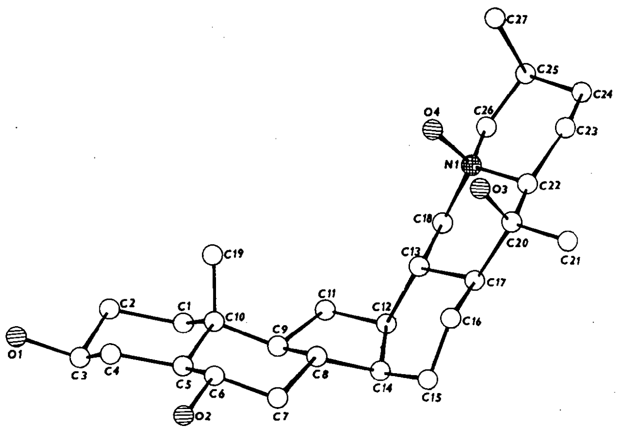

Fig. 1. A perspective view of verticine *N*-oxide in correct absolute configuration, also showing the atom numbering. H atoms are not drawn, for clarity.

molecular structure is similar to that of other related structures (Brisse, 1970; Itô, Fukazawa & Miyashita, 1976; Kettman, Mašterová & Tomko, 1982). Thus, the presence of an *N*-oxide arrangement did not change the usual *trans* configuration at the *E*/*F* ring junction as already observed with quaternization of verticinone with CH_3Br (Itô, Fukazawa & Okuda, 1968), obviously due to a smaller steric volume of the O atom compared with the methyl group.

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Structure of (1*R*,5*R*)-1-*p*-Menth-3-yloxy-2,4-dimethyl-*cis*-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione*

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Abstract. $C_{16}H_{28}N_4O_3$, M_r = 324·43, monoclinic, $P2_1$, a = 10·488 (3), b = 18·432 (6), c = 9·429 (3) Å, β = 90·63 (2)°, V = 1823 (1) Å^3, Z = 4, D_x = 1·182 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 6·38 cm^{-1}, F(000) = 704, room temperature, R = 0·051 for 2914 unique reflections [$I \geq 5\sigma(I)$]. The asymmetric unit contains two independent molecules. The title compound is the first example of a derivative of the bicyclol tautomer in the allantoin series and the key intermediate in the asymmetric synthesis of (−)-(*R*)-1,3-dimethylallantoin; the results of the X-ray structure determination confirm its diastereomeric identity and establish the absolute (1*R*,5*R*) configuration.

Experimental. The title compound was characterized by its melting point (550–551 K), $[\alpha]_D^{25^\circ C}$ −28° (*c* 1·6, Me_2SO), IR, ^{1}H- and ^{13}C-NMR spectra, as well as by regiospecific conversion into (−)-(*R*)-1,3-dimethylallantoin, $[\alpha]_D^{25^\circ C}$ −75° (*c* 3, H_2O) (Modrić, Drake & Poje, 1989). Recrystallization from ethanol;

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* *p*-Menth-3-yl is (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* U_{eq} (Å$^2 \times 10^3$) *values*

