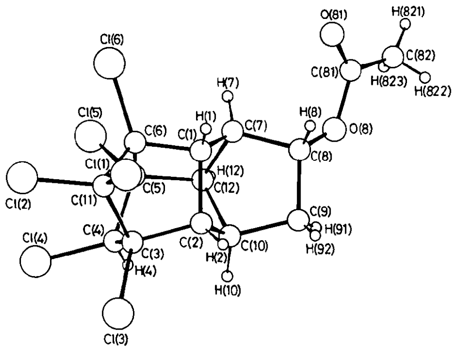

Fig. 1. Molecular configuration and atom-numbering scheme for (V).

away from the molecule. Torsion angles associated with the acetate side chain are −169·3 (7)° for C(9)—C(8)—O(8)—C(81) and +171·1 (9)° for C(8)—O(8)—C(81)—C(82).

The changes in the distance and angular parameters which result from the conversion of the unsaturated hexachloro-8,9,10-trinorbornene nucleus [with C(4)=C(5)] to the saturated bridged cyclopentane ring are largely in the distortion of the molecular cage framework. Although the intra-ring angles at C(11) [92·6 (5)], C(3) [106·2 (6)] and C(6) [105·6 (5)°] are comparable with the mean of those found equivalent in the ring for the cyclodiene series of insecticides (Smith, 1978), the difference in the angles at C(4) [96·5 (5)] and C(5) [105·0 (5)°] reflects the constraints imposed by the bridge between C(5) and C(12). Other distances and angles are similar to those of the parent compound aldrin (DeLacy & Kennard, 1972), its stereoisomer isodrin (Kennard, Smith & Hovmöller, 1979) and other 'cyclodiene' analogues (Smith, 1978).

Packing in the unit cell emphasizes the non-associated nature of the molecules, a common feature among this series of compounds. No intermolecular contacts shorter than 3 Å exist.

The authors wish to thank the Universities of Queensland and Western Australia for the use of facilities and financial support, Mr Stephen Stewart for technical assistance and the Queensland Institute of Technology for the time allowed for one of us (GS) to work on this project.

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(1*S*,5*R*,9*R*)-2-Cyclopropylmethyl-2′-hydroxy-5,9-dimethyl-8-oxo-6,7-benzomorphan Hydrochloride Monohydrate (Ketazocine),* $C_{18}H_{23}NO_2.HCl.H_2O$†

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Abstract. $M_r = 339·86$, orthorhombic, $P2_12_12_1$, $a = 14·367$ (5), $b = 13·673$ (4), $c = 8·941$ (3) Å, $V = 1756$ (1) Å^3, $Z = 4$, $D_m = 1·28$, $D_x = 1·285$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·236 mm^{-1}, $F(000) = 728$, room temperature. The structure was determined by Patterson synthesis and direct methods and refined to $R = 0·049$ for 2347 observed reflections. The cyclopropylmethyl side chain adopts the same conformation as in gemazocine.

Introduction. As part of a structure–activity study on 6,7-benzomorphans, the structure of ketazocine was

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* *Chemical Abstracts* name: 3-cyclopropylmethyl-3,4,5,6-tetrahydro-8-hydroxy-2,6-methano-6,11-dimethyl-3-benzazocin-1(2*H*)-one hydrochloride monohydrate.

† Structural Studies of Substituted 6,7-Benzomorphan Compounds. VII. Part VI: Peeters, De Ranter & Blaton (1982).

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determined. Ketazocine is a putative opiate kappa-agonist and displays the same pharmacological profile as (–)-(1*R*,5*R*,9*R*,13*S*)-*N*-(tetrahydrofurfuryl)normetazocine (Merz & Stockhaus, 1979; Peeters, De Ranter & Blaton, 1982).

