Steric Factors in the Azidolysis–Thermolysis of Some 5-Tosyloxymethylbicyclo[2.2.2]oct-2-enes to yield 4-Azatetracyclo[4.4.0.0^{2,4}.0^{3,8}]decanes

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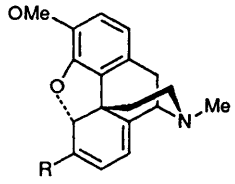
Azidolysis of C-19 diastereoisomer tosylesters of morphine derivatives possessing a bridged ring C has been studied and 4-azatetracyclo[4.4.0^{2,4}.0^{3,8}]decanes **6b**, **6d** and **6f** were formed *via* the substitution and subsequent intramolecular cyclization of the (*R*)-C-19 tosylesters **4b**, **4d** and **4f**, and primarily the ethylidene derivatives **7a**, **7b** and **7c** were obtained from (*S*)-C-19 tosylesters **4c**, **4e** and **4g**. According to our experience the course of the reaction depends on the configuration of the C-19 centre of chirality and on the spatial requirement of the substitutent on C-6

In our previous paper[1] the synthesis of a new substituted 4-azatetracyclo[4.4.0^{2,4}.0^{3,8}]decane ring system **6a** *via* an intramolecular cycloaddition was reported. Azide **5a** was obtained by the azidolysis of the 7α-tosyloxymethyltetrahydro-6,14-*endo*-ethenothebaine **4a**;[2] thermal cyclization of azide **5a** in turn afforded compound **6a**, probably through a triazoline intermediate. In this paper the dependence of the azidolysis and ring-closure reaction of diastereoisomeric secondary tosylesters **4b**–**4g** on the configuration of the C-19 centre of chirality ($R^1 \neq R^2$) and on the character of substituent at C-6 (R^3 = OMe, Cl and H) are described. (*R*)-C-19 tosate **4b**[3] and (*S*)-C-19 tosate **4c**[4] were prepared from thebaine by known procedures. Reaction product **2c**[5] of 6-demethoxythebaine **1c**[6] and methyl vinyl ketone was reduced by sodium borohydride to yield a 1:1 mixture of secondary alcohols **3e** and **3f**,[7] which were separated after tosylation to afford compounds **4f** and **4g**. Tosates **4d** and **4e** were similarly obtained from 6-chloro-6-demethoxythebaine **1b**.[8] The configuration at C-19 of the diastereoisomeric tosylesters has been determined by using the differences in their ^{1}H NMR spectra,[9] *viz.* the dd signal of the C-8 α-proton appears at lower field in the *S*- than in the *R*-diastereoisomer. Azidolysis of the (*R*)-C-19 tosates **4b**, **4d** and **4f** was carried out in *N*,*N*-dimethylformamide (DMF) at 100 °C for 24 h and azatetracyclodecane derivatives **6b**, **6d** and **6f** were obtained, respectively. The (*S*)-C-19 azides **5b**, **5d** and **5f**, formed by inversion in the first step, were detected by TLC but only compound **5d** was isolated. This compound is unstable and spontaneously converts into the ring-closed product **6d**. Azidolysis of the (*S*)-C-19 tosates **4c**, **4e** and **4g** has been carried out under similar reaction conditions. All compounds gave the respective



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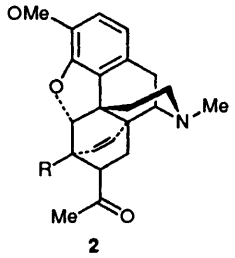

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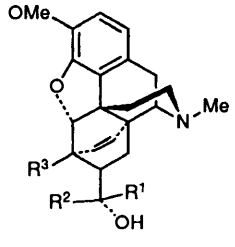
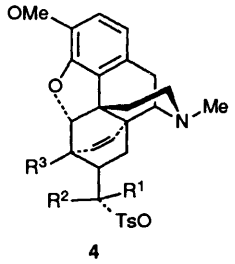
1 and **2** **a**; R = OMe
b; R = Cl
c; R = H



	R^1	R^2	R^3
3a;	H	Me	OMe
b;	Me	H	OMe
c;	H	Me	Cl
d;	Me	H	Cl
e;	H	Me	H
f;	Me	H	H



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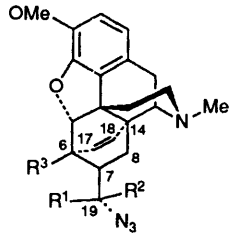

