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EXOZOLINE, A NEW CARBAZOLE ALKALOID FROM THE LEAVES OF *MURRAYA EXOTICA*

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Key Word Index—*Murraya exotica*; exozoline; carbazole alkaloid.

The isolation of a number of coumarins [1–5], indoles [6, 7], flavanoids [8–10] and carotene [11] from various parts of *Murraya exotica* Linn (syn. *M. paniculata* (L.) Jack.) has been reported earlier. The present report relates to the structure of a new carbazole alkaloid isolated from the leaves of the same plant.

Exozoline (**1**), $C_{23}H_{27}NO$ (M^+ 333), mp 180–182° was isolated from the alcoholic extract of the leaves of *M. exotica* by CC on alumina. The homogeneity of exozoline was checked by TLC using various solvent systems. The UV absorption spectrum of exozoline in EtOH with λ_{max} at 242 (log ϵ 4.47), 256 (log ϵ 4.18) and 306 nm (log ϵ 3.97) was strikingly similar to that of 2-methoxy carbazole or its equivalent chromophore [12].

The IR spectrum of exozoline showed absorption peaks at ν_{max}^{KBr} 3440 cm^{-1}: (—NH— function), 1625, 1615, 1445 (aromatic residue), 1380 (C-methyl) and 780, 740 (substituted benzene derivative).

The NMR spectrum of exozoline (60 MHz in $CDCl_3$) showed signals for one indolic proton (*br s*, δ 7.8 confirmed by D_2O exchange), one aromatic proton (*s*, δ 7.54), four aromatic protons (*m*, δ 7.28 6.98), one benzylic proton (*m*, δ 3.34), three protons of an aromatic C-methyl group (*s*, δ 2.28), four deshielded methylene protons of a cyclohexane system (*d*, δ 1.82 and 1.76); three protons of a C-methyl group on a carbon atom linked to an oxygen function (*s*, δ 1.39) and three protons of a methyl group of the isopropyl moiety (*d*, δ 0.62). The other methyl group of the isopropyl moiety appeared at δ 1.36 and was overlapped by the signal for the O—C—CH_3 group at δ 1.39 [13]. The appearance of one of the aromatic protons as a singlet (δ 7.54) clearly indicated the position of the aromatic methyl at C-3 [14]. The NMR spectrum of exozoline has a strong similarity with that of cyclomahanimbine [13] except that the two methylene protons at δ 4.72 had disappeared; instead a doublet for three protons appeared at δ 0.62. The MS had the molecular ion peak at *m/e* 333 (98.50%) plus two other significant peaks at 248 (100% and 210 (21.5%) which can be represented by the species **3** and **4**.

The available evidence suggests that exozoline is a pentacyclic alkaloid built on a 2-hydroxy-3-methyl carbazole skeleton to which a monoterpene is attached to the carbazole at C-1, the terpenoid fragment forms the part of the bicyclic system having a benzylic hydrogen and a cyclohexane ring system with an isopropyl group attached. Therefore exozoline can be represented by structure **1**.

The structure of exozoline was confirmed by the superimposable IR spectrum of dihydrocyclomahanimbine obtained by hydrogenation of cyclomahanimbine (**2**) and also by mmp determination of exozoline with dihydrocyclomanhanimbine.

EXPERIMENTAL

Isolation of exozoline. The defatted plant material was extracted with EtOH. The conc extract was digested with 10% HCl for 3 hr, the soln filtered, washed with H_2O until free from acid and dried. The dark green residue was extracted with C_6H_6 and the extract was concd and chromatographed over Brockmann alumina. The column was successively eluted with petrol and C_6H_6. Exozoline was obtained from the petrol elute and crystallized from petrol–C_6H_6, mp 180 182°. [Found: C, 82.46; H, 8.26; N, 4.29. Calc. for $C_{23}H_{27}ON$: C, 82 84, H, 8.16; N, 4.20%].