Experimental. Crystals obtained at room temperature from an equimolar ethyl acetate–methanol solution; this mixture contained 0·5% water. Density measured by flotation in *n*-heptane/CCl_4, crystal ~0·4 × 0·4 × 0·2 mm, Syntex $P2_1$ computer-controlled diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω-scan technique ($2\theta_{\max} = 60°$, $0 \leq h \leq 20$, $0 \leq k \leq 19$, $0 \leq l \leq 12$), cell dimensions by least-squares refinement of the setting angles of 15 reflections with $6° < 2\theta < 18°$, space group $P2_12_12_1$ from systematic absences *h*00, 0*k*0, 00*l*, for *h, k* and *l* odd respectively; one standard reflection measured periodically showed no discrepancies during data collection (overall e.s.d. 1·4%); 2898 independent reflections measured, 2347 of which considered as observed [$I > 2\sigma(I)$]; Lorentz–polarization corrections but not absorption, scattering factors from Cromer & Mann (1968), and Stewart, Davidson & Simpson (1965) (for H); scattering factor for Cl^- was corrected for anomalous dispersion (*International Tables for X-ray Crystallography,* 1974).

The position of the chloride obtained from a sharpened Patterson synthesis served as input for *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). The resulting *E* map showed all non-hydrogen atoms present in the asymmetric unit. A water molecule was also revealed; its presence was suspected from a comparison between D_m and D_x (before, D_x was 1·23 Mg m^{-3}). Refinement with XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) by block-diagonal least squares on *F*, first with isotropic temperature factors and then anisotropically; full matrix least-squares refinement finally executed; H positions from ΔF synthesis included in refinement with fixed positions and overall temperature factors; $w = (50{\cdot}0 + |F_o| + 0{\cdot}050|F_o|^2)^{-1}$, final $R = 0{\cdot}049$, $R_w = 0{\cdot}062$ and $S = 0{\cdot}29$; $(\Delta/\sigma)_{\text{ave}} = 0{\cdot}03$, $(\Delta/\sigma)_{\max} = 0{\cdot}24$, final $\Delta\rho$ excursions $\leq |0{\cdot}50|$ e Å^{-3} (rejection ratio = 0·3).

Discussion. The atomic-numbering scheme is given in Fig. 1 and parameters are listed in Table 1.* Bond lengths and angles are given in Tables 2 and 3. Compared with previously determined benzomorphan compounds, the structure does not reveal any outstanding features. It should be remarked, however, that the bond lengths in the cyclopropyl ring are significantly shorter (at the 99% significance level) than in gemazocine (Gelders, De Ranter & Schenk, 1979). The torsion angles* reveal that the side chain adopts the same conformation as in gemazocine, but differs from that found in cyclazocine (Karle, Gilardi, Fratini & Karle, 1969). An *ORTEP* (Johnson, 1965) stereoview of the molecule is shown in Fig. 2. The most striking feature is the position of the carbonyl oxygen O(8) which is clearly 7° out of the plane of the aromatic ring. Intramolecular potential-energy calculations using the program *EENY* (Motherwell, 1974) and empirical constants from Giglio (1969) show that the conformation corresponds to a minimum in the energy map (Fig. 3) for varying C(1)—N(2)—C(12)—C(13) and N(2)—C(12)—C(13)—C(14) angles.

The packing of the molecules in the crystal is essentially achieved by hydrogen bonds between the chloride ion and the phenolic O of one molecule and the N atom of the neighbouring molecule. The chloride ion is also bonded to a water molecule. Endless chains are thus formed parallel to **a**. {N(2)···Cl 3·145 (3), H(2)···Cl 2·032 Å, ∠N(2)—H(2)···Cl 157·4°, O(2′)···Cl^i 3·055 (3), H(2′)···Cl^i 2·138 Å, ∠O(2′)—H(2′)···Cl^i 161·2°, O(16)···Cl^{ii} 3·280 (4), H(16*A*)···Cl^{ii} 2·533 Å, ∠O(16)—H(16*A*)···Cl^{ii} 162·9° [symmetry operations: (i) $x + \frac{1}{2}, -y + 1\frac{1}{2}, -z + 1$; (ii) $-x, y - \frac{1}{2}, -z + 1\frac{1}{2}$].} The packing of the molecules is shown in Fig. 4.