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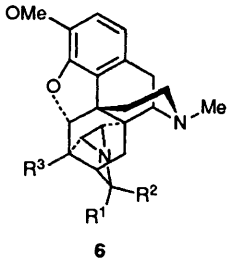

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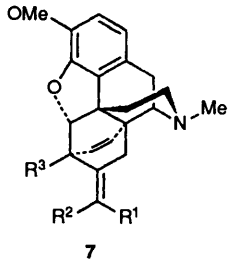

7

	R^1	R^2	R^3
a;	H	H	OMe
b;	H	Me	OMe
c;	Me	H	OMe
d;	H	Me	Cl
e;	Me	H	Cl
f;	H	Me	H
g;	Me	H	H

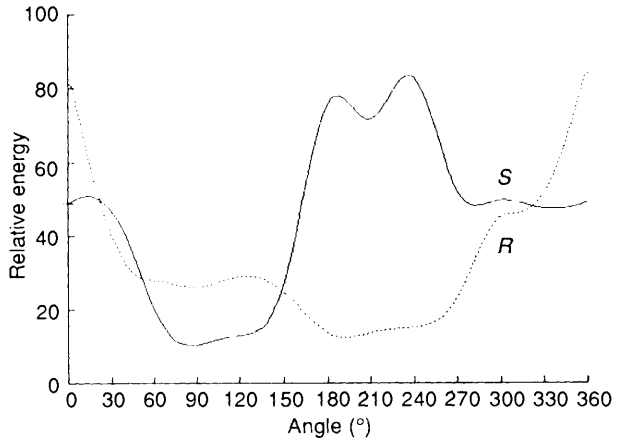

Fig. 1 Conformational energy changes in tosates **4d** and **4e** by rotation of C-19 about C-7–C-19. On the *x*-axis is shown the dihedral angle between 19-H and 7-H.

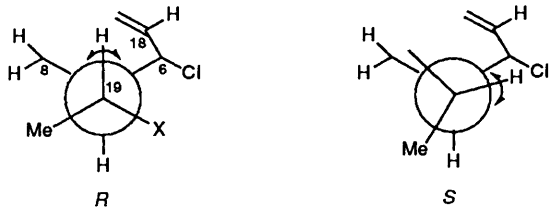

Fig. 2 Energetically preferred conformations of tosates **4d** and **4e** (X = OTs), viewed along the C-19–C-7 axis

ethylidene derivatives **7b**, **7d**, or **7f**, as a major product *via* elimination. This is in accord with the results of detosylation of the 6-methoxy tosate **4c** with potassium t-butoxide.[4] In the azidolysis of the diastereoisomeric tosylesters **4** the different behaviour of the *R* and *S* isomers can be explained by simple molecular mechanics calculations. The structure of 6-chloro-tosates **4d** and **4e** has been minimized by the MMP2 method; C-19 was rotated about the C-19–C-7 axis and energy changes originating from strains and Van der Waals interactions during the rotation were calculated. Results are shown in Fig. 1. On this basis the energetically most favourable arrangement of the (*R*)-C-19 isomer **4d** is that where the dihedral angle of 19-H–C-19–C-7–7-H is 180–200°. In this case the relative arrangement of 7-H and the tosyloxy group is unfavourable towards elimination (Fig. 2) but the (*S*)-C-19 azide **5d** formed by inversion in an S_N reaction, can easily be converted into an aziridine derivative **6d**. On the other hand, for the (*S*)-C-19 isomer **4e** in the most favourable arrangement (19-H–C-19–C-7–7-H angle is 60–90°) the tosyloxy group and the C-7 hydrogen are nearly antiperiplanar, which is favourable for elimination. Parallel with the elimination a ring-closure reaction was observed as well. In the azidolysis of the 6-methoxytosate **4c** the ratio of the ethylidene derivative **7b** to the cyclic product **6c** was 10:0.5, while in the case of the 6-chloro tosate **4e** the formation of the cyclic product could be detected only by TLC. Azidolysis of tosate **4g** afforded a **7f**:**6g** 2:1 mixture, indicating that there is no steric hindrance if R^3 = H. In the case of all isolated cyclic products, complete ^{1}H and ^{13}C NMR assignments were performed by means of COSY, HETCOR, LR-INEPT, NOESY, and homonuclear NOE methods. In the Table the most characteristic ^{1}H and ^{13}C shifts are summarized. It can be seen that the 8α- and 8β-H shifts, and the C-8, C-19, and 19-Me ^{13}C-values respectively, are significant for assignment of the C-19 configuration.