$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

	x	*y*	*z*	U_{eq}
C(101)	4079 (4)	2160 (0)	7665 (4)	45 (1)
O(101)	4348 (3)	2571 (2)	6448 (3)	49 (1)
N(102)	4731 (3)	2525 (2)	8814 (4)	50 (1)
C(102)	4539 (5)	3291 (2)	9132 (5)	60 (1)
C(103)	5545 (3)	2088 (2)	9535 (4)	48 (1)
O(103)	6207 (3)	2254 (2)	10556 (4)	63 (1)
N(104)	5492 (3)	1415 (2)	8942 (4)	56 (1)
C(104)	6277 (6)	821 (3)	9385 (8)	85 (2)
C(105)	4667 (3)	1379 (2)	7722 (4)	44 (1)
N(106)	3565 (3)	926 (2)	7877 (4)	52 (1)
C(107)	2489 (3)	1313 (2)	8106 (4)	44 (1)
O(107)	1439 (3)	1065 (2)	8389 (3)	56 (1)
N(108)	2753 (3)	2032 (2)	7890 (3)	46 (1)
C(109)	3497 (4)	2554 (3)	5238 (4)	55 (1)
C(110)	3854 (4)	3212 (3)	4327 (5)	64 (1)
C(111)	2949 (6)	3202 (4)	3002 (4)	87 (2)
C(112)	3080 (6)	2516 (5)	2177 (6)	92 (2)
C(113)	2780 (5)	1861 (5)	3068 (6)	99 (2)
C(114)	3642 (6)	1849 (3)	4407 (5)	72 (1)
C(115)	2945 (14)	1183 (7)	2210 (9)	160 (4)
C(116)	3837 (6)	3924 (3)	5152 (7)	78 (1)
C(117)	4346 (9)	4565 (4)	4287 (10)	118 (3)
C(118)	2545 (8)	4123 (5)	5782 (9)	112 (2)
C(201)	908 (3)	− 1724 (2)	8269 (4)	47 (1)
O(201)	645 (3)	− 2139 (2)	7062 (3)	54 (1)
N(202)	277 (3)	− 2084 (2)	9416 (4)	53 (1)
C(202)	460 (5)	− 2847 (2)	9745 (5)	61 (1)
C(203)	− 520 (4)	− 1645 (2)	10128 (5)	51 (1)
O(203)	− 1182 (3)	− 1802 (2)	11148 (4)	68 (1)
N(204)	− 487 (3)	− 974 (2)	9516 (5)	61 (1)
C(204)	− 1237 (6)	− 377 (3)	9989 (9)	96 (2)
C(205)	316 (4)	− 947 (2)	8298 (5)	49 (1)
N(206)	1392 (3)	− 480 (2)	8415 (5)	60 (1)
C(207)	2505 (4)	− 855 (2)	8606 (4)	49 (1)
O(207)	3563 (3)	− 588 (2)	8775 (4)	60 (1)
N(208)	2242 (3)	− 1581 (2)	8512 (4)	49 (1)
C(209)	1516 (4)	− 2139 (3)	5869 (5)	58 (1)
C(210)	1118 (5)	− 2787 (3)	4937 (5)	65 (1)
C(211)	2020 (6)	− 2801 (4)	3671 (6)	83 (2)
C(212)	1966 (7)	− 2099 (5)	2848 (7)	92 (2)
C(213)	2310 (7)	− 1459 (4)	3759 (7)	89 (2)
C(214)	1464 (6)	− 1433 (3)	5074 (6)	74 (1)
C(215)	2242 (12)	− 753 (6)	2958 (10)	152 (4)
C(216)	1042 (6)	− 3517 (3)	5753 (6)	76 (1)
C(217)	460 (8)	− 4119 (4)	4844 (10)	111 (2)
C(218)	2311 (7)	− 3743 (4)	6398 (8)	101 (2)

crystal dimensions: 0·36 × 0·26 × 0·25 mm. Philips PW 1100 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters from 18 reflections ($19 \le \theta \le 26°$).

Data were collected using θ–2θ scan technique, scan width 1·2°, scan speed 0·04° s^{-1}, $8 \le 2\theta \le 140°$, $0 \le h \le 12$, $0 \le k \le 22$, $-11 \le l \le 11$. 3568 unique reflections were measured of which the 2194 with $I \ge 5\sigma(I)$ were used in the calculations; 22 reflections ($21\bar{1}$, $12\bar{1}$, 210, 020, 120, 001, 101, 201, 011, 111, 211, 121, 102, 012, 112, $11\bar{2}$, $11\bar{1}$, $10\bar{2}$, $10\bar{1}$, 140, 031, 202) were ignored due to secondary extinction. Three standard reflections monitored every 2 h showed no significant variation in intensity. Data corrected for Lorentz and polarization effects (locally written program) but not for absorption. Two independent molecules were located by direct methods using *SIR* (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985); triplet invariants were estimated by *PTEN* (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984) and the solution with the highest combined figure of merit revealed 41 atoms; the remaining non-H atoms were located from the *XRAY76* Fourier map (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Refinement by block-matrix least squares on F to minimize $\sum w(|F_o| - |F_c|)^2$ led to $R = 0{\cdot}051$ and $wR = 0{\cdot}069$ for 2914 reflections with $I \ge 5\sigma(I)$. H atoms located from ΔF maps were included but not refined and were given the isotropic thermal parameters of the atom to which they were attached; all non-H atoms were refined anisotropically. Number of refined parameters 415. $w = \sigma^{-2}(F_o)$, $S = 2{\cdot}91$, $(\Delta/\sigma)_{\max} = 2{\cdot}1$ [U_{11} of C(111)], $(\Delta/\sigma)_{\rm av.} = 0{\cdot}4$, $(\Delta\rho)_{\max} = 0{\cdot}09$, $(\Delta\rho)_{\min} = -0{\cdot}11$ Å^{-3}. Large thermal factors for terminal methyl groups and for C111–C113 can be attributed to slight disorder. Atomic scattering factors as defined by *XRAY76* (Stewart *et al.*, 1976); hydrogen modelling and geometrical considerations by *CSU* (Vicković, 1988). All calculations were carried out using a Univac 1110/42 computer. Final non-H atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.[*] An *ORTEP* (Johnson, 1976) drawing of the molecule with the numbering scheme is shown in Fig. 1. The