The authors thank Sterling-Winthrop, Brussels, for providing the title compound.

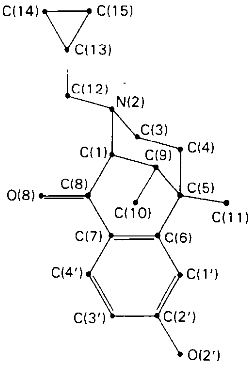

Fig. 1. Atomic-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H, mean-plane data and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38755 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s of the refined parameters in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Cl	−1982	8819	9820	3·33 (1)
C(1′)	342 (2)	7756 (2)	3187 (3)	2·50 (6)
C(2′)	967 (2)	7121 (2)	2474 (4)	2·73 (7)
O(2′)	1473 (1)	7514 (2)	1342 (3)	3·88 (6)
C(3′)	1054 (2)	6161 (2)	2946 (3)	2·78 (7)
C(4′)	498 (2)	5820 (2)	4082 (4)	2·66 (7)
C(1)	−1358 (2)	6752 (2)	6854 (3)	2·36 (6)
N(2)	−848 (1)	7162 (2)	8196 (3)	2·46 (5)
C(3)	−1 (2)	7748 (2)	7735 (3)	2·78 (7)
C(4)	−266 (2)	8525 (2)	6601 (3)	2·72 (7)
C(5)	−819 (2)	8139 (2)	5239 (3)	2·30 (6)
C(6)	−203 (2)	7432 (2)	4375 (3)	2·07 (5)
C(7)	−137 (2)	6442 (2)	4813 (3)	2·26 (6)
C(8)	−728 (2)	6038 (2)	6004 (3)	2·48 (6)
O(8)	−757 (2)	5165 (1)	6308 (3)	3·73 (6)
C(9)	−1684 (2)	7594 (2)	5852 (3)	2·40 (6)
C(10)	−2346 (2)	7204 (2)	4668 (4)	3·25 (8)
C(11)	−1121 (2)	9021 (2)	4299 (4)	3·37 (8)
C(12)	−592 (2)	6397 (2)	9354 (4)	3·20 (8)
C(13)	−1387 (3)	5732 (3)	9787 (4)	3·98 (9)
C(14)	−1452 (3)	5420 (3)	11390 (4)	4·14 (10)
C(15)	−2135 (3)	6128 (4)	10747 (5)	5·00 (12)
O(16)	3492 (2)	4211 (2)	2494 (3)	4·87 (8)

Table 2. *Bond lengths* (Å)

C(1′)–C(2′)	1·403 (4)	C(4)–C(5)	1·546 (4)
C(1′)–C(6)	1·392 (4)	C(5)–C(6)	1·521 (4)
C(2′)–O(2′)	1·356 (4)	C(5)–C(9)	1·549 (4)
C(2′)–C(3′)	1·384 (5)	C(5)–C(11)	1·533 (4)
C(3′)–C(4′)	1·374 (4)	C(6)–C(7)	1·413 (4)
C(4′)–C(7)	1·408 (4)	C(7)–C(8)	1·470 (4)
C(1)–N(2)	1·513 (4)	C(8)–O(8)	1·224 (4)
C(1)–C(8)	1·533 (4)	C(9)–C(10)	1·520 (4)
C(1)–C(9)	1·531 (4)	C(12)–C(13)	1·510 (5)
N(2)–C(3)	1·514 (4)	C(13)–C(14)	1·498 (6)
N(2)–C(12)	1·516 (4)	C(13)–C(15)	1·478 (6)
C(3)–C(4)	1·516 (4)	C(14)–C(15)	1·493 (6)

Table 3. *Bond angles* (°)

