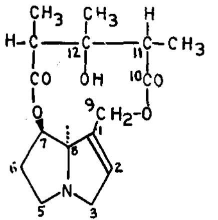
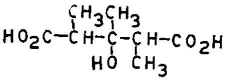
Genus *Crotalaria* XXI[1]. Isocromadurine, a Novel Pyrrolizidine Alkaloid of *C. madurensis* R. Wight

The seeds of *C. madurensis* have been reported[1–3] to contain 4 alkaloids: namely, cromadurine, madurensine, fulvine and crispatine. In this communication we wish to record the isolation and structure of a new macrocyclic pyrrolizidine alkaloid isocromadurine (I).

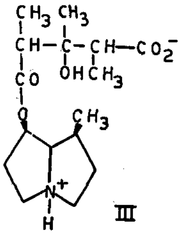
Alcoholic extract of the defatted seeds (containing 1.9% alkaloids) was processed to give alkaloid mixture, which on crystallization from methanol-acetone yielded cromadurine followed by fulvine. The mother liquor, after removal of cromadurine and fulvine, was evaporated to dryness. The residue was crystallized from petroleum ether to give colourless crystals of isocromadurine, m.p. 135–136° $(\alpha)_D^{15}$ + 43.54 (C, 0.85%, ethanol), TLC (silica gel G treated with N/10 NaOH, methanol) showed single spot of Rf 0.22 (cf. monocrotaline 0.22). The elemental analyses of isocromadurine and its picrate (m.p. 204–205°) conform to the molecular formula $C_{16}H_{23}O_5N$, M^+309. The IR-spectrum (KBr) of the base exhibited peaks due to ester carbonyls (1730 cm^{-1}) and –OH group (3400 cm^{-1}).



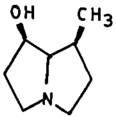
I



II



III



IV

The NMR-spectrum (60 MHz, $CDCl_3$) of isocromadurine exhibits signals at δ 1.17 (s, CH_3–C–OH), 1.27 (d, J 7.5 Hz, 2×CH_3–CH), 2.00 (m, H6), 4.60 (ABq, J 12 Hz, H9) and 5.97 (m, H2). The presence of –OH group at δ 4.50 was shown by D_2O exchange. In the MS (M^+ 309) of isocromadurine, the peaks at *m/e* 80, 93, 95, 119, 120, 121, 136 and 138 suggested it to be an ester of retronecine type amino alcohol. The location of –OH group at C–12 is strongly supported[4] by the presence of ion *m/e* 236 (43%).

The base on hydrolysis with 2 *N* methanolic NaOH at room temperature gave retronecine and isocromaduric acid (II), $C_8H_{14}O_5$, m.p. 129–130° (ether- pet. ether), $(\alpha)_D^{32}$ + 14.9° (C, 0.91%, methanol). The NMR- and IR-spectra of isocromaduric acid were identical with those of cromaduric acid[1], m.p. 138–139°, $(\alpha)_D^{32°}$ − 14.5° (methanol).

When hydrogenated over reduced PtO_2 in ethanol, isocromadurine absorbed 2 moles of hydrogen to give the zwitter ion (III), m.p. 183–184° (ethanol-acetone), $\nu_{max}^{CHCl_3}$ 3550 (–OH), 1720 (CO), 1460 cm^{-1} (–N^+ H). The zwitter ion on hydrolysis[5] with 2 *N* sodium hydroxide in methanol yielded retronecanol (IV), picrate m.p. 207–208° and isocromaduric acid[6].

Zusammenfassung. Strukturaufklärung eines neuen Pyrrolizidinalkaloids, Isocromadurin, aus dem Samen von *Crotalaria madurensis* R. Wight. isoliert.

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[1] For part XX see: P. G. RAO, R. S. SAWHNEY and C. K. ATAL, Indian J. Chem. in press (1975).

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[6] We wish to thank Dr. NITYA ANAND, Director, C.D.R.I., Lucknow for IR-, NMR- and to Dr. B. D. TILAK, Director, NCL, Poona for the mass spectrum.

Sterols of the Lobster (*Homarus americanus*) and the Shrimp (*Pandalus borealis*)[1]

The diversity of sterols in marine invertebrates is of interest from the viewpoint of both chemotaxonomy and comparative biochemistry. There are, however, only a few reports on the sterol composition of marine crustacea, although this class consists of a great number of species and is a major contributor to the biomass of the oceans[2–6]. In this paper we report the isolation of two new sterols, 24-methylcholesterol and 24-ethylcholesterol, from two species of continental shelf crustacea, the lobster (*Homarus americanus*), and the shrimp (*Pandalus borealis*) and discuss possible sources of these two sterols.

Methods. Lobsters were collected in June, 1973, from Vineyard Sound, Massachusetts. Shrimp were collected from 42°43′N, 65°09′W using No. 41 bottom trawls and immediately frozen on the R/V ALBATROSS IV, Cruise 73–3 in May of 1973.

The live lobsters and frozen shrimp were extracted for sterols by a modified procedure of KRITCHEVSKY[4], and IDLER and WISEMAN[5]. Further purification of the sterols was accomplished by formation of their digitonide derivatives[7]. After cleavage of the sterol digitonides to the free sterols and conversion of the sterols to their respective trimethylsilylated derivatives, gas chromatographic analyses were performed[8].

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[1] Woods Hole Oceanographic Institution Contribution Number 3494.

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