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# ISOQUINOLINE ALKALOIDS, DECUMBENINE B AND C, FROM *CORYDALIS DECUMBENS*

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**Key Word Index**—*Corydalis decumbens*; Papaveraceae; isoquinoline alkaloids; decumbenine B and C.

**Abstract**—From the roots of *Corydalis decumbens* two new isoquinoline-type alkaloids, decumbenine B and C were isolated. Their structure elucidation was based on spectroscopic evidence.

## INTRODUCTION

The roots of *Corydalis decumbens* Pers are used in Chinese folk herbal medicine for treatment of paralytic stroke and rheumatic arthritis. In recent years, the crude alkaloid extract of the plant has been shown to have a significant activity against teenage nearsightedness. As a result of searching for new bioactive compounds, we isolated more than 11 isoquinoline-type alkaloids. Among them, two are new isoquinoline alkaloids, decumbenine B (**1**) and C (**2**). In this paper, we report the isolation and structural elucidation of compounds **1** and **2**.

## RESULTS AND DISCUSSION

Decumbenine B (**1**) was isolated as needles, mp 222–224°. The HR mass spectrum showed a $[M]^+$ at *m/z* 323.0776 corresponding to the molecular formula $C_{18}H_{13}NO_5$ (calcd 323.0792). The IR spectrum of **1** suggested the presence of hydroxyl (3250 $cm^{-1}$) and aromatic ring (1600, 1570 $cm^{-1}$) groups. The $^1H$ NMR spectrum exhibited two methylenedioxy groups at $\delta$6.10 (2H, *s*) and 6.26 (2H, *s*), two pairs of aromatic protons with an AB pattern at $\delta$6.85, 7.14 (each 1H, *d*, $J$ = 8.0 Hz) and 7.30, 7.62 (each 1H, *d*, $J$ = 8.6 Hz), two aromatic single protons at $\delta$7.81 (1H, *s*), 9.14 (1H, *s*) as well as two protons at $\delta$4.54 (2H, *s*). Its UV spectrum and unsaturation degree suggested that the base might be a phenyl isoquinoline-type alkaloid. According to the known substitution patterns [1], the one proton singlet at $\delta$9.14 could be assigned to H-1 and this was supported by the signal at $\delta_C$ 151.3 (*d*). There was no signal at around $\delta$8.50 thus indicating that the proton at C-3 must be replaced by a phenyl group. A 14.9% NOE enhancement of the signal at $\delta$7.62 was observed on irradiation of signal at $\delta$9.14 due to H-1 indicating that an ABq at $\delta$7.62 and 7.30 should be designated as H-8 and H-7, respectively. Hence, another one proton singlet at $\delta$7.81 was due to H-4. The H-4 signal displayed a NOE (17.9%) with the signal at $\delta$7.14 establishing that the ABq at $\delta$7.14 and 6.85 was due to H-6′ and H-5′, respectively. The signal at $\delta$4.54 (2H, *s*) must be due to a proton at the carbon atom bearing a hydroxyl group and this was supported by a signal at $\delta_C$ 56.4 (*t*). The hydroxyl group of **1** was transformed into its acetate with difficulty and we deduced that the hydroxyl group might form a hydrogen bond with a nitrogen atom. Thus, the group $CH_2OH$ should be placed at position C-2′. The $^{13}C$ NMR data of **1** was corresponded to the structure **1**.

Decumbenine C (**2**), a new phthalideisoquinoline alkaloid, has the formula $C_{19}H_{11}NO_6$ ($M^+$ 349.0548), mp 211–213; and was isolated as brown woolly crystals. From the IR spectrum it appeared that compound **2** contained a $\gamma$-lactone (1760 $cm^{-1}$), an aromatic ring (1500, 1475 $cm^{-1}$) and a methylenedioxy group (940 $cm^{-1}$). The $^1H$ NMR spectrum of **2** exhibited two methylenedioxy groups with signals at $\delta$6.21 (2H, *d*, $J$ = 7.5 Hz) and 6.12 (2H, *d*, $J$ = 7.5 Hz), two pairs of aromatic AB type protons at $\delta$6.82, 7.06 (each 1H, *d*, $J$ = 8.0 Hz) and 7.53, 8.31 (each 1H, *d*, $J$ = 6.0 Hz), and three one-proton singlets at $\delta$7.12 (2 × 1H, *s*) and 7.40 (1H, *s*). The UV spectrum of compound **2** showed the same absorption as that of papaverine [2]. Hence, we deduced that an isoquinoline moiety was present in decumbenine C. In the $^1H$ NMR spectrum, the signal at $\delta$8.31 was assigned to H-3, because the chemical shift of H-3 in an isoquinoline ring can only be placed at such a downfield value according to the known information in this class of alkaloids [1]. On the basis of the UV and IR spectra, together with the biogenetic capabilities of this plant, decumbenine C should be a phthalideisoquinoline alkaloid. The result of decoupling experiments showed that a signal at $\delta$7.53 was due to H-4. So, the signals of the remaining two aromatic protons with an AB pattern should be at $\delta$6.82 and 7.06, respectively. In NOE differ-

