

## **Narcissus Alkaloids, XV. Roserine from *Narcissus pallidulus***

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NARCISSUS ALKALOIDS, XV.<sup>1</sup> ROSERINE FROM  
*NARCISSUS PALLIDULUS*

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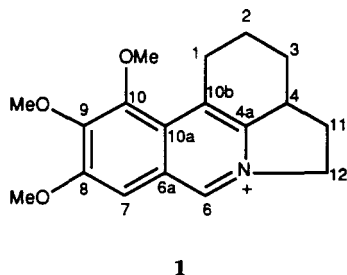
ABSTRACT.—The MeOH extract of *Narcissus pallidulus* afforded a novel compound, roserine [1]. The structure of 1 was elucidated by spectroscopic methods, including 2D nmr analyses.

In a previous work on the alkaloid composition of *Narcissus pallidulus* Graells we reported the isolation and structure elucidation of mesembrenone [2] (2), an unexpected alkaloid in the family Ama-

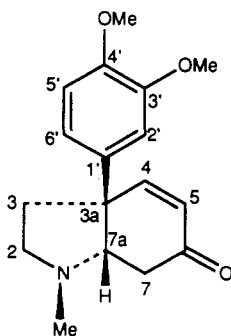
ryllidaceae. This was unusual because mesembrine-type alkaloids were thought to be restricted to Aizoaceae-Mesembryanthemoideae (Dicotyledoneae) (3). We now describe the characterization from this plant of another alkaloid, for which the name roserine [1] is proposed.

Flash chromatography of the alkaloidal extract D (see Experimental) afforded compound 1, C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub> from hreims. Its eims showed the parent peak at *m/z* 300, and fragmentations at *m/z* 285 and 270 by loss of Me groups. The <sup>1</sup>H-nmr spectrum recorded in CDCl<sub>3</sub> (Table 1) exhibited the presence of three singlets at δ 3.90, 4.05, and 4.15 for the aromatic MeO groups at δ 3.90, 4.05, and 4.15 for the aromatic MeO groups and two signals at lower fields assigned as two aromatic protons. The disposition of the MeO groups in the aromatic ring was clarified on the basis of the H-6 and H-7 correlation observed in a complete COSY experiment. The deshielding observed for C-6 and C-12 protons confirmed their α disposition with respect to the nitrogen of the isoquinolinium salt.

The aliphatic zone presented a complex multiplicity which was completely assigned by means of the 2D COSY experiment. The plot showed correlation between H-1β (δ 3.13) with a ddd at δ 2.85 for H-1α and with two multiplets



1



2

<sup>1</sup>For part XIV in this series, see Bastida *et al.* (1).

TABLE 1.  $^1\text{H}$ -nmr Chemical Shift Assignments for Roserine [1] ( $\text{CDCl}_3$ ).

Proton	$\delta_{\text{H}}^a$ ( $J$ ) <sup>b</sup>
H-1 $\alpha$ . . . . .	2.85 ddd (16.0, 6.0, 1.5)
H-1 $\beta$ . . . . .	3.13 dd (16.0, 6.0)
H-2 $\alpha$ . . . . .	1.80–1.95 m
H-2 $\beta$ . . . . .	2.25–2.40 m
H-3 $\alpha$ . . . . .	1.38 qd (11.0, 2.0)
H-3 $\beta$ . . . . .	2.25–2.40 m
H-4 . . . . .	3.40–3.50 m
H-6 . . . . .	9.50 s
H-7 . . . . .	6.95 s
H-11 $\alpha$ . . . . .	2.05 ddd (11.0, 10.0, 6.0)
H-11 $\beta$ . . . . .	2.70 dt (11.0, 6.0)
H-12 . . . . .	4.75–4.95 m
OMe . . . . .	3.90 s
	4.05 s
	4.15 s

<sup>a</sup>Values in ppm.<sup>b</sup>Values in Hz.

at  $\delta$  2.25–2.40 and 1.80–1.95 ppm, which led us to assign them as H-2 $\beta$  and H-2 $\alpha$ , respectively. The larger deshielding of H-1 $\beta$  with respect to its geminal proton could be due to the influence of the oxygen electrons of the MeO group at C-10, which is in out-of-plane conformation. Likewise, correlation of H-12 protons with signals at  $\delta$  2.70 and 2.05, assignable to the H-11 protons, was also observed.

