angle P—N(3)—C(1)′′—C(6)′′ [−97·7 (8)°] indicates that the phenyl substituent on N(3) rotates by about 90° (angle between oxaza ring and phenyl ring is 83·3°). Since the conformation of the oxaza ring is forced to be a half chair, the above rotation occurs so as to avoid interactions with the axial oxygen. The angle between the oxaza ring and the phenyl substituent on the C atom is 3·3° which shows the extent of π delocalization in the molecule due to to the presence of the double bond in the oxaza ring. The angle between the two phenyl rings is 80·5°. The packing of the molecules in the unit cell essentially involves van der Waals contacts.

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Structure of (—)-7α-Acetyl-4,5α-epoxy-3-methoxy-*N*-methyl-6,14-ethenoisomorphinan, $C_{22}H_{25}NO_3$

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Abstract. $M_r = 351{\cdot}45$, trigonal, $P3_2$, $a = 10{\cdot}899$ (2), $c = 13{\cdot}422$ (5) Å, $V = 1380{\cdot}4$ Å^3, $Z = 3$, $D_x = 1{\cdot}27$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}091$ mm^{-1}, $F(000) = 564$, $T = 293$ K, final $R = 0{\cdot}039$ for 2022 unique observed reflections. The acetyl substituent is in the 7α position of the 6,14-ethenomorphinan skeleton. This means that the Diels–Alder reaction of methyl vinyl ketone with (—)-6-demethoxythebaine affords one isomer. There are no unusual bond lengths or angles.

Introduction. The title compound (2) was prepared by Diels–Alder reaction of (—)-6-demethoxythebaine (1) with methyl vinyl ketone (Hutchins, Cooper, Pürro &

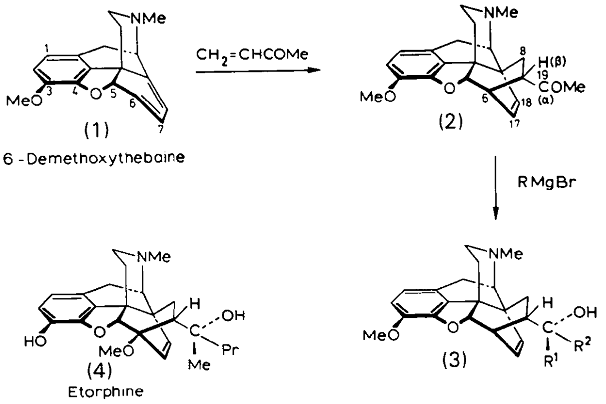

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
C(1)	0·4305 (3)	0·4278 (3)	0·2887 (3)	0·054 (3)
C(2)	0·3869 (3)	0·4471 (3)	0·3817 (2)	0·052 (3)
C(3)	0·2459 (3)	0·4062 (3)	0·4012 (2)	0·049 (3)
C(4)	0·1498 (3)	0·3354 (3)	0·3246 (2)	0·042 (2)
C(5)	−0·0387 (3)	0·2617 (3)	0·2194 (2)	0·042 (3)
C(6)	−0·0549 (3)	0·3736 (3)	0·1610 (2)	0·049 (3)
C(7)	−0·1143 (3)	0·3000 (3)	0·0573 (2)	0·042 (2)
C(8)	0·0001 (3)	0·2857 (3)	−0·0003 (2)	0·044 (2)
C(9)	0·2451 (3)	0·3019 (4)	0·0293 (2)	0·053 (3)
C(10)	0·3715 (3)	0·3535 (4)	0·1050 (3)	0·058 (3)
C(11)	0·3332 (3)	0·3555 (3)	0·2133 (2)	0·045 (3)
C(12)	0·1933 (3)	0·3027 (3)	0·2380 (2)	0·038 (2)
C(13)	0·0727 (3)	0·2369 (3)	0·1660 (2)	0·037 (2)
C(14)	0·1274 (3)	0·3275 (3)	0·0700 (2)	0·037 (2)
C(15)	0·0196 (4)	0·0804 (3)	0·1445 (3)	0·051 (3)
C(16)	0·1270 (4)	0·0593 (4)	0·0867 (3)	0·074 (4)
C(17)	0·0860 (3)	0·5020 (3)	0·1440 (2)	0·051 (3)
C(18)	0·1796 (3)	0·4791 (3)	0·0979 (2)	0·041 (2)
C(19)	−0·1757 (3)	0·3763 (3)	−0·0004 (2)	0·050 (3)
C(20)	−0·2931 (5)	0·3868 (6)	0·0485 (3)	0·085 (5)
C(21)	0·2779 (6)	0·1316 (6)	−0·0639 (5)	0·113 (8)
C(22)	0·2899 (5)	0·4981 (6)	0·5660 (3)	0·090 (6)
O(1)	0·0122 (2)	0·3072 (3)	0·3220*	0·054 (2)
O(2)	0·1931 (3)	0·4320 (3)	0·4861 (2)	0·069 (3)
O(3)	−0·1397 (3)	0·4203 (3)	−0·0833 (2)	0·086 (3)
N	0·1796 (3)	0·1526 (3)	0·0008 (2)	0·068 (3)

