Crabtree, R. H. & Moorehouse, S. M. (1986). *Inorg. Synth.* **24**, 173–176.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Vineyard, B. D., Knowles, W. S., Sabacky, M. J., Bachman, G. L. & Weinkauff, D. J. (1977). *J. Am. Chem. Soc.* **99**, 5946–5952.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1991). C**47**, 439–440

The Structure of a Key Intermediate† in the Total Synthesis of Dendrobine

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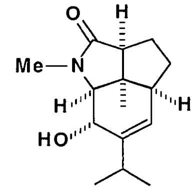
Abstract. $(1R^*,4R^*,5S^*,8R^*,11S^*)$-3,11-Dimethyl-5-hydroxy-6-isopropyl-3-azatricyclo[6.2.1.0^{4,11}]undec-6-en-2-one, $C_{15}H_{23}NO_2$, $M_r = 249{\cdot}35$, monoclinic, $P2_1/c$, $a = 7{\cdot}782\,(2)$, $b = 23{\cdot}119\,(4)$, $c = 7{\cdot}932\,(2)$ Å, $\beta = 101{\cdot}53\,(2)°$, $V = 1398{\cdot}1\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}184$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}7259$ cm^{-1}, $F(000) = 544$, $T = 298$ K, $R = 0{\cdot}0464$ for 1887 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. The molecules are H-bonded into infinite columns parallel to **c** involving the hydroxyl group and the carbonyl O atom [O15···O13$(x,y,z-1)$ 2·756 (2); H15···O13 1·84 (3) Å; O—H···O 173 (3)°]. The bonds from the bridgehead atom of the tricyclic ring to other ring atoms appear to be elongated [av. 1·549 (2) Å] compared to the other Csp^3–Csp^3 bonds in the molecule.

Experimental. (1) was synthesized in two steps from a tricyclic precursor that was prepared by an intramolecular Diels–Alder reaction of an unsaturated dienamide. Details of the synthetic procedure are described elsewhere (Li, 1988).



(1)

The data crystal was a colorless block that was cut from a larger crystal and had approximate dimensions 0·31 × 0·34 × 0·38 mm. Crystals were obtained by slow evaporation from ether. The data were collected at room temperature using graphite-monochromatized Mo $K\alpha$ radiation on a Nicolet $P3$ diffractometer. Lattice parameters were obtained from the least-squares refinement of 24 reflections with $22{\cdot}2 < 2\theta < 30{\cdot}0°$. Data were collected using the ω-scan technique (5330 reflections, 2457 unique, $R_{\text{int}} = 0{\cdot}0169$), with a 2θ range 4·0–50° in 2θ, over a 1·2° ω scan at 10° min^{-1} ($h = 0\rightarrow9$, $k = -27\rightarrow27$, $l = -9\rightarrow9$). Four reflections (061; $11\bar{2}$; 022; $10\bar{2}$) were remeasured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was < 1%). The data were also corrected for Lp effects but not for absorption. Data reduction and decay correction were perfomed using *SHELXTL-Plus* (Sheldrick, 1988). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (570 reflections). The structure was solved by direct methods and refined by full-matrix least squares (Sheldrick, 1976). The non-H atoms were refined with anisotropic thermal parameters. Initially, the H atoms were calculated in ideal positions but were allowed to refine without constraint in the final refinement cycles. All H atoms were refined with isotropic thermal parameters. In all, 255 parameters were refined. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = (0{\cdot}5kI^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}02I)^2\}^{1/2}$. The intensity, I, is given by $(I_{\text{peak}} - I_{\text{background}}) \times$ (scan rate); 0·02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times \text{(scan rate)}]$. The final $R = 0{\cdot}0464$ for 1887 reflections, $wR = 0{\cdot}0512$ ($R_{\text{all}} = 0{\cdot}0645$, $wR_{\text{all}} = 0{\cdot}0551$) and goodness of fit = 1·663. Max. $|\Delta/\sigma| < 0{\cdot}1$ in the final refinement cycle and min. and max. peaks in the final ΔF map were −0·15 and 0·16 e Å^{-3}, respectively. Scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with anomalous-dispersion corrections from

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† IUPAC name: $(1R^*,4R^*,7R^*,10S^*,11S^*)$-10-hydroxy-9-isopropyl-2,11-dimethyl-2-azatricyclo[5.3.1.0^{4,11}]undec-8-en-3-one.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms of* (1)