The  $^{13}\text{C}$ -nmr spectrum of **1** (Table 2) presented two methine carbons in the aromatic zone assigned at C-6 and C-7. The shielding of the carbon C-7 in relation to other para unsubstituted alkaloids (4) is due to the effect of the MeO group in that position. Furthermore, the MeO groups flanked by two ortho substituents have higher  $\delta$   $^{13}\text{C}$  nmr values (62.4, 62.5 ppm) than those with one ortho substituent (56.8 ppm). These measurements indicated that the MeO groups with two ortho substituents acquire the out-of-plane conformation, while those without this kind of substituents or with one ortho substituent exist in the planar conformation (5).

## EXPERIMENTAL

### GENERAL EXPERIMENTAL PROCEDURES.—

TABLE 2.  $^{13}\text{C}$ -nmr Chemical Shift Assignments for Roserine [1] ( $\text{CDCl}_3$ ).

Carbon	$\delta_{\text{C}}^a$
C-1 . . . . .	31.7
C-2 . . . . .	21.8
C-3 . . . . .	23.0
C-4 . . . . .	40.0
C-4a . . . . .	162.4
C-6 . . . . .	138.5
C-6a . . . . .	119.3
C-7 . . . . .	96.8
C-8 . . . . .	150.5
C-9 . . . . .	146.8
C-10 . . . . .	142.0
C-10a . . . . .	127.1
C-10b . . . . .	135.5
C-11 . . . . .	26.8
C-12 . . . . .	57.4
8-OMe . . . . .	56.8
9-OMe . . . . .	62.4
10-OMe . . . . .	62.5

<sup>a</sup>Values in ppm.

$^1\text{H}$ - (250 MHz) and  $^{13}\text{C}$ - (62.5 MHz) nmr spectra were recorded on a Brüker AC250 spectrometer using TMS as internal standard. Chemical shifts are reported in  $\delta$  (ppm) values and coupling constants ( $J$ ) in Hz. EIMS was obtained with a Hewlett-Packard 59865 A instrument operating at 70 eV. Analytical and preparative tlc was carried out on Si gel 60 F<sub>254</sub> plates (Merck). Si gel 60 Merck (70–230 mesh) and Si gel SDS Chromagel 60 A CC (230–400 mesh) were used for cc and flash cc, respectively. Spots on chromatograms were detected by Dragendorff's reagent and under uv light (254 nm).

PLANT MATERIAL.—*N. pallidulus* was collected in the Cáceres Province, Spain, in March 1990, when plants were flowering. The species was authenticated by Prof. Javier Fernández Casas, Real Jardín Botánico de Madrid. A voucher specimen (No. 32937b) is on deposit at the Herbarium of the Faculty of Pharmacy, University of Barcelona, Spain.

EXTRACTION AND ISOLATION.—Fresh aerial parts and bulbs (2.6 kg) were crushed and subjected to continuous Soxhlet extraction for 10 h using MeOH. After evaporation of the solvent, the extract was dissolved in 2% HCl. The mixture was filtered, and the neutral material was removed with Et<sub>2</sub>O. The acidic solution was then extracted with CHCl<sub>3</sub> to provide extract A (1.4 g). The former aqueous acidic solution was made basic (pH 8–9) with Na<sub>2</sub>CO<sub>3</sub> and extracted with CHCl<sub>3</sub>-MeOH (3:2). The organic solution was concentrated in vacuo and taken to dryness to yield extract D (221 mg).

The chromatographic and spectroscopic behavior of the alkaloid detected in extract A was identical to that of a standard sample of **2**. Extract D was separated by flash chromatography on a Si gel column eluting with  $\text{CHCl}_3$ -MeOH (8.5:1.5). After elution, fractions were monitored by tlc. Fractions 37-79 showed the presence of a single alkaloid and were combined to provide 44 mg of impure product. Purification of this compound by preparative tlc, eluting from Si gel with  $\text{CHCl}_3$ -MeOH (9:1) in an  $\text{NH}_3$  saturated atmosphere, yielded the new alkaloid **1** (5 mg).

ROSERINE [**1**].—Hrms  $m/z$  300.1604 (calcd 300.1600 for  $\text{C}_{18}\text{H}_{22}\text{NO}_3$ ); ms  $m/z$  (rel. int.)  $[\text{M}]^+$  300 (2), 286 (11), 285 (40), 284 (21), 271 (38), 270 (100), 256 (18), 254 (17), 242 (32), 239 (19), 228 (24), 225 (11), 199 (16), 171 (21), 170 (11), 154 (10), 143 (10), 142 (11), 115 (13), 93 (8), 73 (10);  $^1\text{H}$  nmr see Table 1;  $^{13}\text{C}$  nmr see Table 2.

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