

# THE MAJOR ALKALOID OF *CROTALARIA LABURNIFOLIA* SEEDS

R. N. GANDHI, T. R. RAJAGOPALAN AND T. R. SESHADRI

Department of Chemistry, University of Delhi, Delhi-7

THE seeds of *Crotalaria laburnifolia* have been in use as a cure for snake and scorpion bites.<sup>1</sup> They were earlier reported<sup>2</sup> to contain an alkaloid with m.p. 184–186° (d) and molecular formula  $C_{16}H_{23}O_5N$ . Later Subramanian *et al.*<sup>3</sup> confirmed its occurrence and named it Crotalaburnine. They also recorded the presence of  $\beta$ -sitosterol and lutexin in the seeds.

In view of the importance of the drug, a detailed study of the alkaloid components was considered necessary. We have therefore examined the seeds procured from Kerala State. The following method of extraction has now been adopted.

The coarsely powdered seeds (2 kg.) were percolated with hot ethanol and the percolate concentrated to small bulk. It was acidified with an equal volume of 10% aqueous citric acid and the remaining ethanol distilled off under reduced pressure. After extraction with petroleum-ether and ether to remove waxes, sterols and fatty components, the solution was made basic with ammonia and the alkaloids extracted exhaustively with chloroform. The extract was dried and evaporated yielding a yellowish residue which gave an orange-red precipitate with Dragendorff reagent. Its solution in acetic anhydride was pale yellow and remained unchanged on boiling, showing the absence of N-oxides. T.L.C. (silica gel G) of the residue using methanol as solvent gave four spots, one of which belonged to a predominantly major component. When the residue was crystallised twice from absolute ethanol, it yielded the major alkaloid as colourless plates (T.L.C. single), m.p. 197–199° (d); yield 4.0 g;  $[\alpha]_D^{25}$ , + 29.7 (abs. ethanol),  $[\alpha]_D^{25}$ , – 19.0 (chloroform). We tentatively retain the name crotalaburnine for the pure alkaloid. It formed a golden-yellow picrate, m.p. 222–224° (d) and a colourless methiodide, m.p. 220–222° (d). The elemental analysis of the pure alkaloid and its m.wt. (Rast) agreed with the formula  $C_{18}H_{25}O_6N$ . It had no methoxyl but had three C-methyl groups. The i.r. spectrum (KBr) showed saturated and unsaturated ester carbonyls at 1750 and 1720  $cm^{-1}$  respectively and hydroxyl at 3500, 3620  $cm^{-1}$ .

On hydrolysis with aqueous barium hydroxide crotalaburnine gave a necic acid which crystallised from ethylacetate and petroleum-ether, m.p. 144–145°;  $[\alpha]_D^{26}$ , + 9.8 (abs. ethanol). It had the composition  $C_{10}H_{11}O_5$ , i.r. (KBr) showed hydroxyl at 3600 and carbonyl at 1720,

1740  $cm^{-1}$ . In all these properties it agreed closely with senecic acid. [Lit.<sup>4</sup> m.p. for senecic acid, 146° and  $[\alpha]_D^{25}$ , + 10.9 (abs. ethanol)]. The identity was confirmed by converting it into lactone, m.p. 153–154°,  $[\alpha]_D^{26}$ , + 37.1 (abs. ethanol). [Lit.<sup>4</sup> m.p. for senecic acid lactone 156° and  $[\alpha]_D^{25}$ , + 36.5° (abs. ethanol)]. Using a sample of senecic acid kindly supplied by Dr. C. C. J. Culvenor direct comparison has been made; m.m.p. was undepressed and i.r. spectra were identical.

The necine obtained by the hydrolysis of the alkaloid crystallised from absolute ethanol as colourless prisms, m.p. 195° (d),  $[\alpha]_D^{26}$ , + 38.8 (abs. ethanol). Its elemental analysis agrees with the formula  $C_8H_{13}O_3N$ ; i.r. (KBr) showed hydroxyl at 3510  $cm^{-1}$ .

The alkaloid on hydrogenolysis using  $PtO_2$  catalyst in absolute ethanol gave a product which crystallised from absolute ethanol, m.p. 179–180° (d);  $[\alpha]_D^{34}$ , – 20.0 (chloroform). Its elemental analysis agrees with the formula  $C_{18}H_{29}O_6N$ . It has four C-methyls, i.r. (KBr) showed hydroxyl at 3580, carbonyl at 1720 and an absorption characteristic of a zwitter ion at 1610  $cm^{-1}$ . The reduction has therefore split only one of the ester groups as earlier known in the case of several senecio alkaloids.

Based upon the above evidence the major alkaloid from *Crotalaria laburnifolia* is a cyclic diester of the pyrrolizidine group with senecic acid as the acid part, the necine ( $C_8H_{13}O_3N$ ) having hydroxymethyl group in the 1-position and a hydroxyl in the 7-position; the position of the 3rd hydroxyl is unsettled. Recently Culvenor *et al.*<sup>5</sup> isolated an alkaloid anacrotine from *Crotalaria anagyroides* seeds, yielding crotanecine and senecic acid on hydrolysis. Only partial data are available on this alkaloid and necine. There is considerable resemblance in properties between this pair and crotalaburnine and its necine, though there are some differences also (m.p. and i.r.). The n.m.r. spectra have great similarity but more data will be required to establish identity or otherwise and work is in progress with this end in view.

1. Iyer, T. K. A. *National Medical Journal*, Dec. 1963.
2. Emmanuel, J. and Ghosh, M. N., *Indian J. Phar.*, 1964, **26**, 322.
3. Snehata, S., Ghosh, M. N., Nagarajan, S. and Subramanian, S. S., *Ibid.*, 1966, **28**, 277.
4. Adams, R. and Govindachari, T. R., *J. Am. Chem. Soc.*, 1949, **71**, 1953.
5. Atal, C. K., Kapur, K. K., Culvenor, C. C. J. and Smith, L. W., *Tetrahedron Letters*, 1966, p. 537.