Since these ring systems are highly strained and rigid, the proton–proton distances can easily be calculated by means of molecular geometric programs and by energy minimization.[10]

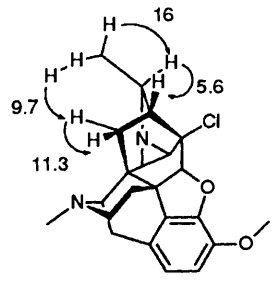

Fig. 3 MMP2-minimized structure of compound **6d**, together with some important ^{1}H-{^{1}H} NOE data

Table Characteristic ^{1}H and ^{13}C NMR chemical shifts, coupling constants (Hz) in parentheses

	Compound				
	6b	**6c**	**6d**	**6f**	**6g**
8-H	1.59d (12.5)	1.25d	1.61d (12.5)	1.54d (12.5)	1.12d (12.5)
8-H	1.91m	2.42m	1.98m	1.80m	2.25m
17-H	1.18dd	1.30m	1.10dd	1.04m	1.17m
18-H	2.10d	2.22d	2.13d	1.99dd	1.98dd
19-Me	1.26d	1.17d	1.27d	1.28d	0.98d
C-6	88.84	87.33	77.10	43.07	39.35
C-8	20.19	32.51	21.25	20.65	32.82
C-17	37.60	38.06	38.08	35.70	38.52
C-18	38.29	39.36	41.49	35.48	34.71
C-19	56.80	66.64	56.94	59.12	65.81
19-Me	15.02	20.07	14.86	15.01	19.55

The configuration of the C-19 can be confirmed by homonuclear NOE measurements. In the case of compound **6d** the average proton–proton distance calculated for the (*S*)-C-19 configuration is $r_{19\text{-Me},8\alpha\text{-H}} \approx 0.26$–0.27 nm, and would be 0.41–0.42 nm for the *R*-configuration. Measured $f_{8\alpha\text{-H}}$(19-Me) = +9.7% NOE values correspond to the *S*-configuration only (Fig. 3). The distance between the 19-Me and the C-7 proton is not sensitive to configurational change although this distance is longer by 0.01 nm in the *S*-isomer than in the *R* one. In the case of the 6-unsubstituted compounds, for the (*S*)-C-19 aziridine **6f** $f_{8\alpha\text{-H}}$(19-Me) is +6% and no other NOE (except for 19-H) can be measured if the 19-Me is irradiated, while the following values were determined for the *R* configuration: $f_{8\alpha\text{-H}}$(19-Me) ≈ 0, $f_{6\text{-H}}$(19-Me) +9.8%, corroborating the *cis*-arrangement of the 6-H and 19-Me, *i.e.* the *R*-configuration for C-19. This means that the homonuclear NOE measured on irradiation of the 19-Me group is essential for the determination of the C-19 configuration. It is worth mentioning that the vicinal coupling value is $J_{7,19} \approx 3.7$ Hz for the *S*-configuration and zero for the *R* one. Similar coupling values were obtained in the case of the 6-methoxy diastereoisomeric pair **6b**/**6c** as well. Since a dihedral angle of 55–60° was calculated between 19-H and 7-H the coupling constants are not enough for the determination of the C-19 configuration.

Experimental

M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Merck 5554 silica gel F_{254} foils with benzene–methanol (8:2 v/v) developing mixture. The detecting agent was Dragendorff's reagent. IR spectra were recorded on a Perkin-Elmer 283B spectrometer. Mass spectra were measured with a VG-7035 (GC-MS-DS) instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WP 200 SY spectrometer operating at 200.13 MHz and 50.3 MHz,

respectively; chemical shifts are reported in ppm (δ) from internal $SiMe_4$. For the standard 2D correlation measurements 1M word (COSY) and 256 K (HETCOR) data tables and magnitude representation were used. The ^{13}C 1D spectra were measured by using the *J*-modulated spin-echo technique to obtain the number of coupled protons. For the measurement of the 1D NOE difference spectra 15–20 of preirradiation time was used and the lines of the multiplets were saturated line-selectively with 35–45 dB/0.2 W attenuation using frequency cycling.[11] Long-range INEPT experiments[12] optimized for 6–8 Hz couplings were used to assign the quaternary carbon atoms.

