

ANADOLINE, A NEW SENECIO ALKALOID FROM SYMPHYTUM ORIENTALE

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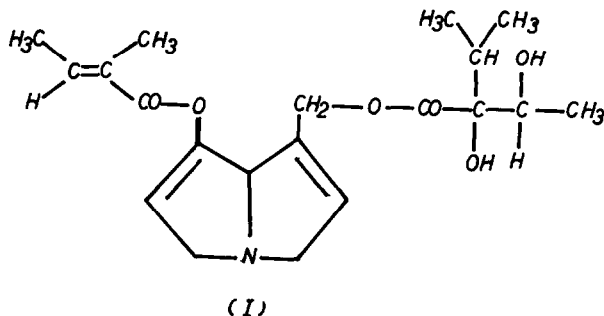
(Received in UK 14 May 1970; accepted for publication 27 May 1970)

A survey of the literature to date would indicate that, S.orientale has not been investigated whereas other symphytum species such as S.officinalis (1,2,3,4,5) and S.asperum (6) have been studied and senecio alkaloids namely symphytine and echimidine were isolated and determined.

An alcoholic extract of the roots of the plant yielded a mixture of seven alkaloids, one of which was found to be a new alkaloid.

Anadoline (I), m.p 186°C (degradation), $(\alpha)_D^{22} + 9.2$ (c=0.7, CHCl₃), has a molecular formula of C₂₀H₂₉NO₆.H₂O from the elementary analysis and the mass spectra with a molecular ion peak at 379 which corresponds C₂₀H₂₉NO₆. Anadoline shows λ_{max} 226 nm (log.ε 3.26) and infrared peaks (KBr) at 3450 (OH), 1740 and 1700 (two ester carbonyl), 1650 (double bond), 1387 cm⁻¹ (isopropyl group). NMR spectrum (in CDCl₃) of I reveals the presence of five methyl groups at 0.9 and 1.07 δ (3H each, d, j=7 cps) (-CH(CH₃)₂), at 1.30 δ (3H, d, j=6.5 cps) (-CH-CH₃), at 1.90 δ (6H, s, with slight divisions at the peak) (CH₃HC=CCH₃-). D₂O exchange shows the presence of two OH groups at 4.8 δ (2H, s, with slight divisions at the peak), a vinylic proton is at 6.8 δ (1H, m) (CH₃HC=CCH₃-). The other protons are as follows: C₂ at 5.92 δ (1H, s); C₃ at 4.02 and 4.2 δ (1H each a pair of doublets, j=9cps); C₅ at 2.1 and 2.4 δ (1H each, m); C₆ at 5.1 δ (1H, t); C₈ at 4.7 δ.

NMR spectra of anadoline is quite similar to that of symphytine and echimidine. Conformation of the structure was obtained by hydrolysis and by hydrogenolysis of the base.



The hydrolysis of anadoline was performed with a 10 % aqueous solution of NaOH. The acid and the amino alcohol parts were separated in a usual way. A white crystalline material was obtained from the acid part, m.p 64°C, composition $C_5H_8O_2$. Preparative thin layer chromatography yielded another acid, m.p 90°C, molecular formula $C_7H_{14}O_4$. The acids were found to be tiglic and trachelantic respectively by mixed m.p's and the IR curve comparison with the standard samples.

Amino alcohol part was not obtained as a crystalline compound. Comparison with the standard samples of retronecine and heliotridine did not give the same R_f values as it was expected. Instead of one double bond, the amino alcohol contains two double bonds, as it was proved by hydrogenation.

Hydrogenolysis of anadoline in dilute sulfuric acid using platinum oxide as catalyst consumed four moles of hydrogen, showing the presence of two double bonds in amino alcohol. This type of senecio alkaloids always contain one double bond at C_1 position. According to NMR findings the second double bond could only be present at C_6 . There are three vinylic hydrogens, one of which belongs to tiglic acid, the other is at C_2 position and the third could be at C_6 . If the double bond was found at C_5 , than the NMR spectrum should show one more vinylic proton.

The hydrogenolysis product was oily, which formed a picrate with a composition $C_{13}H_{23}O_2N \cdot C_6H_3O_7N_3$, m.p 199-201°C. When this was compared with the

picrate of a compound obtained similarly from echimidine, the mixed m.p. undepressed. The compound is 7-(2'-methyl butyryl)retronecanol. All of the findings are in agreement with the proposed structure.

Acknowledgements

This investigation was supported by the Scientific Research Council of Turkey (TAG-96). The authors thank Prof. Dr. C. C. J. Culvenor (Melbourne-Australia) for various samples of senecio alkaloids and acids. Prof. Dr. H. Wagner (München-Germany) for NMR and mass spectra. Also we thank Prof. Dr. A. Baytop (Istanbul-Turkey) and Ass. Prof. Dr. N. Tanker (Ankara-Turkey) for the identification of the plant.

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