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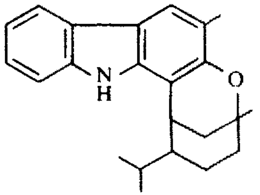

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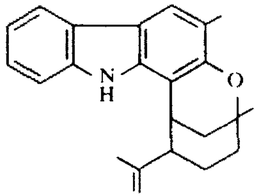

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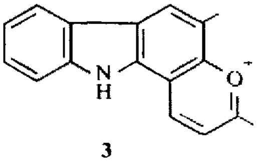

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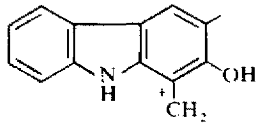

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(−)-(*TRANS*-4′-RHAMNOSYLOXY-3′-METHOXYCINNAMYL)LUPININE, A NEW LUPIN ALKALOID IN *LUPINUS LUTEUS**

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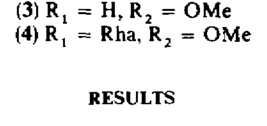
Key Word Index—*Lupinus luteus*; Leguminosae; alkaloid; glycoside; ( )-(*trans*-4′-rhamnosyloxy-3′-methoxycinnamyl)lupinine.

INTRODUCTION

We have recently isolated two ester alkaloids, (−)-(*trans*-4′-hydroxycinnamyl)lupinine (**1**) and its 4′-rhamnoside (**2**), from the young seedlings of *Lupinus luteus* [1, 2]. An enzymatic system for the formation of **1** in *Lupinus* seedlings has also been described [3]. We have now established the presence of (−)-(*trans*-4′-rhamnosyloxy-3′-methoxycinnamyl)lupinine (**4**) in the fresh seedlings of *Lupinus luteus*.



Scheme 1. Lupinine derivatives found in the fresh seedlings of *Lupinus luteus*.

(1) $R_1 = H, R_2 = H$
(2) $R_1 = Rha, R_2 = H$
(3) $R_1 = H, R_2 = OMe$
(4) $R_1 = Rha, R_2 = OMe$

RESULTS

From the EtOH extracts of the fresh 9-day-old seedlings of *Lupinus luteus*, grown in the dark at 28°, **4** was isolated as a colourless amorphous solid, $[\alpha]_D^{22}$ $-78°$, by repeated chromatography of the basic fraction. It gave a single grayish green with *p*-anisaldehyde–H_2SO_4 reagent for reducing sugars on TLC.

The MS spectrum of **4** showed an M^+ ion at *m/e* 491 (1%) and fragment ions corresponding to the loss of the rhamnosyl-moiety below the ion at *m/e* 345 closely resembled those of (−)-(*trans*-4′-hydroxy-3′-methoxycinnamyl)lupinine (**3**), which coexists with **4** in the same seedlings.

The sugar obtained by controlled hydrolysis of **4** with 3% HCl was identified as L-rhamnose by co-chromatography on PC and by Si–TLC. The aglycone was also confirmed as **3** by comparing MS, TLC and HPLC of the natural compound with synthetic material [6].

The PMR spectrum of **4** revealed the presence of a methyl-group of the rhamnosyl-moiety at δ 1.27 (3H, *d*, $J = 6$ Hz), anomeric proton at δ 5.50 (1H, *bs*) and two sharp peaks of three protons for a methoxyl group at δ 3.86 and 3.88.

From these results, the structure of **4** can be represented as (−)-(*trans*-4′-rhamnosyloxy-3′-methoxycinnamyl)lupinine (**4**), a new natural product. It was subsequently inferred from its large negative optical rotation ($[\alpha]_D^{22}$ -78.5; **3**; $-8.5°$) that the configuration at the anomeric center of the rhamnosyl-unit in **4** involves an α-L-rhamnosidic linkage (see [2]). Furthermore, the PMR spectrum of **4** showed two pairs of AB-doublets due to *cis* and *trans* olefinic protons of the cinnamyl-moiety: from the data of chemical shifts, coupling constants and absorption intensities, it was proved that **4** was a mixture of *cis* and *trans* isomers at the ratio of *ca* 1:3, respectively. The conversion of *trans*-cinnamates, such as **1** [1], **2** [2], **3**, **4** and desmethoxyabresolines [4], into the *cis*-isomers during a treatment of the samples in daylight is unavoidable.

The concentration of **4** in the dry seeds of *Lupinus luteus* is extremely low, but its concentration increased rapidly along with those of **1**, **2** and **3** during the first 4–9 day's growth of seedlings at 28°.

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* This work was presented partly at the 96th Annual Meeting of the Pharmaceutical Society of Japan, 6 April 1976 (Meeting Abstracts, II, p. 210).