

## SENECIO MAGNIFICUS F. MUELL., A SOURCE OF SENECTIONINE\*

By C. C. J. CULVENOR†

A prerequisite for the greatly increased attention given to the biological properties of the pyrrolizidine alkaloids during the last decade has been the provision of substantial amounts of pure alkaloids. This is greatly facilitated by the location of plant sources from which particular alkaloids may be obtained readily in high yield and purity. Heliotrine, lasiocarpine, and monocrotaline are conveniently available from *Heliotropium europaeum* and *Crotalaria retusa* (Culvenor, Drummond, and Price 1954; Culvenor and Smith 1957) but senecionine, which is the commonest constituent of *Senecio* species and is representative of the large group of pyrrolizidine adipic esters, has been difficult to obtain in quantity from the Australian species investigated previously. Investigation of *Senecio magnificus* from Alice Springs, N.T., kindly supplied by Mr. G. Chippendale, Animal Industry Branch, Northern Territory Administration, has disclosed that this species is an excellent source of senecionine. From two samples, the yields of pure alkaloid have been 1.5 and 0.5% dry weight respectively. At least two other alkaloids were present in minor amounts but have not been isolated.

### Experimental

The microanalysis was performed by the C.S.I.R.O. and Melbourne University Microanalytical Laboratory. The solvent used for paper chromatography is the upper phase resulting from shaking butanol with an equal volume of 5% acetic acid.

(a) *Preliminary Assay.*—When assayed by the procedure of Culvenor and Smith (1955), dried whole plant gave “unreduced” and “reduced” alkaloid fractions amounting to 0.97 and 2.06% respectively. Paper chromatography of these fractions gave spots of  $R_F$  0.68, 0.59, 0.42 (very faint), and  $R_F$  0.60 (strong), 0.42 (very faint), respectively. The spot of  $R_F$  0.59 or 0.60 is due to senecionine which crystallized (m.p. 240 °C, without further purification) from both fractions. The spot of  $R_F$  0.68 in the “unreduced” alkaloid is ascribed to senecionine *N*-oxide since it is not present in the “reduced” alkaloid and senecionine *N*-oxide is one of the *N*-oxides known to be at least partially extracted from aqueous solution by chloroform. As judged by relative spot intensities, nearly half of the “unreduced” fraction is due to *N*-oxide and the tertiary base content of the plant is only about 0.5%.

(b) *Isolation of Senecionine.*—Milled plant material (63 lb of aerial parts, a different sample from that assayed) was extracted with methanol at 50 °C, the methanol removed under reduced pressure, and the residue extracted with dil.  $H_2SO_4$ . The aqueous solution was made 1.5N with respect to  $H_2SO_4$  and stirred for 4 hr with zinc dust. After filtration the solution was made alkaline with  $NH_3$  and extracted with chloroform. Concentration of the extract and cooling gave crude senecionine (153 g),  $R_F$  0.60, m.p. 240 °C. Recrystallization from ethanol gave the pure alkaloid (113 g), m.p. 249 °C (in an evacuated capillary), undepressed on admixture with an authentic specimen of senecionine,  $[\alpha]_D^{20} -51^\circ$  (c, 2.02 in chloroform) (Found: C, 64.6; H, 7.6; N, 4.4%. Calc. for  $C_{18}H_{25}O_5N$ : C, 64.5; H, 7.5; N, 4.2%).

\* Manuscript received October 7, 1961.

† Division of Organic Chemistry, C.S.I.R.O. Chemical Research Laboratories, Melbourne.

The mother liquors yielded an additional 40 g of crystalline but lower-melting material showing a second spot on a paper chromatogram at  $R_F$  0.44. Non-crystalline alkaloid residues (94 g) showed a major spot at  $R_F$  0.64 (senecionine) and minor spots at  $R_F$  0.58 and 0.42.

### References

- CULVENOR, C. C. J., DRUMMOND, L. J., and PRICE, J. R. (1954).—*Aust. J. Chem.* **7**: 277.  
CULVENOR, C. C. J., and SMITH, L. W. (1955).—*Aust. J. Chem.* **8**: 556.  
CULVENOR, C. C. J., and SMITH, L. W. (1957).—*Aust. J. Chem.* **10**: 464.

## ALKALOIDS OF THE GRAMINEAE: *THELEPOGON ELEGANS*\*

By W. D. CROW†

The immense economic importance of the grasses has led to a large number of investigations, but these are primarily concerned with the use of such plants as pasture materials. The possibility that alkaloids might be present in grasses has nevertheless not been entirely overlooked. The occurrence of the indole bases, gramine in barley (von Euler and Hellstrom 1932) and 5-methoxy-*N*-methyltryptamine in *Phalaris arundinacea* L. (Wilkinson 1958), are recorded in the literature, as also is the occurrence of perloline,  $C_{20}H_{18}O_4N_2$  (Melville and Grimmett 1941) in *Lolium perenne*. The same compound was later shown to occur in two other species of *Lolium*, as well as in *Festuca arundinacea* and *Setaria lutescens* by Reifer and White (1945), who examined a number of grasses specifically for alkaloids. More recently, Yunusov and Akramov (1960) have isolated the pyrrolizidine derivatives loline, lolinine, and lolinidine from *Lolium cuneatum*.

The observation that *Thelepogon elegans*, a sample of which was available from the Plant Introduction Section, C.S.I.R.O., contained alkaloids, was therefore followed up by extraction and isolation of the constituents. Paper chromatography showed the presence of at least five bases, two of which were isolated in sufficient amount for purification. Thelepogine ( $C_{20}H_{31}ON$ ) showed the presence of an hydroxyl group ( $3300\text{ cm}^{-1}$ ) in the infrared, but was transparent at  $M/20000$  in the ultraviolet. The associated base thelepogidine ( $C_{18}H_{29}O_2N$ ) showed no evidence of hydroxyl or carbonyl absorption in the infrared, so that both oxygen atoms must be in the form of ether linkages.

In view of the shortage of material a heavy atom derivative of thelepogine was prepared for X-ray diffraction studies. The methiodide was examined by Fridrichsons and Mathieson (1960) of these Laboratories who have reported the structure (I) as a result of their investigations, and have indicated a possible

\* Manuscript received July 28, 1961.

† Division of Organic Chemistry, C.S.I.R.O. Chemical Research Laboratories, Melbourne; present address: Chemistry Department, Australian National University, Canberra, A.C.T.