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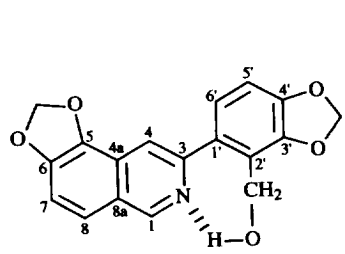
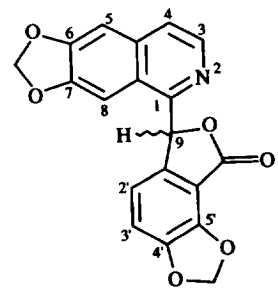
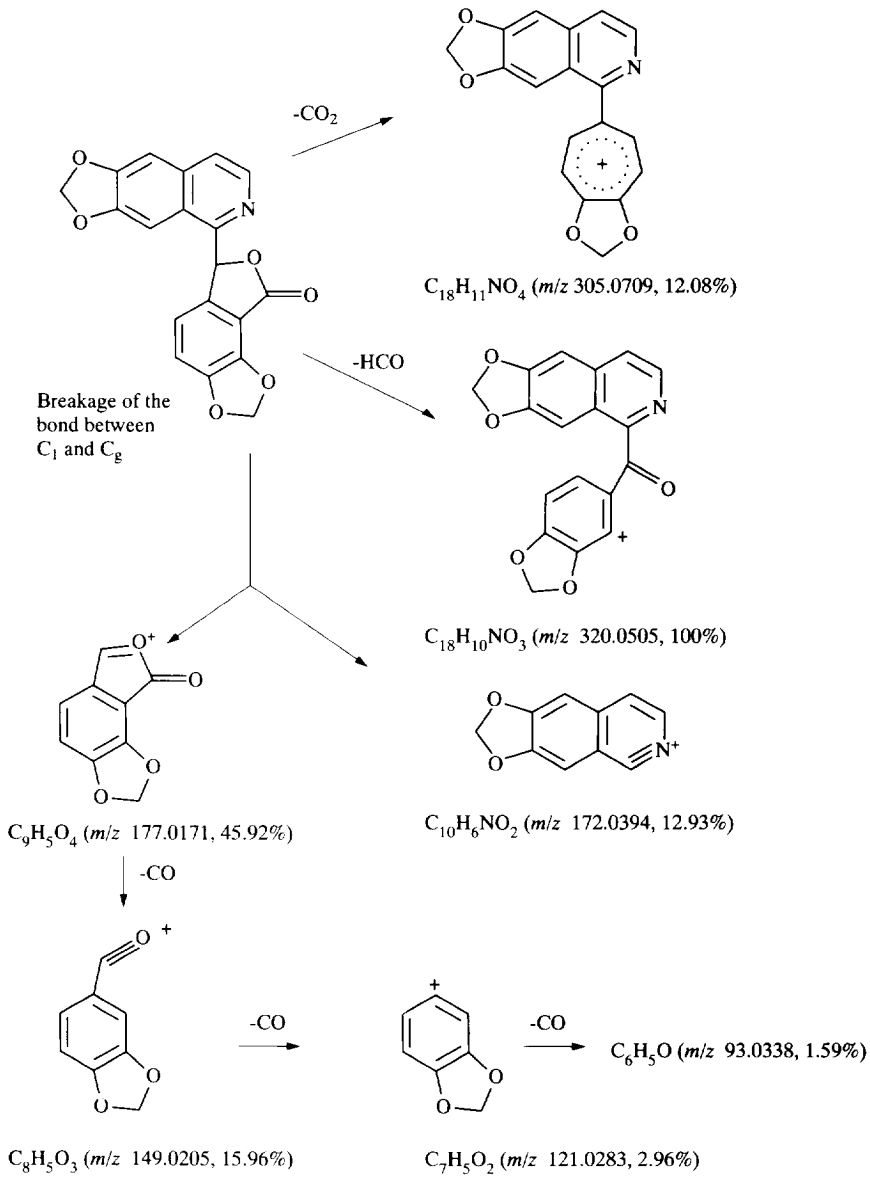


1



2


-CO2
-HCO
Breakage of the bond between C1 and C8
C18H11NO4 (m/z 305.0709, 12.08%)
C18H10NO3 (m/z 320.0505, 100%)
C10H6NO2 (m/z 172.0394, 12.93%)
C9H5O4 (m/z 177.0171, 45.92%)
-CO
-CO
-CO
C8H5O3 (m/z 149.0205, 15.96%)
C7H5O2 (m/z 121.0283, 2.96%)
C6H5O (m/z 93.0338, 1.59%)

Scheme 1.

ence experiments, 3.7 and 6.5% NOE enhancements for signals at $\delta$8.31 (H-3) and 7.40 on irradiating H-4 ($\delta$7.53) indicated that the signal at $\delta$7.40 was due to H-5. Also, 5.6% NOE enhancement for the signal at $\delta$6.82, one of two aromatic protons with an AB pattern, and 2.3% for the signal at $\delta$7.12 were observed on irradiation of the signal at $\delta$7.06, which represents another aromatic proton with an AB pattern, thus establishing that the signals at $\delta$7.06, 6.82 and 7.12 were due to H-2′, H-3′ and H-9, respectively. The signal of H-8 was also located at $\delta$7.12, overlapping with signal of H-9. A putative mass spectral fragmentation of alkaloid **2** is given in Scheme 1.