7α-*Acetyl*-6-*chloro*-6-*demethoxytetrahydro*-6,14-endo-*etheno-thebaine* **2b**.—A mixture of 6-chloro-6-demethoxythebaine **1b**[8] (1.0 g, 3.2 mmol), methyl vinly ketone (2.7 cm^3, 32 mmol) and anhydrous toluene (20 cm^3) was refluxed for 24 h, the solvent was evaporated off, and the residue was triturated with diethyl ether (20 cm^3). The insoluble material was filtered off and the solvent was evaporated off. The residue was dissolved in anhydrous ethanol (10 cm^3), acidified with ethanol (10 cm^3) saturated with hydrochloric acid, and the precipitate was filtered off and dissolved in water (10 cm^3). The aq. solution was alkalized with aq. ammonium hydroxide and the precipitate was filtered to yield *compound* **2b** (0.94 g, 89.5%), m.p. 63–64 °C (from Et_2O) (Found: N, 3.45; Cl, 9.3. $C_{22}H_{24}ClNO_3$ requires N, 3.63; Cl, 9.19%); $\delta_H(CDCl_3)$ 2.20 (3 H, s, 19-Me), 2.40 (3 H, s, NMe), 3.81 (3 H, s, OMe), 4.40 (1 H, s, 5-H), 5.50 (1 H, d, 17-H), 5.82 (1 H, d, 18-H) and 6.52 (2 H, dd, ArH).

General Procedure for the Preparation of C-19-*Diastereo-isomeric Secondary Alcohol Mixtures* **3c**/**3d** *and* **3e**/**3f**.—To a methanolic solution (100 cm^3) of a 7α-acetyl derivative **2a–2c** (10 mmol) at 0 °C was added sodium borohydride (45 mmol) and the mixture was stirred at this temperature for 30 min, then water (200 cm^3) was added and the organic substance was extracted with chloroform (3 × 50 cm^3); the extract was dried (Na_2SO_4) and evaporated. Tosates were prepared from the oily mixture (1:1) of the isomeric alcohols without purification.

General Procedure for the Preparation of Tosates **4d**, **4e**, **4f** *and* **4g**.—To a stirred, cooled mixture of diastereoisomeric secondary alcohols (10 mmol) in anhydrous pyridine (8.0 cm^3) was added a solution of toluene-*p*-sulphonyl chloride (15 mmol) in anhydrous pyridine (6.0 cm^3). The mixture was left at room temperature for one day (**4f** and **4g**) or for 6 days (**4d** and **4e**) and then poured into saturated aq. $NaHCO_3$ (400 cm^3). The organic material was extracted with chloroform (3 × 100 cm^3), washed with brine, dried, and evaporated. The residue was purified by column chromatography (Kieselgel 40, 200 g) with benzene–methanol (9:1) as eluent to obtain the appropriate tosates.

6-*Chloro*-6-*demethoxy*-7α-[(1R)-1-p-*tolylsulphonyloxyethyl*]-6,-14-endo-*ethanotetrahydrothebaine* **4d**. M.p. 177–178 °C (from Et_2O) (Found: N, 2.6; S, 5.8. $C_{29}H_{32}ClNO_5$ requires N, 2.58; S, 5.92%); $\delta_H(CDCl_3)$ 1.01 (3 H, d, 19-Me), 1.25 (1 H, dd, 8α-H), 2.40 (3 H, s, NMe), 2.49 (3 H, s, C_6H_4Me), 3.85 (3 H, s, OMe), 4.25 (1 H, s, 5-H), 5.15 (1 H, m, 19-H), 5.40 (1 H, d, 17-H), 5.58 (1 H, d, 18-H), 7.38 (2 H, d, ArH) and 7.85 (2 H, d, ArH); $[\alpha]_D^{24}$ −4° (*c* 0.1, $CHCl_3$).

6-*Chloro*-6-*demethoxy*-7α-[(1S)-1-p-*tolylsulphonyloxyethyl*]-*tetrahydro*-6,14-endo-*ethenothebaine* **4e**. M.p. 175–178 °C (from Et_2O) (Found: N, 2.6; S, 5.9%); $\delta_H(CDCl_3)$ 1.48 (3 H, d, 19-Me), 1.95 (1 H, dd, 8α-H), 2.40 (3 H, s, NMe), 2.45 (3 H, s, C_6H_4Me), 3.85 (3 H, s, OMe), 4.28 (1 H, s, 5-H), 5.11 (1 H, d, 17-H), 5.25 (1 H, d, 18-H), 5.30 (1 H, m, 19-H), 7.28 (2 H, d, ArH) and 7.77 (2 H, d, ArH); $[\alpha]_D$ −15° (*c* 0.1, $CHCl_3$).

