Formation de IXa—e a partir de VIIIa—e——Selon la technique utilisée pour la préparation de VIa—e à partir de Va—e, on obtient IXa—e à partir de VIIIa—e (Tableau III). Ces alcoyl-6 δ-lactones sont identiques à celles que nous avons déjà préparées à partir de la dihydrorésorcine.

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Integerrimine from *Cacalia hastata* L. *subsp. orientalis* KITAMURA

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Constituents of four species of the genus *Cacalia* (Compositae), *C. decomposita*,[2] *C. floridana*,[3] *C. hastate*,[4] and *C. rubsta*,[5] were examined and naphthofurantype derivatives, secopyrrolizidine alkaloids, and pyrrolizidine alkaloid hastacine (I) were detected. The pyrrolizidine alkaloid the so-called senecio alkaloid, is well known for its strong hepatotoxity. Japanese *C. hastate* L. *subsp. orientalis* KITAMURA (Japanese name "Yobusumasoh") has been used as edible wild plant in northern Japan, and it seemed of interest to compare the difference in the component between Russian and Japanese *C. hastate*.

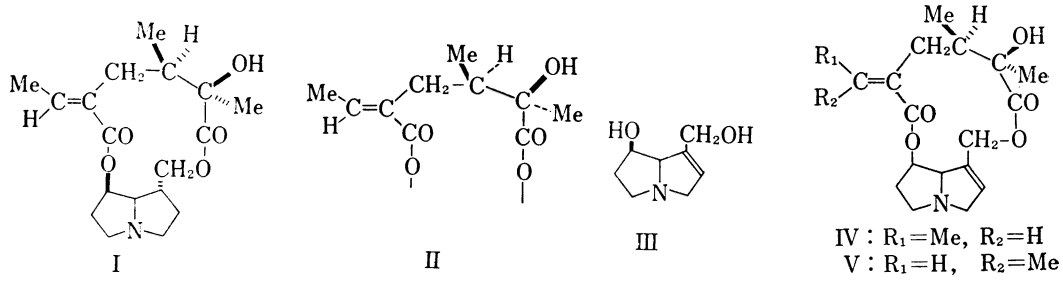

Chart 1

The fresh terrestrial parts of the plant were extracted with ethanol. After several procedures, crude alkaloid was obtained from acetone as prisms, mp 168—169°, $[\alpha]_D$—21.4°, $C_{18}H_{25}O_5N$, positive to the Dragendorff reagent. The melting point and *Rf* values[5] on paper chromatography (PPC) and thin-layer chromatography (TLC) of this alkaloid were very similar to those of hastacine (I) but $[\alpha]_D$ value[6] was different. Hydroxyl group and α,β-unsaturated ester group were found in its infrared (IR) spectrum (3535, 1725, 1710 and 1655 cm^{-1}). Nuclear magnetic resonance (NMR) spectrum, δ 0.93 (3H, d,[7] J=6.6 Hz), 1.33 (3H, s), 1.75 (3H, d, J=7.2 Hz), and 6.57 (1H, q, J=7.2 Hz) ppm and ultraviolet (UV) absorption at 210.3 nm (ε, 10,600) suggested the presence of hastanecic (or integerrinecic) acid

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7) s, d, q, and m are abbreviations for singlet, doublet, quartet, and multiplet, respectively.

(II) moiety. The signals at δ 6.22 (1H, m, vinylic) and 5.44, 4.12 (AB type d, J=12 Hz, attached to lactonic oxygen) ppm however, suggested that necine portion of this compound is not hastanecine as first expected but retronecine (III), and it was deduced that this alkaloid is integerrimine [8](IV). The mass spectrum of the alkaloid is superimposable with that of senecionine (V)[9] which is the isomer with respect to the double bond of α,β-unsaturated lactone in IV.

While Manske[8a] reported the $[\alpha]_D$ value of integerrimine (IV) as +4.3°, and Gonzalez[10] +3.19°, Gellert[11] and Montidome[12] reported the values of −22.1° and −19.4°, respectively. Direct comparison of our alkaloid with the authentic sample kindly supplied by Prof. Culvenor resulted in agreement of their spectra, mp (by mixed fusion), and $[\alpha]_D$ value (Culvenor's sample: −23.0°). The mother liquor of integerrimine (IV) showed the spot besides that of (IV) on TLC and PPC, and the spot did not seemed to be that of hastacine (I) as judged by the behavior on the both chromatograms. Further examination could not be made due to the small amount of the sample available.

Experimental[13]

Extraction of Integerrimine——Fresh terrestrial part (9 kg) of the plant was extracted with EtOH, concentrated to *ca.* 3 liters and extracted with benzene. Aqueous layer was evaporated to dryness and a dark brownish tar was obtained. This tarry residue was dissolved in 2 liters of 2N H_2SO_4 and reduced with 300 g of granular zinc (about 20 mesh).[14]

Recrystallization from CH_3COCH_3 gave 180 mg of Dragendorff-positive colorless prisms, mp 168—169°,[15] $[\alpha]_D$ −21.4° (c=9.00, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{25}O_5N$: C, 64.46; H, 7.51; N, 4.18. Found: C, 64.31; H, 7.55; N, 4.19. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3535, 1725, 1710, and 1655. UV λ_{max}^{MeOH} nm (ε): 210.3 (10600). NMR (in $CDCl_3$) δ: 0.93 (3H, d, J=6.6 Hz) 1.33 (3H, s), 1.75 (3H, d, J=7.2 Hz, Me–CH=C), 5.04 (1H, m, O–CH–), 5.44 (1H, d, J=12 Hz, –C–CH_2–O–), 6.22 (1H, m, vinylic H) and 6.57 (1H, q, J=7.2 Hz, Me–CH=C). Mass Spectrum m/e: 335 (M^+), 291, 248, 220, 153, 138, 137, 136, 121, 120, 119, 95, 94, 93. Picrate mp 205—212.5°; Methiodide, mp 237.5—238°. Rf values on TLC: 0.39 (Silica gel G, 10 g; 0.1 N NaOH 20 ml. stand for over one day before use, solvent MeOH), Rf PPC: 0.57 (5% AcOH: BuOH=1: 1). Rotation value of Culvenor's sample: $[\alpha]_D$ −23.0° (c=5.23, $CHCl_3$). TLC and PPC of the mother liquor of integerrimine; Rf TLC: 0.39 (integerrimine) 0.20, PPC: 0.57 (integerrimine), 0.66.

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14) Activated by Fieser's procedure. L.F. Fieser and W.S. Johnson, *J. Am. Chem. Soc.*, **62**, 575 (1940).
15) Uncorrected.