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STUDIES ON ORCHIDACEAE ALKALOIDS VII*

Structure of a glucosidic alkaloid from Malaxis congesta comb. nov. (Rchb. f.)

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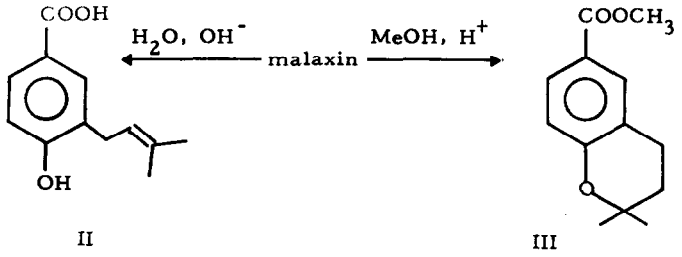
Most of the species of the subfamily Liparidinae have been shown to contain alkaloids [2-5]. From Malaxis congesta comb. nov. (Rchb. f.) we have isolated a crystalline alkaloid for which we propose the name malaxin (I); m.p. 151-159°, $[\alpha]_D^{22}$ -31° (c 2.7, ethanol). Malaxin was shown by elemental analysis and high resolution mass spectrometry to have the empirical formula $C_{26}H_{37}NO_8$.

The UV spectrum ($\lambda_{max}^{ethanol}$ 209 mμ, ε 20000; 254 mμ, ε 17000) and the IR absorption at 1710 cm^{-1} suggest that the alkaloid is an aromatic ester. Hydrolysis with aqueous alkali (4 M NaOH, 100°, 15 h) yielded 4-hydroxy-3-(3-methyl-2-butenyl)-benzoic acid (II) [6,7], m.p. 99-102°, exhibiting maxima at 259 mμ in acidic ethanol and 288 mμ in alkaline ethanol [8]. Acid methanolysis afforded 2,2-dimethyl-6-methoxycarbonylchroman (III) [7], m.p. 79-80°. The structures of II and III were further confirmed by NMR, IR and mass spectra.



II III

Acid hydrolysis of I yielded laburnine and glucose. Laburnine [9] was identified by its m.w. 141 (mass spectrometry, intensities of all peaks identical with those of lindelofidine), optical rotation $[\alpha]_D^{22}$ +19.5° (c 1.3, ethanol), picrate m.p. 169-173° and methiodide m.p. 303-305°. Paper chromatography (ethyl acetate, acetic acid, water; 3:1:1, v/v) showed the sugar to have the same R_f-value as glucose. The sugar was further reduced with sodium borohydride and the product acetylated.

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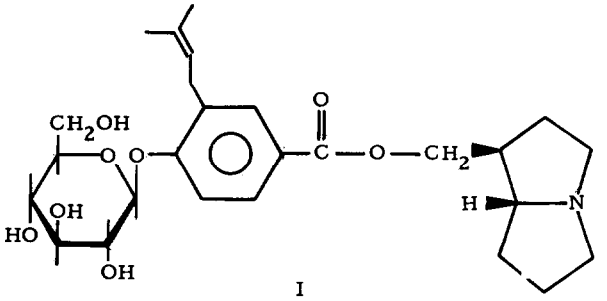
*Number VI of this series see Ref. 1.

The retention time [10] and mass spectrum [11] of the acetyl derivative were identical with those of glucitol hexaacetate. An aqueous solution of the sugar had a positive rotation and hence the sugar must be D-glucose. The strong negative molecular rotation ($[M]_D^{22}$ -151°) of I and the small positive molecular rotation ($[M]_D^{22}$ +27.5°) of laburnine indicate the presence of a β-glucosidic linkage. The fact that the glucosidic linkage was broken during the alkaline treatment is also consistent with a β-glucoside [12]. Hence we propose the following structure for I:



I

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