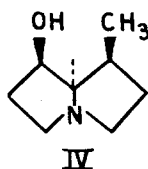
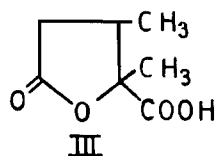
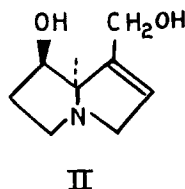
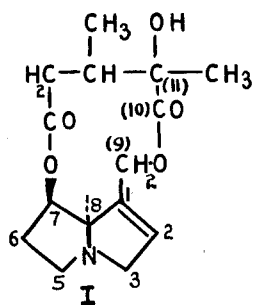


Genus *Crotalaria* XIII¹. Crobarbatine, a New Pyrrolizidine Alkaloid of *C. barbata* R.

In continuation of our systematic chemical studies on the genus *Crotalaria* (Leguminosae) we have isolated several new pyrrolizidine alkaloids. These bases are well known for their diverse biological activities². In this communication we wish to record the structure of a new macrocyclic pyrrolizidine alkaloid crobarbatine (I)³, isolated from the seeds of *C. barbata* R.



The alcoholic extract of the defatted seeds (containing 0.39% of alkaloids) was processed⁴ to give crude alkaloid mixture consisting mainly of two alkaloids. The mixture when chromatographed over neutral alumina yielded the title compound from the benzene eluted fractions. The base on crystallization from benzene afforded colourless crystals m.p. 142–143°, TLC (silica gel G treated with *N*/10 NaOH, methanol) showed single spot of R_f 0.44 (cf. monocrotaline R_f 0.41). The elemental analyses of

Further support for structure (I) was attained by hydrolysis and hydrogenolysis of crobarbatine. The base was hydrolyzed with 10% hydrochloric acid by heating on steam bath for 6 h and ether extractions of the reaction mixture yielded a new necic acid, now called crobarbatic acid (III). The residual aqueous solution was evaporated to dryness to give necine hydrochloride which on crystallization from ethanol-ether afforded colourless crystals, m.p. 161–162°, undepressed on admixture with retronecine (II) hydrochloride. Further the identity was confirmed by superimposable IR-spectrum.

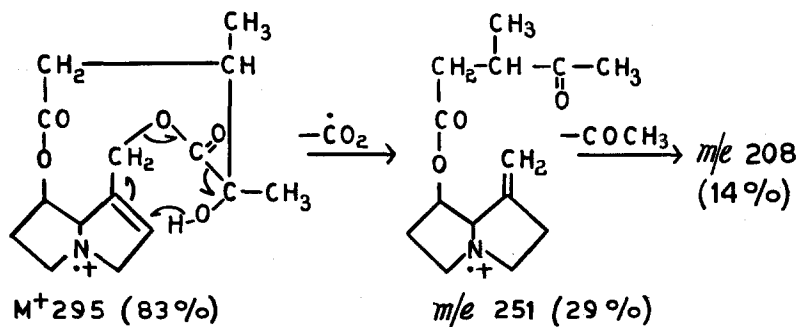
Crobarbatic acid, m.p. 177–178°, C₇H₁₀O₄, did not respond to ferric chloride test⁵ for α -hydroxy acids thus indicating it to be a lactone. The IR (KBr) of acid showed peaks at 1757 (γ -lactone), 1422 (CH₂CO)⁶, 3225 and 1738 cm⁻¹ (COOH). The NMR (100 MHz, D₂O) displayed peaks at δ 1.16 (CH₃-CH-, d, J 7 Hz), 1.72 (CH₃-C-COOH, s) and 2.72 (-CH₂-CH-, m). When measured in CDCl₃, in addition to above protons the NMR of crobarbatic acid revealed the presence of one carboxylic proton at δ 7.44.

Crobarbatine absorbed 2 moles of hydrogen when hydrogenated in 0.5N H₂SO₄ solution over reduced PtO₂ catalyst. The reaction product was basified with dil. NaOH and extractions with ether yielded retronecanol (IV), picrate m.p. 207–208° which did not depress an admixture with authentic retronecanol picrate. The aqueous layer was again acidified with dil. HCl and extractions with ether afforded crobarbatic acid⁷.

Zusammenfassung. Strukturaufklärung eines neuen Pyrrolizidinalkaloids, Crobarbatin, welches aus dem Samen von *Crotalaria barbata* R. isoliert wurde.

S. C. PURI, R. S. SAWHNEY and C. K. ATAL

Regional Research Laboratory, CSIR,
Jammu-Tawi (India), 19 June 1972.



crobarbatine and its picrate (m.p. 237°) conform to the molecular formula C₁₅H₂₁NO₅, M⁺ 295. The IR-spectrum (KBr) of the base exhibited peaks due to ester carbonyls (1735 cm⁻¹) and -OH group (3330 cm⁻¹).

The NMR-Spectrum (60 MHz, D₂O) revealed the presence of CH₃-CH- (δ 1.07, d, J 6.5 Hz), CH₃-C(OH)- (δ 1.32, s), H6 (δ 2.10, m), H9 (δ 4.81; 5.28, AB quartet, J 16 Hz) and H2 (δ 6.27, m). The difference in chemical shifts of H9 protons (Δ H₉ = 0.47 ppm) is in accord with a 11 membered macrocyclic pyrrolizidine diester². The mass spectrum (M⁺ 295) of crobarbatine displayed characteristic peaks at *m/e* 80, 93, 95, 119, 120, 121, 136 and 138 which indicated it to be an ester of retronecine (II) type aminoalcohol. The location of -OH group at C₁₁ is strongly supported by the ion *m/e* 251².

¹ For part XII see: R. S. SAWHNEY and C. K. ATAL, J. Indian Chem. Soc. 48, 887 (1971).

² L. B. BULL, C. C. J. CULVENOR and A. T. DICK, in *The pyrrolizidine Alkaloids* (North-Holland Publishing Co., Amsterdam 1968).

³ Presented at 23rd Indian Pharmaceutical Conference held at Manipal in February 1972.

⁴ R. S. SAWHNEY and C. K. ATAL, J. Indian Chem. Soc. 45, 1052 (1968).

⁵ M. KROPAN, L. NOVELLIE, S. M. CHRISTIE and F. L. WARREN, J. chem. Soc. 1949, 1704.

⁶ N. B. COLTHUP, L. H. DALY and S. E. WIBERLEY, in *Introduction to Infrared and Roman Spectroscopy* (Academic Press, New York 1964).

⁷ We thank Mr. L. W. SMITH, C.S.I.R.O., Melbourne for the NMR and to Dr. B. D. TILAK, Director, National Chemical Laboratory, Poona for the mass spectrum.