

This represents the first example of a pyrrolidino-flavonol. So far four flavonoid alkaloids have been described: ficine and isoficine from *Ficus pantoniana* [4], phyllospadine, from *Phyllospadix iwatensis* [5] and vochysine from *Vochysia guaijanensis* [6]. The first three are *N*-methyl-pyrrolidinoflavones and vochysine is a pyrrolidinoflavan.

EXPERIMENTAL

The plant material, *Lilium candidum* L., was collected in South Slovakia and the herbarium specimen is deposited in the Department of Pharmacognosy and Botanics of the Pharmaceutical Faculty, Comenius University, in Bratislava. Mps are uncorrected.

Extraction and isolation of lilaline. Dry flowers (1500 g) were macerated several times at room temp. with a 96 % and 70 % EtOH [1]. The filtered extract was evaporated and then freeze-dried. The substances present in the ethanolic macerate were extracted successively with petrol, ether, chloroform and chloroform-ethanol (2:1).

Chromatography on silica gel of the ethereal extract using benzene-acetone for elution gave a fraction rich in lilaline. Rechromatography of this fraction on Sephadex LH-20 with methanol and crystallization from acetone afforded 26 mg of yellow crystals of lilaline. Mp 247°, $[\alpha]_{D}^{27} +65^{\circ}$ (methanol, c 0.2), $C_{20}H_{17}NO_7$. UV λ_{max}^{MeOH} nm (log ϵ): 272 (4, 36), 322 (4, 10), 371 (4, 31), + NaOMe: 285, 322, 424, + AlCl₃: 276, 312, 357, 436 + AlCl₃-HCl: 273, 308, 353, 432 + NaOAc: 282, 322, 402 + H₃BO₃-NaOAc: 272, 320, 372. ¹H NMR (300.13 MHz,

CD₃OD): δ 1.29 (3H, d, $J = 7.4$ Hz, CH₃), 2.17 (1H, ddd, $J = 12.9, 8.9$ and 4.9 Hz, H-4a"), 2.57 (1H, ddd, $J = 12.9, 9.7$ and 5.9 Hz, H-4b"), 2.77 (1H, dgd, $J = 9.7, 7.4$ and 4.9 Hz, H-3"), 5.56 (1H, dd, $J = 8.9$, and 5.9 Hz, H-5"), 6.24 (1H, s, H-6), 6.91 (2H, d, $J = 9.0$ Hz, H-3' and H-5'), 8.01 (2H, d, $J = 9.0$ Hz, H-2' and H-6'). ¹³C NMR (75.47 MHz, CD₃OD): δ 17.5(CH₃), 35.9 (C-4"), 38.5 (C-3"), 48.1 (C-5"), 99.3 (C-6), 104.8 (C-4a), 106.8 (C-8), 116.5 (C-3', C-5'), 123.6 (C-1'), 130.8 (C-2', C-6'), 137.1 (C-3), 148.5 (C-2), 155.9 (C-5), 160.7 (C-4'), 161.8 (C-8a), 163.7 (C-7), 177.5 (C-4), 183.9 (C-2").

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AN OXINDOLE FROM THE ROOTS OF *CAPPARIS TOMENTOSA**

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Key Word Index—*Capparis tomentosa*; Capparaceae; root; new oxindole; ¹³C NMR.

Abstract—The structure of 3-hydroxy-3-methyl-4-methoxyoxindole isolated from the roots of *Capparis tomentosa* has been determined by spectrometric methods.

INTRODUCTION

Capparis tomentosa Lam. (woolly caper-bush) is one of the best-known trees among African peoples for its supposed magico-medicinal properties and has the reputation of curing a variety of complaints ranging from coughs and colds to barrenness and impotence [1].

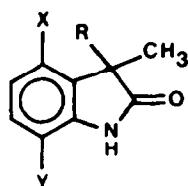
This paper deals with the structural elucidation of a new oxindole **1** from the roots *C. tomentosa*. Anticonvulsant properties have been reported for a number of 3-alkylated 3-hydroxyoxindoles [2, 3]. Compound **1**, however, showed only slight, if any, anticonvulsant activity.