* Parameter was kept fixed during refinement.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *concerning the non-hydrogen atoms*

C(1)–C(2)	1·388 (5)	C(9)–C(14)	1·543 (5)
C(1)–C(11)	1·391 (4)	C(9)–N	1·463 (5)
C(2)–C(3)	1·394 (5)	C(10)–C(11)	1·515 (5)
C(3)–C(4)	1·393 (4)	C(11)–C(12)	1·375 (4)
C(3)–O(2)	1·369 (4)	C(12)–C(13)	1·495 (4)
C(4)–O(1)	1·372 (4)	C(13)–C(14)	1·550 (4)
C(4)–C(12)	1·368 (4)	C(13)–C(15)	1·530 (5)
C(5)–O(1)	1·475 (3)	C(14)–C(18)	1·501 (4)
C(5)–C(6)	1·532 (6)	C(15)–C(16)	1·514 (7)
C(5)–C(13)	1·546 (5)	C(16)–N	1·453 (5)
C(6)–C(7)	1·576 (4)	C(17)–C(18)	1·320 (5)
C(6)–C(17)	1·490 (4)	C(19)–O(3)	1·198 (4)
C(7)–C(8)	1·539 (5)	C(19)–C(20)	1·492 (7)
C(7)–C(19)	1·515 (5)	C(21)–N	1·483 (8)
C(8)–C(14)	1·547 (4)	C(22)–O(2)	1·421 (5)
C(9)–C(10)	1·572 (5)		

C(2)–C(1)–C(11)	121·2 (3)	C(11)–C(12)–C(13)	124·8 (3)
C(1)–C(2)–C(3)	121·8 (3)	C(5)–C(13)–C(12)	101·3 (2)
C(2)–C(3)–C(4)	116·2 (3)	C(5)–C(13)–C(14)	111·1 (3)
C(2)–C(3)–O(2)	126·9 (3)	C(5)–C(13)–C(15)	113·0 (2)
C(4)–C(3)–O(2)	116·8 (3)	C(12)–C(13)–C(14)	105·4 (2)
C(3)–C(4)–C(12)	120·5 (3)	C(12)–C(13)–C(15)	114·1 (3)
C(3)–C(4)–O(1)	125·3 (3)	C(14)–C(13)–C(15)	111·3 (2)
C(12)–C(4)–O(1)	113·7 (2)	C(8)–C(14)–C(9)	115·8 (2)
C(6)–C(5)–O(1)	112·6 (3)	C(8)–C(14)–C(13)	108·4 (2)
C(13)–C(5)–O(1)	107·2 (2)	C(8)–C(14)–C(18)	105·5 (3)
C(5)–C(6)–C(7)	103·2 (3)	C(9)–C(14)–C(13)	105·6 (3)
C(5)–C(6)–C(17)	110·6 (3)	C(9)–C(14)–C(18)	113·3 (2)
C(7)–C(6)–C(17)	108·1 (2)	C(13)–C(14)–C(18)	107·9 (2)
C(6)–C(7)–C(8)	110·4 (2)	C(13)–C(15)–C(16)	112·1 (2)
C(6)–C(7)–C(19)	110·7 (3)	C(15)–C(16)–N	111·4 (4)
C(8)–C(7)–C(19)	113·7 (2)	C(6)–C(17)–C(18)	115·1 (3)
C(7)–C(8)–C(14)	108·5 (2)	C(14)–C(18)–C(17)	115·0 (2)
C(10)–C(9)–N	114·8 (4)	C(7)–C(19)–C(20)	116·6 (3)
C(10)–C(9)–C(14)	111·4 (3)	C(7)–C(19)–O(3)	123·2 (4)
C(14)–C(9)–N	107·8 (2)	C(20)–C(19)–O(3)	120·0 (3)
C(9)–C(10)–C(11)	115·3 (3)	C(4)–O(1)–C(5)	106·5 (2)
C(1)–C(11)–C(10)	124·7 (2)	C(3)–O(2)–C(22)	116·8 (3)
C(1)–C(11)–C(12)	115·6 (3)	C(9)–N–C(16)	111·9 (3)
C(10)–C(11)–C(12)	118·8 (2)	C(9)–N–C(21)	109·7 (3)
C(4)–C(12)–C(11)	123·6 (2)	C(16)–N–C(21)	114·8 (4)
C(4)–C(12)–C(13)	109·7 (3)		

Rapoport, 1981). Conversion of (2) with Grignard compounds affords analogs (3) (Crabbendam, Lie, Linders & Maat, 1984) of etorphine (4), an analgesic with an activity over 1000 times greater than morphine. The new compounds are of interest in the study of structure–activity relationships (SAR) of analgesics.

In principle, the Diels–Alder addition yields four isomers, namely with the acetyl substituent in the 7α, 7β, 8α or 8β position. The position of the acetyl substituent could not be determined unambiguously from ^{1}H NMR data. Therefore, a single-crystal X-ray analysis was started, which confirmed structure (2) for the compound obtained from (−)-6-demethoxythebaine (1). This result also enabled us to assign all the ^{1}H NMR signals of compound (2) and the new compounds derived from it.

