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Structure of 8β-Bromo-6,7-didehydro-4,5α-epoxy-3-methoxy-17-methylmorphinan, $C_{18}H_{20}BrNO_2$

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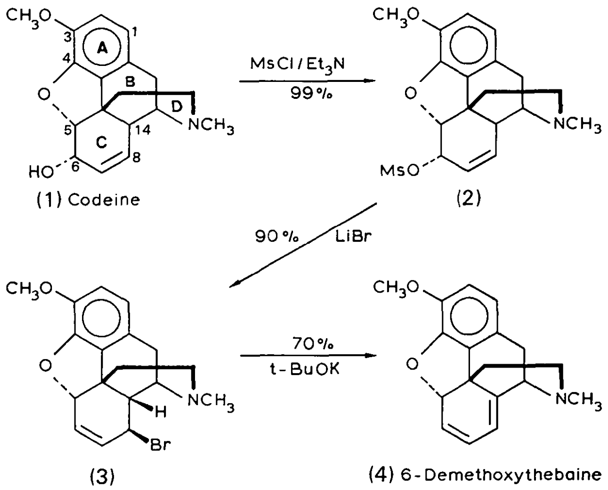
(*Received* 17 *August* 1983; *accepted* 31 *October* 1983)

Abstract. $M_r = 362{\cdot}27$, monoclinic, $C2$, $a = 15{\cdot}284\,(4)$, $b = 7{\cdot}999\,(3)$, $c = 15{\cdot}493\,(4)$ Å, $\beta = 124{\cdot}53\,(2)°$, $V = 1560{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}55$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}80$ mm^{-1}, $F(000) = 744$, $T = 298$ K. Final $R = 0{\cdot}062$ for 1076 observed data. The Br atom is in the 8β-position of the morphinan skeleton.

Introduction. Conversions of the opium alkaloid (—)-codeine (1) have been investigated to prepare (—)-6-demethoxythebaine (4) (Beyerman, Crabbendam, Lie & Maat, 1984). The latter compound plays an important role in the synthesis of etorphine-like Diels–Alder adducts of morphinan-6,8-dienes with a relatively small number of oxygen-containing substituents. So far, the only simple preparation of (4) starts from the difficultly accessible (—)-neopine, a minor alkaloid from opium (Crabbendam, Maat & Beyerman, 1981).

(—)-Codeine was converted quantitatively into 6-*O*-mesylcodeine (2) with mesyl chloride (methanesulfonyl chloride) in the presence of triethylamine. Treatment of the mesyl ester with lithium bromide in toluene and some dimethylformamide produced allylic rearrangement, affording in 90% yield (+)-8β-bromo-6,7-didehydro-4,5α-epoxy-3-methoxy-17-methylmorphinan (3). This compound can be converted easily into (4).

The assignment of the structure (3), especially regarding the position of the Br atom, remained doubtful from NMR data. Therefore, a single-crystal X-ray analysis was started, which confirmed structure (3) for the compound obtained from (—)-codeine.



Experimental. Title compound prepared in the Laboratory of Organic Chemistry starting from natural (—)-codeine and purified by crystallization from ethanol/diethyl ether; colorless crystals grown from acetone, m.p. 432–434 K, $[\alpha]_D^{25\cdot0\,°C} = +47{\cdot}6°$ [chloroform/ethanol 9:1, 1·4 g dm^{-3}], irregular shape, max. edge ~0·5 mm. Systematic absences hkl for $(h + k)$ odd indicated space group Cm or $C2$, latter chosen on basis of distribution of peaks in Patterson function. Cell parameters obtained from diffractometer angular settings of 25 centered reflections ($9 < \theta < 18°$). 1484 independent $hk\pm l$ with $2 < \theta \leq 25°$ ($h_{\max}$ 18, $k_{\max}$ 9, $l \pm 18$); CAD-4 diffractometer

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(graphite-monochromated Mo $K\alpha$ radiation), ω–2θ scan, width = 1·20° + 0·5° tan θ, max. recording time 120 s, $\sigma_{\text{count}}(I)/I < 0{\cdot}02$ requested in a scan; three standard reflections, no significant variations; 1090 reflections with $I > \sigma(I)$. No correction for absorption. Direct methods failed, heavy-atom positions determined from Patterson map, resulting double solution unraveled in several steps by successive Fourier difference maps and least-squares refinement on F of positional and anisotropic temperature factors; no H atoms located. Apparently 14 reflections improperly measured or strongly attenuated by absorption or extinction. Final $R = 0{\cdot}062$ for 1076 observed reflections, equal weights for all reflections, $S = 1{\cdot}44$ (final R for inverted structure = 0·067). $(\Delta/\sigma)_{\max} = 0{\cdot}09$. Final difference map showed two peaks, 0·98 and 0·64 e Å^{-3}, in neighborhood of Br atom. All calculations performed with XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