C(2′)–C(1′)–C(6)	120·7 (3)	C(9)–C(5)–C(11)	110·2 (2)
C(1′)–C(2′)–O(2′)	115·9 (3)	C(1′)–C(6)–C(5)	120·9 (2)
C(1′)–C(2′)–C(3′)	120·4 (3)	C(1′)–C(6)–C(7)	118·6 (2)
O(2′)–C(2′)–C(3′)	123·7 (3)	C(5)–C(6)–C(7)	120·5 (2)
C(2′)–C(3′)–C(4′)	119·7 (3)	C(4′)–C(7)–C(6)	119·6 (2)
C(3′)–C(4′)–C(7)	121·0 (2)	C(4′)–C(7)–C(8)	119·0 (2)
N(2)–C(1)–C(8)	110·0 (2)	C(6)–C(7)–C(8)	121·5 (2)
N(2)–C(1)–C(9)	109·5 (2)	C(1)–C(8)–C(7)	117·5 (2)
C(8)–C(1)–C(9)	111·7 (2)	C(1)–C(8)–O(8)	119·4 (3)
C(1)–N(2)–C(3)	111·7 (2)	C(7)–C(8)–O(8)	123·1 (3)
C(1)–N(2)–C(12)	113·8 (2)	C(1)–C(9)–C(5)	108·9 (2)
C(3)–N(2)–C(12)	110·9 (2)	C(1)–C(9)–C(10)	109·6 (2)
N(2)–C(3)–C(4)	110·6 (2)	C(5)–C(9)–C(10)	115·1 (2)
C(3)–C(4)–C(5)	114·6 (2)	N(2)–C(12)–C(13)	114·0 (3)
C(4)–C(5)–C(6)	108·5 (2)	C(12)–C(13)–C(14)	117·6 (3)
C(4) C(5)–C(9)	107·3 (2)	C(12)–C(13)–C(15)	118·6 (3)
C(4)–C(5)–C(11)	108·0 (2)	C(14)–C(13)–C(15)	60·2 (3)
C(6)–C(5)–C(9)	109·9 (2)	C(13)–C(14)–C(15)	59·2 (3)
C(6)–C(5)–C(11)	112·7 (2)	C(13)–C(15)–C(14)	60·5 (3)

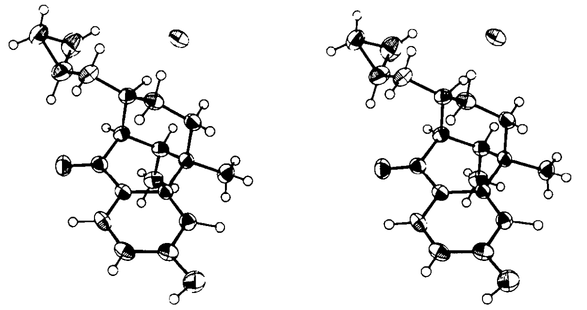

Fig. 2. Stereoscopic view of ketazocine.HCl with 50% probability thermal ellipsoids for the non-hydrogen atoms.

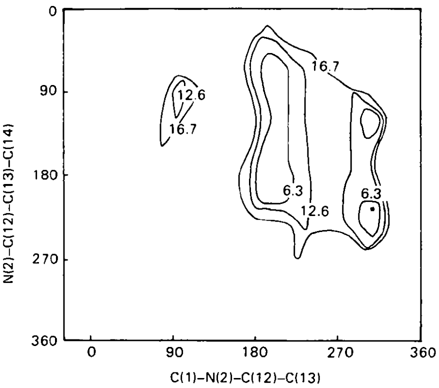

Fig. 3. Map of the intramolecular potential-energy calculations; the contours are in kJ mol^{-1}. The asterisk indicates the conformation adopted in the crystal.

