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LILALINE—A FLAVONOID ALKALOID FROM *LILIUM CANDIDUM*

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Key Word Index—*Lilium candidum*; Liliaceae; flavonoid; alkaloid; 3,5,7,4'-tetrahydroxy-8-(3-methyl-2-oxo-5-pyrrolidinyl)flavone; structure determination.

Abstract—A new flavonoid alkaloid, lilaline, was isolated from the aerial part of *Lilium candidum*. Its structure has been elucidated as 3,5,7,4'-tetrahydroxy-8-(3-methyl-2-oxo-pyrrolidinyl)flavone.

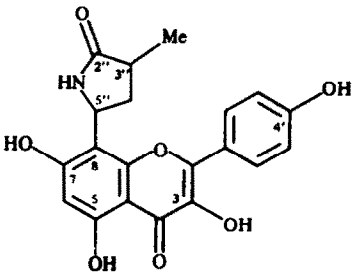
INTRODUCTION

During our search for new medicinal plant components, we investigated the aerial part of *Lilium candidum* L. growing in Czechoslovakia. In a previous publication [1] we described the isolation of a substance with the composition $C_{20}H_{17}NO_7$, while in this paper we describe its structure determination.

RESULTS AND DISCUSSION

A floral extract of white lily afforded an alkaloid which crystallizes from acetone in the form of yellow prisms, $C_{20}H_{17}NO_7$. The substance does not react with Dragendorff's reagent, but it gives a positive reaction with ferric chloride and aluminium chloride. In UV light the compound displays a yellow fluorescence, which becomes more intensive after exposure to ammonia. In the UV spectrum the absorption maxima at 272, 322 and 371 nm are characteristic of flavonols with a free 3-OH and spectral shift reagents [2] indicated free hydroxyl groups at the 5-, 7- and 4'-positions. The IR spectrum shows bands at 3300 cm^{-1} (OH), 1690 cm^{-1} (C=O in a five-membered lactam), 1640 cm^{-1} (C=O of benzopyrone) and 800 and 840 cm^{-1} (aromatic nucleus). The mass spectrum displays peaks at M^+ 383 for $C_{20}H_{17}NO_7$, calculated 383.3610, and further important fragment ion peaks at m/z 339 ($C_{19}H_{15}O_6$), 286 ($C_{15}H_{10}O_6$) and 176 ($C_{10}H_{10}NO_2$). The presence of the fragment ion 286 may be due to kaempferol while that at m/z 97 (C_5H_7NO) corresponds to the alkaloidal moiety.

It is evident from the ^{1}H NMR spectrum of lilaline that the alkaloidal moiety contains the fragment CH_3–/–CH–CH_2–CH–/–heteroatom. This fact and the IR and MS data indicate the presence of a 3-methyl-2-oxo-5-pyrrolidinyl group. The remaining signals in the ^{1}H NMR spectrum belong to the flavonoid moiety and characteristic for kaempferol substituted in position C-8 or C-6 (singlet at δ6.24). A comparison of the corresponding signals in the ^{13}C NMR spectra of lilaline at δ99.3 (C-6) resp. δ106.9 (C-8) and kaempferol [3] at δ98.2 (C-6) resp. δ93.5 (C-8) favour C-8 substitution. The signal at δ183.9 (C-2') confirms the presence of pyrrolidinone in the molecule of lilaline. Thus lilaline is 3,5,7,4'-tetrahydroxy-8-(3-methyl-2-oxo-5-pyrrolidinyl)flavone (1).



1

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 *Phyllosphadix iwatensis* [5] and vochysine from *Vochysia guaianensis* [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°, $[\alpha]_{578}^{27}$ +65° (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, + $AlCl_3$: 276, 312, 357, 436 + $AlCl_3$–HCl: 273, 308, 353, 432 + NaOAc: 282, 322, 402 + H_3BO_3–NaOAc: 272, 320, 372. ^{1}H NMR (300.13 MHz, CD_3OD): δ1.29 (3H, *d*, *J* = 7.4 Hz, CH_3), 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, *dqd*, *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'). ^{13}C NMR (75.47 MHz, CD_3OD): δ17.5(CH_3), 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; ^{13}C 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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