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The Alkaloids of *Senecio paucicalyculatus* Platt.

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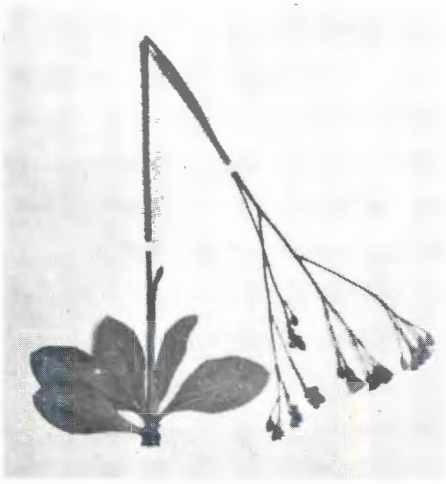
Senecio paucicalyculatus, (National Herbarium No. 27246) which is synonymous with *S. launayaefolius* O. Hoffm., is one of the less common species of the *Paucifolii group*. It occurs only in some parts of Natal, in the Estcourt region and near Pietermaritzburg. During the flowering period the plant is usually from twelve to eighteen inches high. It has a single, erect, leafless stem with only a few leaves at the base. Until flowering, therefore, there is not much danger of animals being poisoned by it, and no case of poisoning from *S. paucicalyculatus* has so far been reported.



Senecio paucicalyculatus Platt.

The material used for this investigation was collected at Cedara near Pietermaritzburg, where a small patch was found growing in a vlei. On account of drought most of the plants did not flower during the 1941 season, so that only a small amount of flowering plants could be collected during November. The rest of the material used was collected during February and March, and consisted of plants which did not flower at all. Plants were dug up, root and all, dried and ground. The root material made up only a relatively small percentage of the total.

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Three alkaloids have been isolated from *S. paucicalyculatus*, viz. *retrorsine* and *isatidine*, both in considerable quantities, and a very small amount of a *new alkaloid*, probably $C_{18}H_{27}O_8N$, which melts at 184° C. The amount of *isatidine* seems to decrease considerably with the age of the plant, whilst the amount of *retrorsine* increases. Whereas the early flowering plants, which were collected in November, contained over 2·5 per cent. crude *isatidine* and 1·0 per cent. crude *retrorsine* in the leaves and roots, those collected during February yielded only a small amount of *isatidine* and 2·3 per cent. *retrorsine*.

Retrorsine and *isatidine* were identified by comparison of their properties with those of authentic specimens of the respective alkaloids isolated from *S. isatideus* and *S. retrorsus*.

The properties of the third alkaloid, for which the name "*paucicaline*" is suggested, are still being investigated. It may, however, be mentioned that it shows much similarity with *isatidine*.

It is very soluble in cold water and insoluble in chloroform. Increased solubility in water with increased number of OH-groups, was also noticed in *isatidine*, $C_{18}H_{25}O_7N$ and *seleratine*, $C_{18}H_{27}O_7N$.

Method of Isolation.

The method used for the extraction of the dry material was the same as the method already described previously (H. L. de Waal and T. P. Pretorius, 1941) for the extraction of *Senecio* alkaloids.

The aqueous extract is filtered and the filtrate, after shaking with ether, concentrated on a waterbath under reduced pressure and filtered again. After alkalinification with 20 per cent. ammonia the alkaloids crystallise out. This crop of crystalline alkaloid is filtered off and the mother liquor left to stand for further crystallisation.

When *isatidine* predominates, the alkaloids are best separated by treating the crude mixture with chloroform, followed by hot ethyl acetate. The chloroform fraction contains *retrorsine*, the ethyl acetate fraction mainly *paucicaline*, whilst *isatidine* remains undissolved. The following method gives good results where the yield of *isatidine* is small.

The total residue is crystallised from absolute alcohol and the first crop of crystals, which is chiefly a mixture of *retrorsine* and *paucicaline*, is filtered off. On evaporation of the mother liquor mostly *isatidine* is obtained. This is further purified by treatment with hot ethyl acetate and recrystallisation from alcohol or water.

The crystalline mixture from the absolute alcohol is dissolved in hot ethyl acetate. The first crystallisation yields almost pure *retrorsine*. On concentration of the mother liquor *paucicaline* crystallises in very fine needle-like crystals, together with a little admixed *retrorsine* which can easily be removed by treatment with chloroform.

Experimental.