## EXPERIMENTAL

Mps: uncorr. UV: MeOH. IR: KBr. $^1$H and $^{13}$C NMR (400 MHz), $CDCl_3$. MS: 70 eV direct inlet. CC: silica gel (200–300 mesh). TLC: silica gel $GF_{254}$ plate (0.25 mm). Spray reagent for TLC: Dragendorff reagent.

*Plant material. Corydalis decumbens* was collected in Jiangxi Province, China in 1989. Voucher specimens are deposited in the Herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

*Extraction and isolation.* Air-dried and ground roots (10 kg) of *Corydalis decumbens* were refluxed × 3 in 95% EtOH. The extract was evapd to dryness and the residue was dissolved with 3% HCl. The acidic extract was basified to pH 10–11 with $NH_3$–water and extracted with $CHCl_3$ to give total alkaloids. A portion (60 g) of the total alkaloids was chromatographed over a column of silica gel (2 kg) eluted with a mixt. of $C_6H_6$–EtOAc (7:3) followed by $CHCl_3$–MeOH (9:1) and finally EtOH. Fractions of 200 ml were collected and frs containing similar TLC profiles were pooled. Fractions 9–12 (500 mg) were chromatographed by prep. TLC ($C_6H_6$–$(Me)_2CO$, 84:4) to yield decumbenine C (**2**, 3 mg). Rechromatography of frs 13–31 (5.9 g) on silica gel (360 g) with elution by $CHCl_3$–$(Me)_2CO$ (84:2) gave decumbenine B (**1**, 30 mg).

*Decumbenine B* (**1**). Needles, mp 222–224°. UV $\lambda_{max}^{MeOH}$ nm: 224, 280, 304, 340. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3250, 1650, 1600, 1570, 1060, 940. $^1$H NMR ($CDCl_3$): $\delta$4.54 (2H, *s*, $CH_2O$), 6.10 (2H, *s*, $OCH_2O$), 6.26 (2H, *d*, $OCH_2O$), 6.85 (1H, *d*, $J$ = 8.0 Hz, H-5′), 7.14 (1H, *d*, $J$ = 8.0 Hz, H-6′), 7.30 (1H, *d*, $J$ = 8.6 Hz, H-7), 7.62 (1H, *d*, $J$ = 8.6 Hz, H-8), 7.81 (1H, *s*, H-4), 9.14 (1H, *s*, H-1). $^{13}$C NMR: $\delta$56.4 (*t*, $CH_2O$), 101.5 (*t*, $OCH_2O$), 102.5 (*t*, $OCH_2O$), 122.1 (*s*, C-1′), 122.8 (*s*, C-8a), 134.8 (*s*, C-4a), 151.3 (*d*, C-1), 152.3 (*s*, C-3), 107.6, 111.6, 111.9, 123.0, 124.0 (*d*, ArCH), 123.6, 140.4, 146.9, 147.5, 147.9 (*s*, ArC); EIMS *m/z*: 323 $[M]^+$ (base peak), 295, 280, 249, 174; HRMS *m/z*: 323.0776 $[M]^+$ (calcd for $C_{18}H_{13}NO_5$ 323.0792).

*Decumbenine C* (**2**). Brown woolly crystals, mp 211–213°. UV $\lambda_{max}^{MeOH}$ nm: 237, 280, 318sh, 332. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1760, 1500, 1475, 1260, 1040, 940. $^1$H NMR ($CDCl_3$); $\delta$8.31 (1H, *d*, $J$ = 6.0 Hz, H-3), 7.53 (1H, *d*, $J$ = 6.0 Hz, H-4), 7.06 (1H, *d*, $J$ = 8.0 Hz, H-2′), 6.82 (1H, *d*, $J$ = 8.0 Hz, H-3′), 7.12 (2H, *s*, H-8 and H-9), 7.40 (1H, *s*, H-5), 6.21 (2H, *d*, $J$ = 7.5 Hz, $OCH_2O$), 6.12 (2H, *d*, $J$ = 7.5 Hz, $OCH_2O$). MS *m/z* (rel. int.); 349 $[M]^+$ (96), 320 (100), 305 (12), 177 (46), 172 (13), 149 (16), 121 (3), 93 (2); HRMS *m/z*: 349.0548 $[M]^+$ (calcd for $C_{19}H_{11}NO_6$ 349.0587).

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2. Shamma, M. (1972) *The Isoquinoline Alkaloids*, p. 309. Plenum Press, New York.