Oh & Maslen, 1966, 1968). Therefore, the configuration of C(4) in the five-membered ring remained unknown. For the total synthesis of (1) (Asaoka, Ishibashi, Yanagida & Takei, 1983), it was required to clarify the relative configuration of C(4). The molecular structure of the title compound, which is the intermediate in the synthesis, has been determined.



(1)



(2)

Experimental. Colorless needle-like crystals from pentane solution, D_m by flotation in aqueous KI solution. Systematic absences: $0k0$, $k = 2n + 1$, $h0l$, $h = 2n + 1$. Crystal dimensions $0{\cdot}4 \times 0{\cdot}3 \times 0{\cdot}2$ mm. Rigaku AFC-3 diffractometer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 15 independent 2θ values ($25 < 2\theta < 30°$). Intensity measurement performed up to $2\theta = 55°$, $-17 \le h \le 17$, $0 \le k \le 11$, $0 \le l \le 12$. ω–2θ scan, scan speed $2°$ min^{-1}(θ), scan width $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$, background measured for 5 s before and after each scan. Three standard reflections monitored before and after data collection, no significant variation in intensities. 2553 reflections measured, 1375 with $|F_o| > 5\sigma(|F_o|)$ considered observed and used for structure determination. $R_{int} = 0{\cdot}040$. Corrections for Lorentz and polarization, absorption ignored. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier calculation. Full-matrix least-squares refinement on F using *SHELX*76 (Sheldrick, 1976), H atoms located on difference map. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(|F_o|) + 0{\cdot}004594|F_o|^2]^{-1}$. Final $R = 0{\cdot}043$, $wR = 0{\cdot}049$ for 1375 observed reflections. $(\Delta/\sigma)_{max} = 0{\cdot}4$. $\Delta\rho$ excursions in the final difference map $< 0{\cdot}2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations carried out on a FACOM-HITAC M-180 computer at this Institute.

Discussion. The final atomic parameters for the non-H atoms are given in Table 1.‡ A stereoscopic drawing of the molecule with the numbering of the atoms is shown in Fig. 1. Bond distances and bond angles are listed in Table 2. The relative configuration is (1*R**, 4*S**, 5*R**,

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‡ Lists of structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42892 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6*S**, 7*R**, 9*S**). The molecule has a unique skeleton, a tricyclo[5.2.2.0^{1,5}]undecane ring. The three six-membered rings adopt boat conformations. Although the average C—C distance in the three rings is 1·545 Å, the length of C(8)—C(9) extends to 1·587 (4) Å because of the short contact of 2·803 (7) Å between C(13) and C(15). The torsion angle C(1)—C(9)—C(15)—C(16) is 151·8 (3)°.

The crystal structure viewed along **b** is shown in Fig. 2. The molecules related by an **a** glide are linked by O—H···O hydrogen bonds. The distances O(17)···O(18) and H(17)···O(18) are 2·878 (4) and 2·08 (5) Å, respectively, and the angle O(17)—H(17)—O(18) is 166 (5)°.

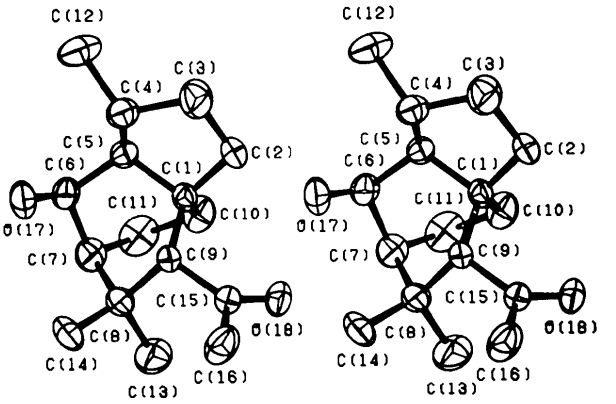

Fig. 1. *ORTEP* (Johnson, 1965) stereoscopic drawing showing numbering of atoms.

Table 1. *Final atomic coordinates* (×10^4) *with their e.s.d.'s and equivalent isotropic temperature factors*

	x	*y*	*z*	B_{eq}(Å^2)
C(1)	9282 (2)	2884 (3)	8445 (2)	3·3
C(2)	9828 (2)	2168 (4)	9563 (3)	4·7
C(3)	9201 (3)	2051 (5)	10671 (4)	6·1
C(4)	8262 (2)	2610 (3)	10242 (3)	4·0
C(5)	8498 (2)	3603 (3)	9151 (3)	3·5
C(6)	7732 (2)	4081 (3)	8201 (3)	4·2
C(7)	8132 (2)	4081 (3)	6857 (3)	4·8
C(8)	8314 (2)	2588 (3)	6339 (3)	4·3
C(9)	8860 (2)	1811 (3)	7479 (2)	2·9
C(10)	9768 (2)	4046 (4)	7718 (4)	5·2
C(11)	9022 (3)	4917 (4)	6986 (5)	6·5
C(12)	7746 (4)	3312 (5)	11304 (4)	6·3
C(13)	8865 (4)	2675 (7)	5113 (4)	7·2
C(14)	7419 (3)	1802 (5)	5983 (5)	6·8
C(15)	9521 (2)	745 (3)	6962 (2)	3·4
C(16)	9146 (3)	−659 (4)	6558 (5)	5·6
O(17)	6958 (1)	3215 (3)	8334 (3)	5·7
O(18)	10332 (1)	970 (2)	6873 (2)	4·8