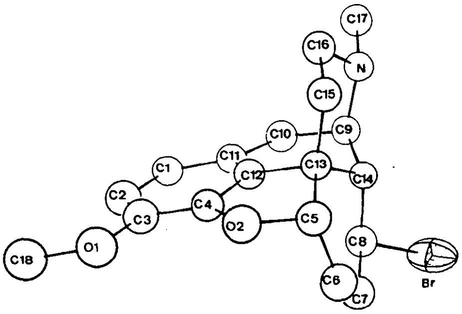

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Br	0·0662 (1)	0	0·2238 (1)	0·083 (2)
C(1)	−0·1574 (12)	0·245 (2)	0·4213 (11)	0·050 (16)
C(2)	−0·1447 (11)	0·410 (2)	0·4572 (11)	0·047 (14)
C(3)	−0·1409 (9)	0·540 (2)	0·4001 (9)	0·049 (16)
C(4)	−0·1465 (8)	0·503 (3)	0·3107 (8)	0·044 (12)
C(5)	−0·1188 (9)	0·501 (3)	0·1800 (8)	0·050 (12)
C(6)	−0·0019 (10)	0·488 (3)	0·2294 (9)	0·054 (15)
C(7)	0·0495 (11)	0·346 (2)	0·2639 (9)	0·055 (16)
C(8)	−0·0024 (9)	0·176 (2)	0·2546 (10)	0·048 (14)
C(9)	−0·1776 (8)	0·033 (2)	0·1822 (9)	0·040 (13)
C(10)	−0·1727 (9)	0·033 (2)	0·2853 (9)	0·049 (14)
C(11)	−0·1680 (9)	0·206 (2)	0·3264 (9)	0·041 (13)
C(12)	−0·1661 (9)	0·340 (2)	0·2732 (9)	0·037 (13)
C(13)	−0·1739 (9)	0·337 (2)	0·1707 (9)	0·039 (13)
C(14)	−0·1217 (8)	0·176 (2)	0·1683 (9)	0·036 (12)
C(15)	−0·2920 (9)	0·338 (2)	0·0772 (9)	0·039 (13)
C(16)	−0·3476 (10)	0·183 (2)	0·0763 (11)	0·044 (15)
C(17)	−0·3502 (14)	−0·119 (2)	0·0728 (13)	0·058 (18)
C(18)	−0·1203 (14)	0·742 (2)	0·5250 (12)	0·080 (20)
N	−0·2892 (7)	0·031 (2)	0·0849 (7)	0·042 (11)
O(1)	−0·1304 (9)	0·704 (2)	0·4280 (8)	0·059 (12)
O(2)	−0·1351 (8)	0·610 (1)	0·2483 (7)	0·055 (10)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·40 (2)	C(8)–C(14)	1·53 (2)
C(1)–C(11)	1·42 (2)	C(9)–C(10)	1·56 (2)
C(2)–C(3)	1·39 (2)	C(9)–C(14)	1·52 (2)
C(3)–C(4)	1·37 (2)	C(9)–N	1·51 (1)
C(3)–O(1)	1·36 (2)	C(10)–C(11)	1·51 (2)
C(4)–O(2)	1·38 (2)	C(11)–C(12)	1·36 (2)
C(4)–C(12)	1·39 (3)	C(12)–C(13)	1·52 (2)
C(5)–C(6)	1·50 (2)	C(13)–C(14)	1·53 (2)
C(5)–O(2)	1·50 (2)	C(13)–C(15)	1·55 (1)
C(5)–C(13)	1·52 (2)	C(15)–C(16)	1·50 (2)
C(6)–C(7)	1·31 (3)	C(16)–N	1·47 (2)
C(7)–C(8)	1·54 (2)	N–C(17)	1·46 (2)
C(8)–Br	1·97 (2)	O(1)–C(18)	1·45 (3)
C(2)–C(1)–C(11)	121 (2)	C(1)–C(11)–C(12)	115 (1)
C(1)–C(2)–C(3)	120 (2)	C(10)–C(11)–C(12)	119 (1)
C(2)–C(3)–C(4)	119 (1)	C(4)–C(12)–C(11)	124 (1)
C(2)–C(3)–O(1)	124 (1)	C(4)–C(12)–C(13)	109 (1)
C(4)–C(3)–O(1)	117 (2)	C(11)–C(12)–C(13)	127 (1)
C(3)–C(4)–C(12)	120 (2)	C(5)–C(13)–C(12)	100 (1)
C(3)–C(4)–O(2)	128 (2)	C(5)–C(13)–C(14)	117 (1)
C(12)–C(4)–O(2)	112 (1)	C(5)–C(13)–C(15)	112 (1)
C(6)–C(5)–C(13)	115 (2)	C(12)–C(13)–C(14)	108 (1)
C(6)–C(5)–O(2)	108 (1)	C(12)–C(13)–C(15)	110 (1)
C(13)–C(5)–O(2)	105 (1)	C(14)–C(13)–C(15)	109 (1)
C(5)–C(6)–C(7)	122 (1)	C(8)–C(14)–C(9)	111 (1)
C(6)–C(7)–C(8)	125 (1)	C(8)–C(14)–C(13)	111 (1)
C(7)–C(8)–C(14)	112 (1)	C(9)–C(14)–C(13)	107 (1)
C(7)–C(8)–Br	110 (1)	C(13)–C(15)–C(16)	111 (1)
C(14)–C(8)–Br	109 (1)	C(15)–C(16)–N	112 (1)
C(10)–C(9)–C(14)	116 (1)	C(9)–N–C(16)	111 (1)
C(10)–C(9)–N	113 (1)	C(9)–N–C(17)	115 (1)
C(14)–C(9)–N	106 (1)	C(16)–N–C(17)	111 (1)
C(9)–C(10)–C(11)	113 (1)	C(3)–O(1)–C(18)	117 (1)
C(1)–C(11)–C(10)	126 (1)	C(4)–O(2)–C(5)	106 (1)

Discussion. The molecular structure is shown in Fig. 1 together with the atom numbering. The final atomic parameters are given in Table 1.* Bond lengths and angles are listed in Table 2.

The Br atom is in the 8β-position of the *C* ring of the morphinan skeleton, which means in the *cis*-position with respect to the proton at C(14). During the allylic rearrangement the 6α-mesyl group splits off and the bromo substituent arrives exclusively at the 8β-position. The product obtained, indeed, proved to be a good starting material for (−)-6-demethoxythebaine.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38956 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.