6-*demethoxy*-7α-[(1R)-1-p-*tolylsulphonyloxyethyl*]*tetrahydro*-6,14-endo-*ethenothebaine* **4f**. M.p. 156–158 °C (from Et_2O) (Found: N, 2.8; S, 6.3. $C_{29}H_{33}NO_5S$ requires N, 2.76; S, 6.32%); $\delta_H(CDCl_3)$ 0.57 (1 H, dd, 8α-H), 1.28 (3 H, d, 19-Me), 2.37 (3 H, s, NMe), 2.45 (3 H, s, C_6H_4Me), 3.81 (3 H, s, OMe), 4.10 (1 H, m, 19-H), 4.40 (1 H, d, 5-H), 5.31 (1 H, dd, 17-H), 5.47 (1 H, d, 18-H), 7.33 (2 H, d, ArH) and 7.78 (2 H, d, ArH); $[\alpha]_D^{24}$ −12° (*c* 0.1, $CHCl_3$).

6-*Demethoxy*-7α-[(1S)-1-p-*tolylsulphonyloxyethyl*]*tetrahydro*-6,14-endo-*ethenothebaine* **4g**. M.p. 130–132 °C (from Et_2O) (Found: N, 2.8; S, 6.3%); $\delta_H(CDCl_3)$ 0.81 (1 H, dd, 8α-H), 1.18 (3 H, d, 19-Me), 2.35 (3 H, s, NMe), 2.42 (3 H, s, PhMe), 3.78 (3 H, s, OMe), 4.38 (1 H, d, 5-H), 4.39 (1 H, m, 19-H), 5.44 (1 H, d, 17-H), 5.59 (1 H, dd, 18-H), 7.31 (2 H, d, ArH) and 7.75 (2 H, d, ArH); $[\alpha]_D^{24}$ −15° (*c* 0.1, $CHCl_3$).

General Procedure for the Azidolysis of Tosates **4b–4g**.—A mixture of a tosate (2 mmol), (10 cm^3), sodium azide (10 mmol) and water (2 cm^3) was heated at 100 °C for 24 h, then poured into water (200 cm^3), and in the case of compounds **4b**, **4d**, **4f** and **4g** was extracted with chloroform (3 × 30 cm^3). After the eluent had been dried the solvent was evaporated off and compounds **6b**, **6f**, **6g** and **7f** were prepared as oily products, while compound **6d** was obtained as crystalline material on purification by column chromatography. Compounds **7b** and **7d** obtained from tosates **4c** and **4e** were purified by crystallization from ethanol. In the case of substrate **4c** the aziridine **6c** was obtained from the aq. mother liquor and was purified by column chromatography. Azidolysis of compound **4d** was interrupted after 1 h, the mixture was poured into water (200 cm^3), the precipitate was filtered off and washed with diethyl ether, and the azide **5d** was isolated from the ethereal solution.

7α-[(1S)-1-*Azidoethyl*]-6-*chloro*-6-*demethoxy*-6,14-endo-*ethenotetrahydrothebaine* **5d**. M.p. 65–67 °C (from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 2100 (N_3); $\delta_H(CDCl_3)$ 1.25 (3 H, d, 19-Me) 2.39 (3 H, s, NMe), 3.85 (3 H, s, OMe), 4.25 (1 H, m, 19-H), 4.35 (1 H, s, 5-H), 5.40 (1 H, d, 17-H), 5.78 (1 H, 18-H) and 6.51 (2 H, dd, ArH).

7-Ethylidenetetrahydro-6,14-*endo*-ethenothebaine **7b**, m.p. 203–205 °C (from EtOH), was identical with authentic material (ref. 4).

6-*Chloro*-6-*demethoxy*-7-*ethylidenetetrahydro*-6,14-endo-*ethenothebaine* **7d**. M.p. 170–174 °C (from EtOH) (Found: N, 3.9; Cl, 9.7. $C_{22}H_{24}NO_2Cl$ requires N, 3.79; Cl, 9.59%); $\delta_H(CDCl_3)$ 1.70 (3 H, d, 19-Me), 2.40 (3 H, s, NMe), 3.82 (3 H, s, OMe), 4.30 (1 H, s, 5-H), 5.48 (1 H, d, 17-H), 5.80 (1 H, d, 18-H) and 6.10 (1 H, m, 19-H); $[\alpha]_D^{24}$ −25° (*c* 0.1, $CHCl_3$).