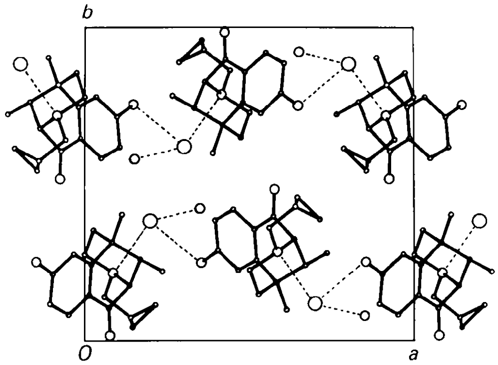

Fig. 4. A view of the crystal structure along **c** showing the packing. Hydrogen bonds are indicated by dashed lines.

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Structure of 5′-*O*-Acetyl-2′,3′-*O*-isopropylideneuridine, $C_{14}H_{18}N_2O_7$

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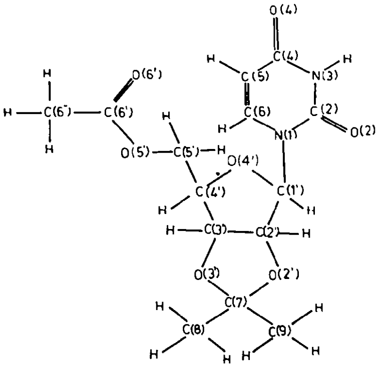
Abstract. $M_r = 326\cdot3$, monoclinic, $P2_1$, $a = 6\cdot510\,(2)$, $b = 8\cdot432\,(2)$, $c = 15\cdot114\,(2)$ Å, $\beta = 101\cdot42\,(3)°$, $Z = 2$, $V = 813\cdot15$ Å^3, $D_x = 1\cdot33$ Mg m^{-3}, $F(000) = 172$, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 0\cdot906$ mm^{-1}, final $R = 6\cdot4\%$ for 1924 observed counter reflections. The conformation about the glycosidic bond is *syn* [torsion angle C(6)—N(1)—C(1′)—O(4′) = −103·9 (3)°]. The sugar pucker is C(2′)-*exo*,C(3′)-*endo* ($^3T_2$). The conformation about the C(4′)—C(5′) bond is *gauche–trans*. An uncommon intermolecular hydrogen bond involving the ribose-ring oxygen O(1′) and the base-nitrogen N(3) stabilizes the crystal structure.

Introduction. We report here the crystal structure of the title compound (I). The investigation was undertaken as part of our studies of isopropylidene derivatives of nucleosides (Katti, Seshadri & Viswamitra, 1981; Gautham, Ramakrishnan, Seshadri, Viswamitra, Salisbury & Brown, 1982; Gautham, Seshadri & Viswamitra, 1983; Gautham, Seshadri, Viswamitra & Salisbury, 1983).



(I)

Experimental. Large crystals by evaporation of an acetone solution of the compound (Sigma Chemical Co.); D_m not determined; crystals characterized by rotation and Weissenberg photographs; unit-cell parameters refined from 2θ values of 25 high-angle reflections measured on an Enraf–Nonius CAD-4 diffractometer; ω–2θ scans, $\theta \leq 60°$; 2000 unique reflections, 1924 [$|F_o| \geq 3\sigma(|F_o|)$] considered observed after Lorentz and polarization corrections; no absorption correction; index range h 0 to 8, k 0 to 10, l −18 to 18; structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980); full-matrix least-squares refinement with anisotropic temperature factors using *SHELX* (Sheldrick, 1976) brought R to 10·32%. High temperature factors observed for atoms of the acetyl group [C(6′), C(6″) and O(6′)]. Successive difference Fourier maps at this stage revealed all the H atoms except those attached to C(5), C(4′), C(8) and one of the C(9) methyl group; these were fixed from geometrical considerations. Further block-diagonal least-squares refinement (Shiono, 1968) of the non-hydrogen atoms alone brought R to 6·4% ($R_w = 8\cdot1\%$); $w(|F_o| - |F_c|)^2$ minimized where $w = 1/(a|F_o|^2 + b|F_o| + c)$ with $a = 0\cdot282$, $b = 1\cdot0$ and $c = 0\cdot032$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961); maximum shift/error ratio = 0·21; residual electron density in final difference map

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