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ALKALOIDS OF LYSICHITON CAMTSCHATCENSE SCHOTT VAR. JAPONICUM MAKINO

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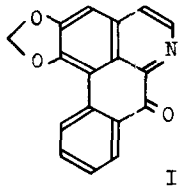
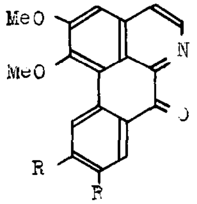
The Araceae plant family has not extensively been investigated and, particularly, no alkaloid appears to have been isolated from Lysichiton species. This report deals with the isolation and characterization of alkaloids from L. camtschatcense Schott var. Japonicum Makino (Japanese name: Mizubasho). A major alkaloid (I) was isolated in 0.01% yield from chloroform extracts of dried roots of the plant. The alkaloid I was crystallized from chloroform as yellow needles, had m.p. 279-281° (decomp.), and was analyzed for $C_{17}H_9O_3N$; mol. wt. 275 (mass). The NMR, IR and UV spectra of this compound were practically the same as those reported on liriodenine (1) which had been isolated from a number of species of Magnoliaceae (2). Chromic acid oxidation of I gave an acid which in turn was converted into benzo[g]-quinoline-5,10-dione (1) on pyrolysis. These facts strongly suggested that the alkaloid I would be liriodenine, and the identity was established by direct comparison (3).

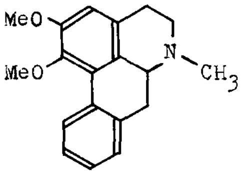


I



II R=H

III R=MeO



IV

The second yellow alkaloid (II) was isolated in 0.005% yield by chromatography of the mother liquors from I on alumina. The alkaloid II was crystallized from ethanol as yellow needles, m.p. 210-211°(decomp.), and analyzed for $C_{18}H_{13}O_3N$. Its IR spectrum had a peak of highly conjugated carbonyl group at 1675 cm^{-1}, and its UV and visible light absorption spectra closely resembled those of I; $\lambda_{max.}^{EtOH}$ 235, 270, 307 and 400 mμ (log ε, 4.47, 4.41, 3.76 and 3.94); $\lambda_{max.}^{0.1N\text{-}HCl\text{-}EtOH}$ 249, 276, 306 and 453 mμ (log ε, 4.33, 4.44, 3.82 and 3.58). These facts indicated that, like I, the second yellow alkaloid II should possess a 7-oxo-dibenzo[de,g]quinoline skeleton. The NMR spectrum of alkaloid II showed absorptions for six protons as two singlets at 6.00 and 5.98 τ, which could be assigned to two methoxyl groups. The base must, therefore, be dimethoxy-(desmethylenedioxy)-liriodenine.

The methoxyl groups could be located, on biogenetic ground, at C-1 and C-2 as represented by II; these positions almost invariably bear oxygen functions in aporphines from which liriodenine type alkaloids are considered to have been derived oxidatively (4,5). As expected from the structure II, absorptions for protons on C-3 and C-5 appeared as a singlet and a doublet at 2.88 and 1.25 τ respectively, and these positions were approximately the same with those reported on O-methylatheroline (III) (5). The final conclusion of its structure was established through synthesis. Thus, 3,4-dihydro-6,7-dimethoxy-1-(o-nitrobenzyl)isoquinoline (6) upon oxidation with selenium dioxide in acetic acid (7) gave 6,7-dimethoxy-1-(o-nitrobenzoyl)isoquinoline, $C_{18}H_{14}O_5N_2$, m.p. 179-181° (from MeOH); $\nu_{max.}^{Nujor}$ 1685 (CO), and 1528 and 1347 cm^{-1} (NO_2). Catalytic reduction of this compound afforded the corresponding 1-(o-aminobenzoyl) derivative which underwent the Pschorr cyclization to yield a product identical in all respects with the alkaloid II*.

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* After we confirmed the structure, we noticed that the alkaloid II should be identical with "oxidation product of nuciferine" (8) obtained by Tomita et al., although, unfortunately, the direct comparison could not be made. In view of the first isolation of this alkaloid from the plant, we wish to designate the compound "lysicamine". We wish to express our thanks to Professor M. Tomita for his kind suggestion that it would be better to give the alkaloid a name related to natural sources.

Furthermore, two colorless crystalline bases were isolated by chromatography on alumina of crude bases which were obtained from methanol extracts of the dried roots; elution with benzene-chloroform (9:1) gave the third alkaloid which was crystallized from ether-hexane as colorless needles, m.p. 52-53° , mol. wt. 200 (mass); $\nu_{max.}^{KBr}$ 1665, 1610, 1585, 1563 and 1485 cm^{-1}; $\lambda_{max.}^{EtOH}$ 225, 270, 305 and 318 mμ (log ε , 4.69, 4.21, 3.87 and 3.75). Identification of this alkaloid is now under investigation.

The fourth alkaloid was isolated from fractions eluted with benzene-chloroform (8:2) and crystallized from ether-hexane as colorless needles, m.p. 161-162°, $\lambda_{max.}^{EtOH}$ 230 and 273 mμ (log ε , 4.22 and 4.10), which were rather unstable and gradually decomposed, when exposed to air. On the basis of the m.p. and spectral behaviors as well as biogenetic considerations, this alkaloid was presumed to be nuciferine (IV) (2). This was established by direct comparison with an authentic sample of the alkaloid (9).

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2) Cf. M.Shamma and W.A.Slusarchyk, *Chem. Rev.*, **64**, 59 (1964).

3) We express sincere thanks to Dr. W.I.Taylor and Professor I.R.C.Bick for the direct comparison.

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9) We express sincere thanks to Professor M.Tomita for the direct comparison.