Experimental. Title compound prepared in the Laboratory of Organic Chemistry starting from (−)-6-demethoxythebaine and methyl vinyl ketone. Crystals grown from ethyl acetate, m.p. 434–435 K, $[\alpha]_D^{25\cdot0\,^\circ\mathrm{C}} = -174^\circ$ (chloroform/ethanol 9:1, 1·0 g dm^{-3}). D_m not measured. Irregular-shaped crystal (approximate size 0·50 × 0·30 × 0·25 mm). Enraf–Nonius CAD-4F diffractometer. Cell parameters from setting angles of 25 reflections with $9^\circ < \theta < 14^\circ$. 2688 independent reflections measured, 2027 with $I > 2{\cdot}5\sigma(I)$. $\theta_{\max} = 30^\circ$, $\omega/2\theta$ scan mode, graphite-monochromated Mo $K\alpha$ radiation, h: 0–13, k: 0–12, l: −18–18. Three reference reflections measured every hour showed no decay (variation <3%). No corrections for absorption or extinction. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined on F by full-matrix least squares; H atoms from difference map; refinement in $P3_2$ demands the same absolute configuration for the morphinan skeleton as in a previous analysis (van Koningsveld, Lie & Maat, 1984); 5 reflections with high F_c/F_o ratios, possibly due to extinction, removed. Refined parameters included positional parameters of all atoms and anisotropic temperature factors for non-hydrogen atoms; H atoms refined with fixed isotropic temperature factor; $wR = 0{\cdot}0385$ for 2022 observed reflections, $w = 1$, $(\Delta/\sigma)_{\max} = 0{\cdot}97$ (0·37 for non-H atoms), $S = 0{\cdot}55$.*

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39277 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

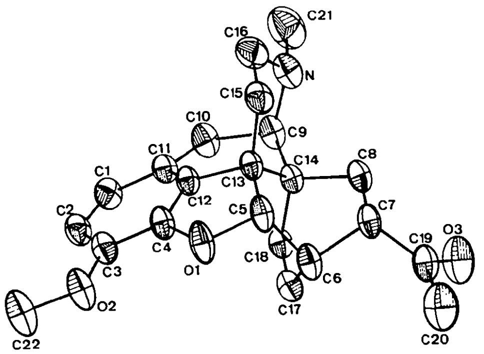

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

Residual density in final difference Fourier map $<0\cdot16$ e Å^{-3}. All calculations performed with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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 bond angles are listed in Table 2.

The acetyl substituent is in the 7α position of the 6,14-ethenoisomorphinan skeleton (2). This means that the Diels–Alder reaction of methyl vinyl ketone with (–)-6-demethoxythebaine (1) affords one isomer. Consequently, the reaction products of the title compound with different Grignard compounds will possess structure (3) with the alkyl methyl carbinol substituent also in the 7α position.

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Structure of 2-Methoxy-6-pentyl-1,4-benzoquinone (Primin), $C_{12}H_{16}O_3$

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Abstract. $M_r = 208\cdot26$, triclinic, $P\bar{1}$, $a = 4\cdot123$ (1), $b = 9\cdot759$ (4), $c = 14\cdot256$ (2) Å, $\alpha = 87\cdot07$ (2), $\beta = 87\cdot38$ (2), $\gamma = 79\cdot15$ (3)°, $V = 562\cdot2$ (5) Å^3, $Z = 2$, $D_x = 1\cdot230$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 0\cdot722$ mm^{-1}, $F(000) = 224$, $T = 296$ K, R is 0·058 for 1518 unique reflections. The structure was solved after several trials by shifting the atomic positions of a correct model along the pentyl chain direction. The angle between the quinonoid ring plane and the pentyl chain plane is 13·4 (4)°. The average dimensions of the C_{sp^3}–C_{sp^3} distances and corresponding angles of the aliphatic chain are 1·523 (5) Å and 112·8 (3)°, those for the quinone ring are C–C 1·477 (4), C=C 1·338 (5), C=O 1·225 (4) Å, C–C–C 118·6 (3), C=C–C 121·1 (3), O=C–C 120·7 (3)°, the shortest intermolecular C···O distance being 3·33 (1) Å.

Introduction. In the course of our investigations on the relationship between chemical structure and allergenic potency of naturally occurring sensitizing 1,4-benzoquinones (Hausen & Schulz, 1977), X-ray structure analysis has been performed for primin (I), (*R*)-3,4-dimethoxydalbergione (II), (*R*,*S*)-4-methoxydalbergione (IV) and (*S*)-4,4′-dimethoxydalbergione (VII) (Schmalle, Jarchow, Hausen & Schulz, 1984), acamelin (V) (Schmalle & Hausen, 1980) and 2,6-dimethoxy-1,4-benzoquinone (VI) (Schmalle, Jarchow & Hausen, 1977). Elucidation of the structures of

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