RESULTS AND DISCUSSION

The IR spectrum (Nujol) of **1** exhibited absorptions characteristic for the hydroxy group (3375 cm⁻¹) and the

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	R	X	Y
1	OH	OCH ₃	H
2	SCH ₃	OCH ₃	H
3	SCH ₃	H	OCH ₃

5-membered lactam group (3210 and 1620 cm^{-1} , NH and 1715 cm^{-1} , C=O). The 80 MHz ^1H NMR spectrum (CD_3SOCD_3) of **1** showed the presence of a methyl (*s*, δ 1.42) and aromatic methoxy (*s*, δ 3.78) and a hydroxy group (*s*, δ 5.95). The aromatic protons appeared as two doublets (δ 6.42, *J* = 7.6 Hz and 6.60, *J* = 8.5 Hz), each showing fine splitting of 0.7 Hz, and a doublet of doublets (δ 7.16, *J* = 7.6 and *J* = 8.5 Hz), indicating that the methoxy group should be in either the 4- or 7-position. The lactam proton appeared as a broad signal at δ 10.14.

A comparison of the ^{13}C NMR chemical shift values (CD_3SOCD_3) (Table 1) of **1** with that of the 4-methoxy (**2**) and 7-methoxy (**3**) [5] derivatives of 3-methyl-3-methylthio-oxindole confirmed the position of the methoxy group of **1** and also allowed assignment of its aromatic carbon signals. A good correlation is obtained for the aromatic carbon frequencies of **1** and **2** (see Table 1); the only significant difference (2.2 ppm) between the resonances of **1** and **2** is observed for C-3a, which is nearest to the hetero atom on C-3. In contrast, the average difference for the best fit between the aromatic carbon frequencies of **1** and **3** is 10.1 ppm.

EXPERIMENTAL

Plant material. Roots of *C. tomentosa* were collected by Dr. A van Wyk on 1 December 1981 at Louis Trichardt, South Africa. A voucher specimen (AvW no. 5208) is on deposit in the Schweickerdt Herbarium of the University of Pretoria.

Extraction and separation. Air-dried plant material (22 kg) was extracted successively with C_6H_6 , EtOAc, MeOH and worked up in the usual fashion [6]. Compound **1** was isolated from a fraction eluted from a silica gel column (silica gel 60) with EtOAc-petrol (4:1).

3-Hydroxy-3-methyl-4-methoxyindole (1). Colourless crys-

Table 1. ^{13}C NMR frequencies of compounds **1** and **2** [5] (CD_3SOCD_3)

Carbons	δ (ppm)*		
	1†	2	1-2
2	179.6 (<i>s</i>)	177.9	1.7
3	72.9 (<i>s</i>)	49.4	
3a	118.4 (<i>s</i>)	116.2	2.2
4	156.6 (<i>s</i>)	156.2	0.4
5	105.6 (<i>d</i>)	105.6	0
6	130.2 (<i>d</i>)	130.2	0
7	103.0 (<i>d</i>)	102.9	0.1
7a	142.5 (<i>s</i>)	142.3	0.2
Me	22.0 (<i>q</i>)	18.8	3.2
OMe	55.3 (<i>q</i>)	55.6	-0.3

* Relative to tetramethylsilane.

† Splitting in the off-resonance proton decoupled spectrum in parentheses; *s* = singlet, *d* = doublet, *q* = quartet.

tals from EtOAc (0.03% yield); mp 230°; IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3375 (OH), 3210 (NH), 1715 (C=O), 1615 (NH); MS m/z (rel. int.): 193.073 [M]⁺ (39) (calc. for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: 193.070), 178 [M - Me]⁺ (25), 165 [M - CO]⁺ (44), 150 [178 - CO]⁺ (100), 135 [150 - Me]⁺ (20); ^1H NMR (80 MHz DMSO- d_6): δ 1.42 (3H, *s*, Me), 3.78 (3H, *s*, OMe), 5.59 (2H, *br s*, OH), 6.42 (1H, *dd*, 6.60 (1H, *dd*, 7.16 (1H, *dd*, 10.14 (1H, *s*, NH).

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