400 gm. coarsely ground plant material (from plants in early flowering stage) was extracted with 1,500 c.c. 96 per cent. alcohol for approximately 30 hours in a glass soxhlet. The alcohol was distilled off under reduced

pressure on a waterbath, the aqueous solution diluted to 2,000 c.c., acidified with citric acid and filtered after two days. The filtrate was shaken successively with ether, concentrated under reduced pressure on a waterbath to 600 c.c. and filtered again. A mixture of alkaloids crystallised out, and and this was filtered off and treated with chloroform. The chloroform insoluble residue was treated with hot ethyl acetate and filtered. The filtrate was evaporated to dryness at room temperature and the residue dissolved in absolute alcohol. A small amount of *paucicaline* crystallised out.

The fraction insoluble in ethyl acetate was crystallised from ethanol. Determination of its chemical properties and those of its derivatives proved it to be identical with *isatidine*.

The mother liquor was exhausted with chloroform and the chloroform shakings added to the chloroform-soluble fraction of the crude akaloid which crystallised from the aqueous solution. After evaporation of the chloroform the residue was crystallised from absolute alcohol followed by ethyl acetate, and identified as *retrorsine*.

2 Kg. of dry material from plants collected during February-March was extracted in the same way except that a slightly modified procedure was used for the separation of the alkaloids. Instead of treating with chloroform, the crude mixture was dissolved in ethanol. The first crop of crystals was recrystallised from ethyl acetate. The mother-liquor residue consisted of a mixture of *retrorsine* and *paucicaline*, which were separated with chloroform. *Isatidine* was obtained from the residue of the alcoholic mother liquor.

Alkaloidal Yield.

(*a*) 400 gm. dry material (young plants) yielded—

isatidine 10·5 gm.
retrorsine 4·0 gm.
paucicaline trace.

(*b*) 2,000 gm. dry material (old plants) yielded—

retrorsine 46·0 gm.
isatidine 2·0 gm.
paucicaline 0·3 gm.

Chemical Properties of Paucicaline.

Paucicaline crystallises from absolute alcohol in very fine needles, which melt with decomposition at 184° C.

It gives precipitates with the reagents of Wagner, Dragendorff, Sonnenschein and Mayer.

It decolourises dilute $KMnO_4$ in $2\frac{1}{2}$ per cent. Na_2CO_3 solution.

Solubility.

Paucicaline is very soluble in cold water, acetic acid and dilute mineral acids. It dissolves readily in ethanol and methanol, and is less soluble in ethyl acetate. It is insoluble in chloroform, acetone and ether.

Micro-analysis.

Found: C = 57·43%, H = 7·41%, N = 3·25%

Calculated for: $C_{18}H_{27}O_8N$: C = 57·60%, H = 7·20%, N = 3·73%

Note by Prof. H. L. de Waal.

This new water-soluble alkaloid *paucicaline* appears to be identical with a new alkaloid isolated by Dr. J. S. C. Marais and the writer from the water-soluble fraction of *S. retrorsus* (ex Inungi, Kokstad, East. Prov.) during an investigation of its alkaloids at Onderstepoort in 1941. This alkaloid was named *lanigerosine* (unpublished) and was separated and isolated in the form of its nitrate, m.p. 245°.

Analysis.

3·555 mgm: 6·249 mgm. CO_2 and 1·843 mgm. H_2O

3·327 mgm: 0·217 ml. N_2 at 22·5° C. and 623·5 mm. Hg.

Found: C 47·94%; H 5·80%; N = 6·18%

Calc. $C_{18}H_{27}O_8N.HNO_3$: C = 48·21%; H 6·15%; N 6·24%

Calc. $C_{18}H_{25}O_8N.HNO_3$: C = 48·44%; H 5·87%; N = 6·27%

The formula for this new alkaloid is more likely $C_{18}H_{27}O_8N$ and it is now proposed to investigate its presence in another senecio member of the Paucifolii group, viz. *S. isatideus* and to establish its identity and products of hydrolysis.

Summary.

1. *Senecio paucicalyculatus* has been examined for toxic alkaloids.

2. Three alkaloids, viz. *retrorsine*, *isatidine* and a new alkaloid, *paucicaline*, have been isolated.

3. *Paucicaline*, probably $C_{18}H_{27}O_8N$, melts at 184° C.

4. The relative amounts of *retrorsine* and *isatidine* seem to vary with the age of the plant.

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