

STRUCTURE OF THE ALKALOID ELEGANTINE

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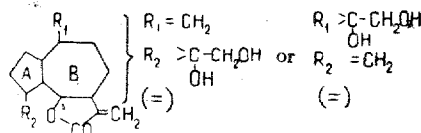
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We have cleaved the alkaloid elegantine [1] into tyramine and lactone A. Lactone A, $C_{15}H_{18}O_4$, mp 148-149° C (ethyl acetate), $[\alpha]_D^{20} +102^\circ$ (c 0.48; chloroform), mol. wt. 282 (mass spectrum) differs from the lactones described in the literature; we have called it eleanin. It contains a γ -lactone ring conjugated with a double bond (1755 cm^{-1}), $\lambda_{\text{max}}^{\text{ethanol}}$ 203 m μ (log ϵ 4.26), three hydrogenatable double bonds (catalytic reduction according to Adams), two of which are terminal (1650, 1420, and 910 cm^{-1}). The ozonolysis of elegantine gave about 2 moles of formaldehyde, identified as the dimedone derivative. Eleanin contains two hydroxy groups (IR spectrum: 3450 cm^{-1}), one of which acetylates with acetyl chloride and acetic anhydride in pyridine. The acetylation product is a chromatographically homogeneous transparent resin and its IR spectra is: 3470 cm^{-1} (hydroxyl), 1730 cm^{-1} (ester carbonyl). The two hydroxyls are on neighboring carbon atoms since eleanin is oxidized by periodic acid. From the volatile products of the reaction, formaldehyde was isolated. Consequently, one hydroxyl is primary and the other, probably, tertiary.

The NMR spectrum of eleanin has no signals from protons of methyl groups.

The dehydrogenation of hexahydroeleanin with selenium gave a mixture of azulenes (blue oil) which was purified through its complex with phosphoric acid followed by chromatography on alumina. UV spectrum of the mixture: $\lambda_{\text{max}}^{\text{ethanol}}$ 350, 368, 600 m μ (log I_0/I , 1.24, 1.15, 0.62).

On the basis of the information obtained and by analogy with the lactones isolated from the genus Saussurea [2-4] we propose the following formula for eleanin:



Since the methylene group conjugated with lactone is very active and forms condensation products with ammonia under very mild conditions [5], we condensed eleanin with ammonia at 0° C. The product obtained behaved as an alkaloid: it dissolved completely in dilute acid, and gave a precipitate with silicotungstic acid and an orange coloration with Dragendorff's reagent.

Consequently we assume that in the alkaloid the lactone is bound to tyramine through the methylene group conjugated with the lactone. This is confirmed by the IR spectra of elegantine (CO band 1765 cm^{-1}) and of eleanin ($\text{C}=\text{O}$ 1755 cm^{-1}).

REFERENCES

1. A. M. Khashimov, L. S. Smirnova, S. F. Matkhalikova, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], **4**, 367, 1968.
2. M. Romanuk, V. Herout, and F. Sorm, Coll., **21**, 894, 1956.
3. S. B. Mathur, S. V. Hiremath, G. H. Kulkarni, G. R. Kelkar, and S. C. Bhattacharyya, Tetrah., **21**, 3575, 1965.
4. V. Herout, Planta Medica (Suppl.), **97**, 1966.
5. G. H. Kulkarni, G. R. Kelkar, and S. C. Bhattacharyya, Tetrah., **20**, 1301, 1964.

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