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Chemical Constituents of *Toddalia aculeata* Pers.*

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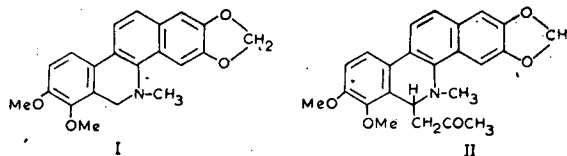
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The base toddalinine from *T. aculeata* Pers. has been identified as dihydrochelerythrine. The acetone addition product of chelerythrine has been isolated as an artefact. Three coumarins not previously reported to occur in the plant have been isolated and identified as pimpinellin, isopimpinellin and 6-(3'-chloro-2'-hydroxy-3'-methyl)-n-butyl-5,7-dimethoxycoumarin. The last of these is an artefact arising from epoxy coumarin aculeatin, by the action of hydrochloric acid used in the alkaloid isolation.

TODDALIA ACULEATA Pers. (Fam. Rutaceae) has been the subject of extensive chemical investigation. Two alkaloids^{1,2}, toddaline and toddalinine, were isolated from the root bark. The former, m.p. 204.5°, was identified² as chelerythrine by direct comparison of the base as well as its pseudocyanide, m.p. 262°. Toddalinine, reisolated by the earlier method² and purified rigorously; has m.p. 165°, and forms a yellow hydrochloride, m.p. 245° (decomp.). The base analyses for the formula C₂₁H₁₉O₂N. It has now been identified as dihydrochelerythrine (I) by direct comparison with an

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authentic sample prepared by the reduction of chelerythrine chloride with lithium aluminium hydride³. Dihydrochelerythrine has since been isolated by Scheuer *et al.*⁴ from *Fagara semiarticulata*.



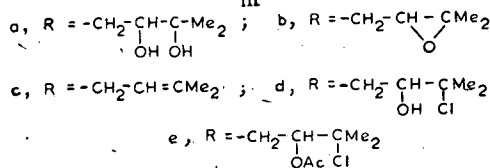
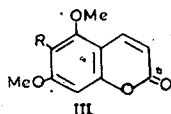
Besides the above two alkaloids, we isolated a small amount of a base, C₂₄H₂₃O₅N; m.p. 193.4°; λ_{max}. 228, 283, 320 (inf.) mμ (log ε 4.52, 4.61, 4.18); ν_{max}. 1610, 1715 cm.⁻¹. Its NMR spectrum showed the presence of six aromatic protons (δ 6.9-7.8), a methylenedioxy group (δ 6.02), two OCH₃ groups (δ 3.90, 3.95), an NCH₃ group (δ 2.64) and a methyl ketone group (δ 2.04). Besides these there was a one-proton quartet (δ 5.1) due to a —N—CH—

and a two-proton multiplet (δ 2.34) due to a methylene group adjacent to a ketone. The mass spectrum of the base showed a molecular ion peak at m/e 405 and a strong peak at m/e 348 (metastable peak at 299.5) due to the elimination of the —CH₂COCH₃ group. The base has been identified as the hitherto unknown acetone addition product (II) of chelerythrine by comparison with an authentic sample prepared by base-catalysed addition of acetone to chelerythrine. The compound is almost

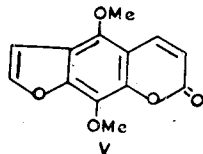
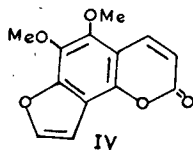
certainly an artefact produced by the action of acetone (used in the isolation) on chelerythrine. It is interesting to note that 9-ethoxychelerythrine, another artefact of chelerythrine, has been isolated by Torto *et al.*⁵ from *F. xanthoxyloides*.

Chromatography over silica gel of the neutral material left after removal of the alkaloids as their hydrochlorides has yielded besides toddalolactone^{1,2,6} (IIIa), three coumarins A, B and C which have not been previously reported to occur in *T. aculeata*.

Compound A, m.p. 118°, C₁₃H₁₀O₅ (mass spectrum, m/e 246, 231, 203, 188, 175, 160, 147, 132), λ_{max}. 219, 251, 304 mμ (log ε 4.32, 4.37, 4.03), ν_{max}.



1575, 1620, 1725 cm.⁻¹, has been identified as pimpinellin (IV) by direct comparison with an authentic sample.



Compound B, m.p. 150°, C₁₃H₁₀O₅ (mass spectrum, m/e 246, 231, 203, 188, 175, 160, 147, 132), λ_{max}. 222, 245, 269, 312 mμ (log ε 4.39, 4.17, 4.26, 4.10), ν_{max}. 1595, 1630, 1730 cm.⁻¹ has been identified

as isopimpinellin (V) by direct comparison with an authentic sample.

Compound C, m.p. 153°, C₁₆H₁₈O₅Cl (mass spectrum, m/e 326, 290, 255, 249, 219, 205, 189, 176, 161, 147), [α]_D +72.26° (c. 2.5, CHCl₃), λ_{max}. 208, 226, 245 (inf.), 254 (inf.), 330 mμ (log ε 4.55, 4.31, 3.87, 3.74, 4.24), ν_{max}. 1605, 1715 cm.⁻¹, is very similar to toddalolactone (IIIa) in its UV spectrum. Its NMR spectrum shows the coumarin protons on C-3 and C-4 as doublets (J=10 cps.) centred at δ 6.23 and 7.86 respectively, one aromatic proton (singlet at δ 6.63), two methoxyls (δ 3.92) and two tertiary C-CH₃ groups (δ 1.68). The compound forms a monoacetate (IIIe), m.p. 79-80°. Compound C evidently has the structure (IIIId) and is an artefact produced by the action of hydrochloric acid (used in the alkaloid isolation) on the epoxy-coumarin aculeatin (IIIb) isolated previously from the plant by Dutta⁷.

During our work we did not encounter any toddaculine⁸ (IIIc) or aculeatinhydrate⁷.

Satisfactory analyses were obtained for all compounds reported in this communication.

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