

DECUMBENSINE AND *EPI*- α -DECUMBENSINE: TWO NEW ALKALOIDS ISOLATED FROM *CORYDALIS DECUMBENS*

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The Chinese medicinal plant *Corydalis decumbens* (Thunb.) Pers. (Papaveraceae) was used in folk medicine for the treatment of central nervous system diseases. As part of a continuing study on the alkaloidal constituents of the plant (1,2), two new alkaloids, decumbensine [**1**] and *epi*- α -decumbensine [**2**], along with three known alkaloids, bicuculine, hydroxyhydrastine, and corydaline, were isolated and their structures elucidated.

The first new alkaloid, decumbensine [**1**], $[\alpha]^{20}_D + 129.0^\circ$ ($c = 1.1$, CHCl_3) was obtained as an amorphous product. According to its molecular peak 342 $[\text{M} + 1]^+$ (cims) and ^{13}C -nmr spectrum, its molecular formula should be $\text{C}_{19}\text{H}_{19}\text{NO}_5$. The mass spectrum showed a base peak at m/z 190, typical of a methylenedioxy isoquinoline moiety. The ir spectrum presented a typical hydroxyl absorption (3450 cm^{-1}) and no carbonyl group.

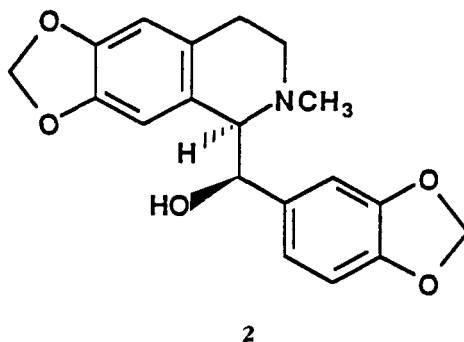
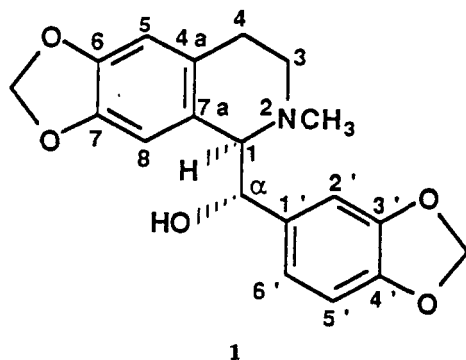
The ^1H -nmr spectrum of **1** showed an *N*-methyl singlet at 2.43 ppm, four peaks between 1.7 and 2.8 ppm for the AA'BB' system of the isoquinoline nucleus, and two doublets ($J = 3.8\text{ Hz}$) at

3.80 and 5.32 ppm. The aromatic region presented two doublets ($J = 7.9\text{ Hz}$) at 5.57 and 6.45 ppm and three singlets at 6.24, 6.51 and 6.72 ppm. The peaks of two methylenedioxy groups appeared at 5.90 and 5.94 ppm.

These data are in agreement with structure **1**. The two doublets at 3.80 and 5.32 ppm are attributed to H-1 and H- α , respectively. The location of the two methylenedioxy groups on the aromatic ring is deduced from the splitting of the aromatic peaks as two doublets and three singlets.

The ^{13}C -nmr spectrum of this compound confirms the proposed structure **1**. We observed two methylene peaks at 22.4 and 46.1 ppm (C-4 and C-3), one methyl peak at 44.1 ppm (N-Me), and two methine signals at 65.1 and 87.1 ppm (C-1 and C- α). The presence of the two methylenedioxy groups is confirmed by two signals at 101.1 and 101.8 ppm.

The isomeric *epi*- α -decumbensine [**2**], the second alkaloid, was isolated in small amounts as an amorphous material, $[\alpha]^{20}_D + 32.5^\circ$ ($c = 0.6$, CHCl_3) and showed spectroscopic characteristics



very close to those of decumbensine [1]. A nearly identical fragmentation was observed in ms.

The ^1H -nmr spectrum of 2 is very similar to that of 1 with the exception of the chemical shifts and the coupling constants of H-1 and H- α . The N-Me peak is shielded (1.95 ppm), while the H-3 and H-4 are deshielded. H-1 and H- α appeared as two singlets at 3.66 and 5.27 ppm. The aromatic portion showed three singlets and an AA' system centered at 6.82 ppm that was attributed to the H-5' and H-6' protons. These data suggested that this alkaloid is epimeric with decumbensine [1] at C-1 or C- α .