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

	x	y	z	U_{eq}
C1	1·0287 (3)	0·39575 (9)	0·9463 (2)	0·0404 (7)
C2	0·8784 (3)	0·43652 (8)	0·9380 (2)	0·0367 (6)
N3	0·8238 (2)	0·45482 (6)	0·7763 (2)	0·0348 (5)
C4	0·9381 (3)	0·43778 (8)	0·6591 (2)	0·0338 (6)
C5	0·8358 (3)	0·41542 (9)	0·4868 (2)	0·0355 (6)
C6	0·7428 (3)	0·35978 (8)	0·5105 (2)	0·0354 (6)
C7	0·8338 (3)	0·32067 (9)	0·6150 (3)	0·0431 (7)
C8	1·0202 (3)	0·32908 (9)	0·7052 (3)	0·0432 (7)
C9	1·0628 (4)	0·29590 (11)	0·8755 (3)	0·0574 (9)
C10	0·9869 (4)	0·33378 (10)	0·9983 (3)	0·0579 (10)
C11	1·0637 (3)	0·39288 (8)	0·7609 (2)	0·0365 (6)
C12	1·2542 (3)	0·40797 (14)	0·7551 (4)	0·0576 (10)
O13	0·8125 (2)	0·45125 (6)	1·0607 (2)	0·0569 (6)
C14	0·6856 (3)	0·49717 (11)	0·7291 (3)	0·0500 (8)
O15	0·9626 (2)	0·40830 (7)	0·3803 (2)	0·0508 (6)
C16	0·5570 (3)	0·35268 (10)	0·4138 (3)	0·0485 (8)
C17	0·5439 (4)	0·3547 (2)	0·2210 (3)	0·0711 (12)
C18	0·4634 (4)	0·30003 (15)	0·4651 (5)	0·0787 (14)

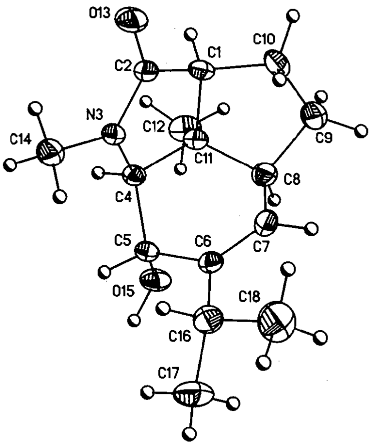

Fig. 1. View of (1) with the atom-labelling scheme. Ellipsoids are scaled to the 30% probability level. H atoms are of arbitrary size.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the non*-H *atoms of* (1)

1	2	3	1–2	1–2–3
C2	C1	C10	1·494 (3)	113·1 (2)
C10	C1	C11	1·543 (3)	107·5 (2)
C11	C1	C2	1·550 (3)	105·66 (15)
N3	C2	O13	1·337 (2)	124·5 (2)
N3	C2	C1		109·7 (2)
O13	C2	C1	1·235 (3)	125·7 (2)
C4	N3	C14	1·463 (3)	122·2 (2)
C4	N3	C2		114·1 (2)
C14	N3	C2	1·448 (3)	122·6 (2)
C5	C4	C11	1·527 (2)	113·8 (2)
C5	C4	N3		112·6 (2)
C11	C4	N3	1·539 (3)	104·54 (14)
C6	C5	O15	1·506 (3)	112·4 (2)
C6	C5	C4		110·82 (15)
O15	C5	C4	1·431 (3)	105·6 (2)
C7	C6	C16	1·331 (3)	125·5 (2)
C7	C6	C5		116·7 (2)
C16	C6	C5	1·504 (3)	117·8 (2)
C8	C7	C6	1·497 (3)	123·6 (2)
C9	C8	C11	1·531 (3)	103·2 (2)
C9	C8	C7		112·0 (2)
C11	C8	C7	1·557 (3)	113·2 (2)
C10	C9	C8	1·515 (4)	103·5 (2)
C1	C10	C9		103·6 (2)
C12	C11	C1	1·532 (3)	111·9 (2)
C12	C11	C4		110·3 (2)
C12	C11	C8		111·3 (2)
C1	C11	C4		104·8 (2)
C1	C11	C8		103·9 (2)
C4	C11	C8		114·26 (14)
C17	C16	C18	1·513 (4)	110·9 (2)
C17	C16	C6		112·0 (2)
C18	C16	C6	1·515 (4)	114·6 (2)

the work of Cromer & Liberman (1970). The scattering factors for the H atoms were from Stewart, Davidson & Simpson (1965). The linear absorption coefficient was calculated from values found in *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55).* Positional and thermal parameters for non-H atoms are listed in Table 1, and the bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labelling scheme is shown in Fig. 1. Other computer programs are listed in reference 11 of Gadol & Davis (1982).

Related literature. The crystal structures of three molecules analogous to (1) have been previously reported (Lynch, Li & Martin, 1988; Lynch, Li, Martin & Davis, 1990).

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References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Gadol, S. M. & Davis, R. E. (1982). *Organometallics*, **1**, 1607–1613.

Li, W. (1988). PhD Thesis, Univ. of Texas, USA.

Lynch, V. M., Li, W. & Martin, S. F. (1988). *Acta Cryst.* **C44**, 187–189.

Lynch, V. M., Li, W., Martin, S. F. & Davis, B. E. (1990). *Acta Cryst.* **C46**, 1155–1157, 1159–1161.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1988). *SHELXTL-Plus88. Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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* Lists of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving the H atoms, torsion angles, structure-factor amplitudes and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53352 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.