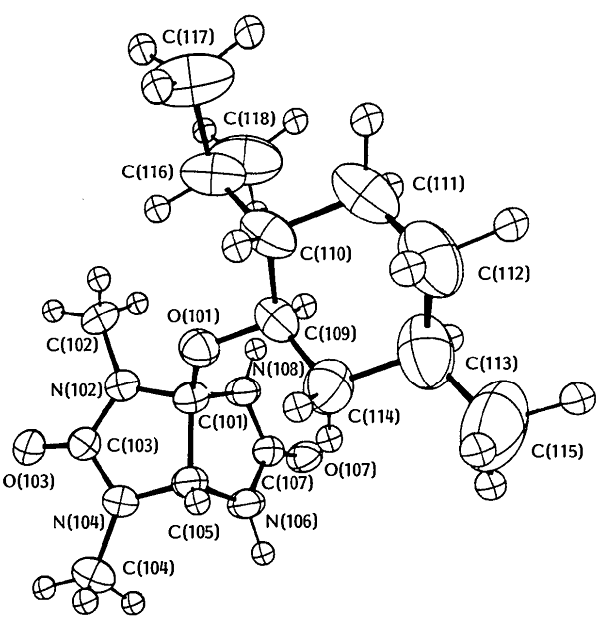

Fig. 1. *ORTEP* view of molecule (1*a*) The orientation of the angular menthyl group with respect to the bicyclic system is described by torsion angles: C(105)—C(101)—O(101)—C(109) = 91·8 (4), N(108)—C(101)—O(101)—C(109) = − 28·3 (5), and C(101)—O(101)—C(109)—C(110) = 163·8 (3)°.

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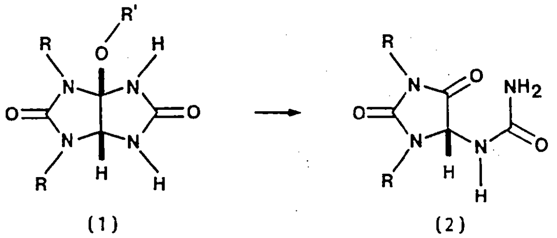
[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances, angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52672 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

absolute (1*R*,5*R*) configuration of the bicylic ether was assigned with reference to the known configuration of the (−)-menthyl moiety.



(1) (2)

(*a*): R = Me, R′ = Menthyl; (*b*): R = R′ = H

Related literature. We recently developed a biogenetically modelled route to (−)-(*R*)-1,3-dimethylallantoin (2*a*) *via* regiospecific cleavage of the intermediate (1*a*) bearing the (−)-menthyl ether unit as a chiral auxiliary (Modrić, Drake & Poje, 1989); the key intermediate (1*a*) is the first example of a derivative of the putative bicyclol tautomer (1*b*) of allantoin (2*b*). An X-ray crystal structure determination of (1*a*) was undertaken in order to establish an absolute configurational standard for correlation with (2*a*) and the related naturally occurring homologue (2*b*). The structure of (±)-allantoin, a prototype of (2), has been reported (Mootz, 1965); the tautomerism (1)$\rightleftarrows$(2) is reminiscent of the formation of cyclol peptides (Cerrini, Fedeli & Mazza, 1971) due to amide–amide interaction.

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Structure of 4-Piperidone Derivatives. II. 2,6-Bis(*p*-methoxyphenyl)-3,5-dimethyl-4-piperidone

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Abstract. $C_{21}H_{25}NO_3$, $M_r = 339{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}031\,(2)$, $b = 11{\cdot}675\,(1)$, $c = 22{\cdot}783\,(2)$ Å, $V = 1870{\cdot}19$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}05$ cm^{-1}, $F(000) = 728$, $T = 295$ K, $R = 0{\cdot}046$, $wR = 0{\cdot}050$ for 1817 unique observed reflections $[I > 3\sigma(I)]$. The 4-piperidone ring has a slightly distorted chair conformation, the mean torsion angle being 57·1°; the puckering is enhanced in the area of N(1) and decreased in the area of C(4). The phenyl rings are planar and all molecular dimensions and van der Waals interactions are normal.

Experimental. Crystals were grown from ethanol at room temperature. Data were collected for a

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† DCB contribution No. 751.

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