6-*Demethoxy*-7-*ethylidenetetrahydro*-6,14-endo-*etheno-thebaine* **7f**. $\delta_H(CDCl_3)$ 1.61 (3 H, d, 19-Me), 2.40 (3 H, s, NMe), 3.82 (3 H, s, OMe), 4.55 (1 H, d, 5-H), 5.56 (2 H, m, 17- and 19-H) and 5.90 (1 H, dd, 18-H).

(2′S,6α,7α,14α)-2′-*Methyl*-5′,6′,6,7-*tetrahydro*-2′H,8H-1′,5′;6′,14-*dicyclopyrido*[3′,4′;7,6]*thebaine* **6b**). $\delta_H(CDCl_3)$ 1.18 (1 H, dd, 5′-H), 1.26 (3 H, d, 2′-Me), 1.59 (1 H, d, 8α-H), 2.10 (1 H, d, 6′-H), 2.35 (3 H, s, NMe), 3.44 (3 H, s, 6-OMe), 3.85 (3 H, s, 3-OMe), 4.99 (1 H, s, 5-H) and 6.65 (2 H, dd, ArH); *m*/*z* 380 (M^+, 20%).

(2′R,6α,7α,14α)-2′-*Methyl*-5′,6′,6,7-*tetrahydro*-2′H,8H-1′,5′;6′,14-*dicyclopyrido*[3′,4′:7,6]*thebaine* **6c**. $\delta_H(CDCl_3)$ 1.22 (3 H, d, 2′-Me), 1.25 (1 H, m, 8α-H), 1.28 (1 H, dd, 5′-H), 2.17 (1 H, d, 6′-H), 2.33 (3 H, s, NMe), 2.97 (1 H, m, 2′-H), 3.48 (3 H, s, 6-OMe), 3.87 (3 H, s, 3-OMe), 4.95 (1 H, s, 5-H) and 6.65 (2 H, dd, ArH); *m*/*z* 380 (M^+, 10%).

(2′S,6α,7α,14α)-6-*Chloro*-6-*demethoxy*-2′-*methyl*-5′,6′,6,7-*tetrahydro*-2′H,8H-1′,5′;6′,14-*dicyclopyrido*[3′,4′:7,6]*thebaine* **6d**. M.p. 170–172 °C (from Et_2O–hexane) (Found: N, 7.1; Cl, 9.0.

$C_{22}H_{25}ClN_2O_2$ requires N, 7.28; Cl, 9.21%); $\delta_H(CDCl_3)$ 1.10 (1 H, dd, 5′-H), 1.27 (3 H, d, 2′-Me), .161 (1 H, d, 8α-H), 2.13 (1 H, d, 6′-H), 2.31 (3 H, s, NMe), 3.85 (3 H, s, OMe), 4.81 (1 H, s, 5-H) and 6.62 (2 H, dd, ArH); $[\alpha]_D^{24}$ −19° (*c* 0.1, $CHCl_3$); *m/z* 384 (M^+, 100%).

(2′S,6α,7α,14α)-6-*Demethoxy*-2′-*methyl*-5′,6′,6,7-*tetrahydro*-2′H,8H-1′,5′;6′,14-*dicyclopyrido*[3′,4′:7,6]*thebaine* **6f**. $\delta_H(CDCl_3)$ 1.04 (1 H, m, 5′-H), .128 (3 H, d, 2′-Me), 1.54 (1 H, d, 8α-H), 2.39 (3 H, s, NMe), 3.85 (3 H, s, OMe), 4.89 (1 H, d, 5-H) and 6.65 (2 H, dd, ArH); *m/z* 350 (M^+, 30%).

(2′R,6α,7α,14α)-6-*Demethoxy*-2′-*methyl*-5′,6′,6,7-*tetrahydro*-2′H,8H-1′,5′;6′,14-*dicyclopyrido*[3′,4′:7,6]*thebaine* **6g**. $\delta_H(CDCl_3)$ 0.98 (3 H, d, 2′-Me), 1.12 (1 H, d, 8α-H), 1.17 (1 H, m, 5′-H), 1.98 (1 H, dd, 6′-H), 2.36 (3 H, s, NMe), 3.84 (3 H, s, OMe), 4.87 (1 H, d, 5-H) and 6.65 (2 H, dd, ArH); *m/z* (350 (M^+, 25%).

Acknowledgements

Financial support from the Alkaloida Chemical Factory (Tiszavasvári, Hungary) is gratefully acknowledged. Our thanks are due to Dr. A. Zékány and Mrs. Zs. Gyulai for their help in the experimental work.

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Paper 0/05042C
Received 9*th November* 1990
Accepted 11*th December* 1990