Tetrahedron Letters No.27, pp. 2597-2600, 1967. Pergamon Press Ltd. Printed in Great Britain.

CHEMOTAXONOMICAL ALKALOID STUDIES II.

STRUCTURES OF KURAMERINE AND KUMOKIRINE

Kunisuke Nishikawa, Mieko Miyamura and Yoshimasa Hirata
Chemical Institute, Faculty of Science
Nagoya University, Chikusa, Nagoya, Japan

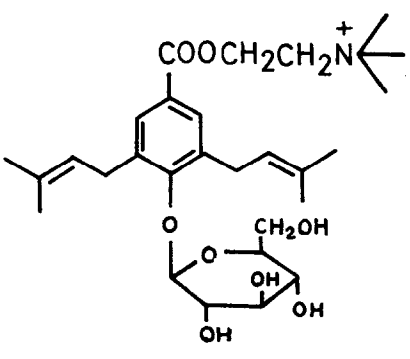
(Received 6 April 1967)

In the previous paper (1), we reported the structure of Nervosine which was isolated from Liparis nervosa Lindl..

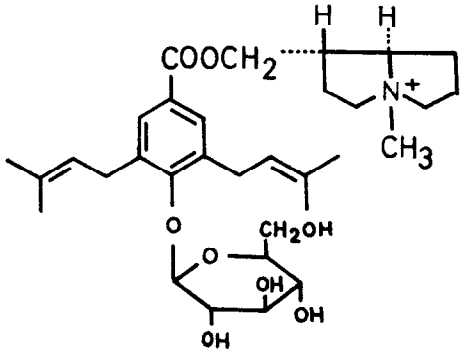
We further studied two plants, Liparis Kurameri French. et. Sav.* and Liparis Kumokiri F. Maekawa**, both of which are Liparis species of the Orchidaceae family, in point of view of plant chemotaxonomy.

From these plants, two new alkaloids, Kuramerine (I) and Kumokirine (VIII), (both named by us), were isolated.

In this communication, we wish to report the structuresof these alkaloids.



(I)



(VIII)

---

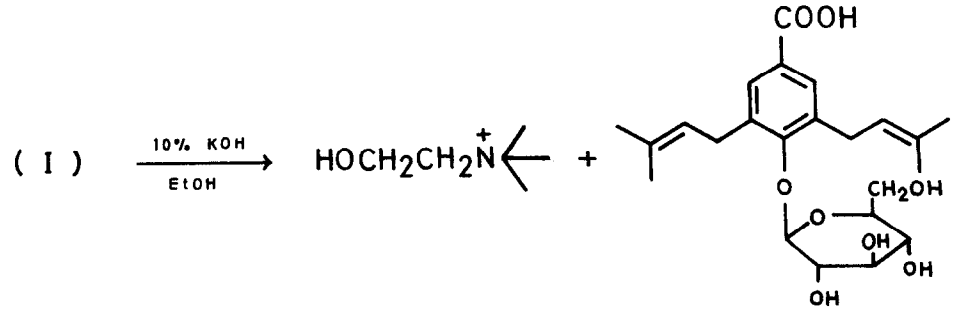
* Japanese name is Zigabachiso.

** Japanese name is Kumokiriso.

Kuramerine (I), ($C_{28}H_{44}O_8N$ - $C_6H_2O_7N_3$, m.p. 105 - 107°, as picrate; $[\alpha]_D^{20}$=-19.7° as HCl salt (methanol); Rf: 0.78 (n-BuOH : AcOH : H_2O = 4 : 1 : 1); pKa': over 12), shows positive Benzidine - HIO_4 and negative Tollens tests.

Other spectral data are as follow: ν_{max}^{KBr} (cm^{-1}) 3400 (strong), 1715, 1120 - 980 (strong); λ_{max} (ε) 248, 280 290 mμ (14000, 2300, 2000) in both neutral and alkaline methanol.

Alkaline hydrolysis of I produced quantitatively two compounds, one of which was a strongly basic II. The other was acidic III.



(II) (III)

The compound II, ($C_5H_{14}ON$ - $C_6H_2O_7N_3$, m.p. 245 - 246°, as picrate), was assumed to be choline from its NMR spectrum in pyridine: 3.52 (9H, singlet), 3.90 (2H, quartet, J_1=6.5, J_2=3.5 cps), 4.34 ppm (2H, multiplet) from internal TMS. It was identified as choline by comparison of its melting point, and the IR spectra of its picrate and chloride with those of authentic samples.

The acidic compound III, Kurameric acid, ($C_{23}H_{32}O_8.H_2O$, m.p. 103 - 105°; pKa': 6.1 (66 % methanol)), exhibits spectral properties similar to those of Nervosinic acid (1). For example: ν_{max}^{KBr} (cm^{-1}) 3350 (strong), 1690, 1605, 1120 - 980 (strong); λ_{max} (ε) 243, 278, 288 mμ (13000, 2300, 2000) in methanol, 235, 278, 288 mμ (12500, 2300, 2000) in alkaline methanol.