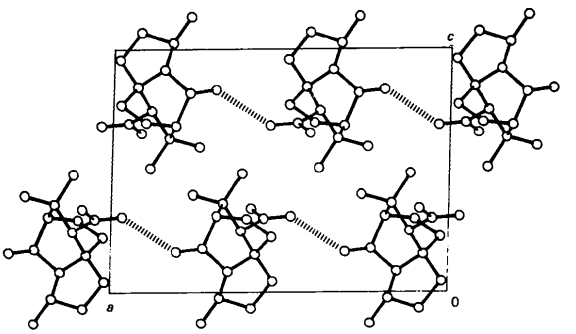

Fig. 2. Crystal structure viewed along **b**.

Table 2. *Bond distances* (Å) *and bond angles* (°)

C(1)—C(2)	1·543 (5)	C(6)—O(17)	1·410 (4)
C(1)—C(5)	1·545 (4)	C(7)—C(8)	1·547 (5)
C(1)—C(9)	1·546 (4)	C(7)—C(11)	1·526 (6)
C(1)—C(10)	1·530 (5)	C(8)—C(9)	1·587 (4)
C(2)—C(3)	1·506 (7)	C(8)—C(13)	1·539 (7)
C(3)—C(4)	1·522 (6)	C(8)—C(14)	1·539 (6)
C(4)—C(5)	1·529 (4)	C(9)—C(15)	1·514 (4)
C(4)—C(12)	1·518 (6)	C(10)—C(11)	1·547 (7)
C(5)—C(6)	1·534 (4)	C(15)—C(16)	1·498 (6)
C(6)—C(7)	1·539 (5)	C(15)—O(18)	1·210 (3)
C(2)—C(1)—C(5)	101·9 (2)	C(6)—C(7)—C(8)	113·2 (3)
C(2)—C(1)—C(9)	112·4 (2)	C(6)—C(7)—C(11)	105·8 (3)
C(2)—C(1)—C(10)	117·2 (3)	C(8)—C(7)—C(11)	110·6 (3)
C(5)—C(1)—C(9)	108·6 (2)	C(7)—C(8)—C(9)	104·8 (2)
C(5)—C(1)—C(10)	106·4 (2)	C(7)—C(8)—C(13)	110·1 (3)
C(9)—C(1)—C(10)	109·6 (2)	C(7)—C(8)—C(14)	112·0 (3)
C(1)—C(2)—C(3)	107·5 (3)	C(9)—C(8)—C(13)	112·5 (3)
C(2)—C(3)—C(4)	108·5 (4)	C(9)—C(8)—C(14)	110·5 (3)
C(3)—C(4)—C(5)	101·9 (3)	C(13)—C(8)—C(14)	107·1 (4)
C(3)—C(4)—C(12)	114·1 (3)	C(1)—C(9)—C(8)	110·8 (2)
C(5)—C(4)—C(12)	113·8 (3)	C(1)—C(9)—C(15)	115·5 (2)
C(1)—C(5)—C(4)	105·9 (2)	C(8)—C(9)—C(15)	110·8 (2)
C(1)—C(5)—C(6)	111·1 (2)	C(1)—C(10)—C(11)	107·5 (3)
C(4)—C(5)—C(6)	118·9 (2)	C(7)—C(11)—C(10)	110·2 (4)
C(5)—C(6)—C(7)	107·1 (3)	C(9)—C(15)—C(16)	117·8 (3)
C(5)—C(6)—O(17)	109·3 (3)	C(9)—C(15)—O(18)	123·3 (2)
C(7)—C(6)—O(17)	115·1 (3)	C(16)—C(15)—O(18)	119·0 (3)

References

ASAOKA, M., ISHIBASHI, K., YANAGIDA, N. & TAKEI, H. (1983). *Tetrahedron Lett.* pp. 5127–5130.

BIRCH, A. J., GRIMSHOW, J. & TURNBULL, T. P. (1963). *J. Chem. Soc.* pp. 2412–2417.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JEFFERIES, P. R., KNOX, J. R. & MIDDLETON, E. J. (1962). *Aust. J. Chem.* **15**, 532–537.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

OH, Y. L. & MASLEN, E. N. (1966). *Tetrahedron Lett.* pp. 3291–3294.

OH, Y. L. & MASLEN, E. N. (1968). *Acta Cryst.* B**24**, 883–896.

PATTENDEN, G. (1978). *Progress in the Chemistry of Organic Natural Products*, pp. 133–198. Vienna: Springer Verlag.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.