The configuration of C-1 was deduced from the cd spectrum, which presented a negative Cotton effect at 240 nm typical of an S configuration (3). Kametani *et al.* (4) have shown that for synthetic products with a hydroxyl on C- α , both methine proton signals of the (1R, α S)-isomer appear at a lower field than those of the (1S, α S)-isomer. In the case of decumbensine [1] and *epi*- α -decumbensine [2] the chemical shifts suggest that decumbensine [1] is the (1R, α S)-isomer. This hypothesis was confirmed by the fact that the N-Me protons of *epi*- α -decumbensine were shielded, showing a signal at 1.95 ppm. This observation can be explained by the anisotropy which is due to the sterically preferred conformation of the pendant aromatic ring, with a hydrogen bond between the lone-pair electrons of nitrogen and the hydrogen of the hydroxyl group.

In the course of this study, another benzyloisoquinoline alkaloid, phyllocryptonine, bearing a hydroxyl on C- α , was isolated from *Cryptocarya phyllostemon* (Lauraceae) (5).

EXPERIMENTAL

GENERAL METHODS.— ^1H -nmr spectra were recorded in CDCl_3 on a Bruker AM-400 NMR spectrometer (400 MHz) (TMS) and ^{13}C -nmr spectra on a Bruker AC-100 NMR spectrometer (22.63 MHz).

PLANT MATERIAL.—The plant material was

collected from Jianxi Province, China, and the sample was identified by Prof. S.L. Huang of our institute. A voucher specimen is deposited in the Department of Pharmacognosy of our institute. The total alkaloids were extracted with EtOH followed by the usual fractionation and were then separated by Si gel chromatography.

DECUMBENSINE [1].—Amorphous, $[\alpha]^{20}_{\text{D}} + 129^\circ$ ($c = 1.1$, CHCl_3); ir (CHCl_3) ν max cm^{-1} 3430, 1500, 1490, 1485, 1250; cims (isobutane) m/z $[\text{M} + 1]^+$ 342, 190, 179, 163; ^1H nmr (CDCl_3) 1.75 (H-4ax, ddd, $J = 13.5$, 11.8, and 4.3 Hz), 1.95 (H-3eq, ddd, $J = 16.8$, 4.3, and 2.0 Hz), 2.32 (H-4eq, ddd, $J = 13.5$, 5.4, and 2.0 Hz), 2.43 (N-Me, s), 2.65 (H-3ax, ddd, $J = 16.8$, 11.8, and 5.4 Hz), 3.80 (H-1, d, $J = 3.8$ Hz), 5.32 (H- α , d, $J = 3.8$ Hz), 5.57 (H-6', d, $J =$ Hz), 5.90 and 5.94 ($2 \times \text{OCH}_2\text{O}$, m), 6.24, 6.51, and 6.72 (H-5, H-8, H-2', 3s), 6.45 (H-5', d, $J = 7.9$ Hz); ^{13}C nmr (CDCl_3) 22.4 (C-4), 44.1 (N-Me), 46.1 (C-3), 65.1 (C-1), 87.1 (C- α), 97.8, 107.4, 108.1, 108.4, and 114.5 (C-5, C-8, C-2', C-5', C-6'), 101.1 and 101.8 ($2 \times \text{-OCH}_2\text{O-}$), 124.1 (C-4), 128.5 (C-1'), 133.1 (C-7a), 141.4, 146.3, 146.5, and 148.1 (C-6, C-7, C-3', C-4').

epi- α -DECUMBENSINE [2].—Amorphous, $[\alpha]^{20}_{\text{D}} + 32.5^\circ$ ($c = 0.6$, CHCl_3); ir (CHCl_3) ν max cm^{-1} 3450, 1500, 1485, 1250; cims (isobutane) m/z $[\text{M} + 1]^+$ 342, 190, 179, 163; ^1H nmr (CDCl_3) 1.95 (N-Me, s), 2.45 (H-4eq, ddd, $J = 15.3$, 3.1 and 2.0 Hz), 2.53 (H-4ax, td, $J = 15.3$ and 3.8 Hz), 2.99 (H-3eq, ddd, $J = 12.4$, 3.8, and 2.0 Hz), 3.18 (H-3ax, ddd, $J = 15.3$, 12.4, and 3.1 Hz), 3.66 (H-1, s), 5.27 (H- α , s), 5.91 and 6.04 ($2 \times \text{-OCH}_2\text{O-}$, m), 6.23, 6.59, and 6.07 (H-5, H-8, and H-2'), 6.82 (2H, s, H-5' and H-6').

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