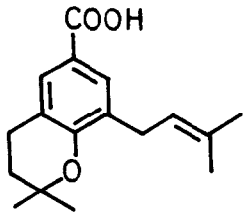
In the NMR spectrum of III in pyridine, two sharp singlets at 1.63 and 1.73 ppm (both 6H), a doublet at 4.02 ppm (4H, J=7 cps) and a triplet at 5.57 ppm (2H, J=7 cps) were observed.

These signals are also present in the NMR spectrum of Nervosinic acid (1).

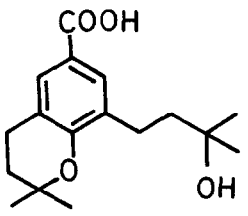
Under catalytic hydrogenation, III was transformed to a tetrahydro derivative (IV), having the original chromophore. The NMR spectrum shows a doublet at 0.90 ppm (12H, J=5 cps), a multiplet at 1.3 - 1.9 ppm (6H) and a broad triplet at 3.20 ppm (4H, J=7 cps) in pyridine.

Treatment of III with 2N hydrochloric acid gave D-glucose and two acidic compounds V and VI. Further, hydrolysis of IV gave D-glucose and VII.

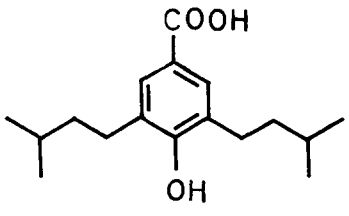
The structures of these degradation products were confirmed by comparison with authentic samples from Nervosine (1).



(V)



(VI)



(VII)

The value of molecular rotation of III ($[M]_D^{20°}$=-7200) indicates a β-linkage of the glycoside bond at the C_1 position of glucose.

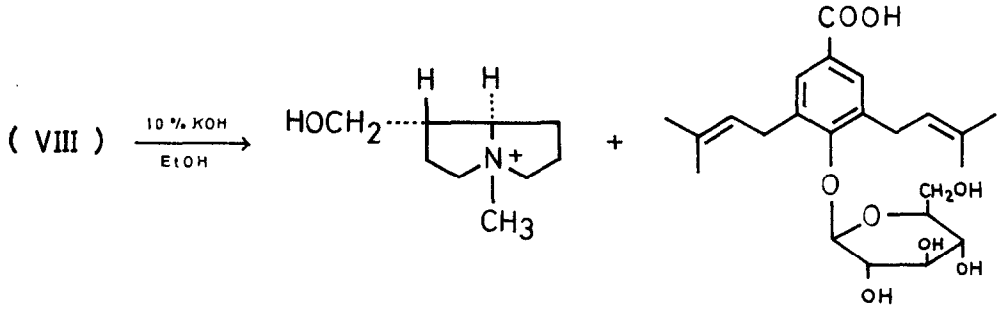
From these results, the structure of Kurameric acid can be assigned as III.

Accordingly, on the basis of the molecular formula and the characteristics of two degradation products, the structure of Kuramerine can be assigned as I which consists of choline (II) and Kurameric acid (III).

Kumokirine (VIII), ($C_{32}H_{48}O_8N.H_2O$ - $C_6H_2O_7N_3$, m.p. 100 - 102°, as picrate; $[\alpha]_D^{20°}$=-23.4° as HCl salt (methanol); Rf: 0.77 (n-BuOH : AcOH : H_2O = 4 : 1 : 1)), shows positive Benzidine - HIO_4 and negative Tollens tests.

Other physical properties are shown below: ν_{max}^{KBr} (cm^{-1}) 3400 (strong), 1710, 1120 - 970 (strong); λ_{max} (ε) 247, 280, 290 mμ (14000, 2300, 2000) in neutral and alkaline methanol.

The high pKa' value (over 12) indicates that Kumokirine (VIII) should be a quarternary amine. Alkaline hydrolysis of VIII gave one mole of a strongly basic compound (IX) and one mole of an acidic compound (X) in quantitative yield.



(IX) (X)

The basic compound (IX), Kumokiridine, ($C_9H_{18}ON$ - $C_6H_2O_7N_3$, m.p. 247 - 248°, as picrate; $[\alpha]_D^{20°}$=+12° (methanol)), exhibits the following NMR spectrum in pyridine: 1.90 - 2.60 (7H, multiplet), 3.39 (3H, singlet), 3.45 - 3.95 (4H, multiplet), 3.88 (2H, doublet, J=4.5 cps), 4.16 ppm (1H, multiplet) from an internal TMS. From this NMR spectrum, the structure of IX can be deduced as N-methyl-1-hydroxymethyl pyrrolizidine.

In fact, this compound was identified as N-methyl d-Tracherantamidine (Laburnine)(2) by the comparison of melting point, IR and NMR spectra and $[\alpha]_D$ value with that of authentic sample.

Another alkaline degradation product (X), m.p. 103 - 105°, is Kurameric acid (III) which was confirmed by the comparison of the IR and NMR spectra with that of an authentic sample.

Accordingly, the structure VIII should be given to Kumokirine.

REFERENCES

(1) K. Nishikawa and Y. Hirata, Tetrahedron Letters

(2) F. Galinovsky, H. Goldberger and M. Pöhm, Monatsh, 80, 558 (1949)
Chem. Abst., 44, 1484 (1950)
Y. Tsuda and L. Marion, Can. J. Chem., 41, 1919 (1963)