The spectrum also contained 3 methoxyl singlets at $\delta 3.76$ (C–6′), 3.92 and 3.94 (C–6 and C–12), 12 methylene protons centered around $\delta 2.90$, 2 methine protons at $\delta 3.59$ and 3.62 (C–1 and C–1′), a high field aromatic proton singlet at $\delta 6.10$ (C–8′), and 9 other aromatic protons between $\delta 6.25$ and 7.20. The absence of a high field methoxyl resonance between $\delta 3.02$ and 3.20 confirmed that a hydroxyl function was present at C–7. Since the C–6′ methoxyl appears at $\delta 3.76$, the existence of thaligine in either the (+ −) or (− +) form was suggested[4]; and indeed *O*-methylation with diazomethane afforded (+)-isotetrandrine of known absolute configuration[5]. The two samples of isotetrandrine were identical in terms of Rf values, UV-, NMR- and mass spectra, and ord curves.

*Résumé.* Le nouvel alcaloïde thaligine (**1**) a été tiré du *Thalictrum polygamum* Mulh. (Ranunculaceae).

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*8 January 1973.*

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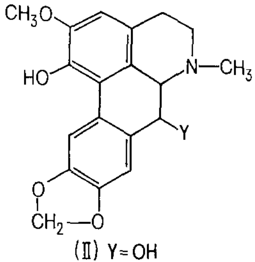
## Structure of Nandazurine, from *Nandina domestica* Thumb.

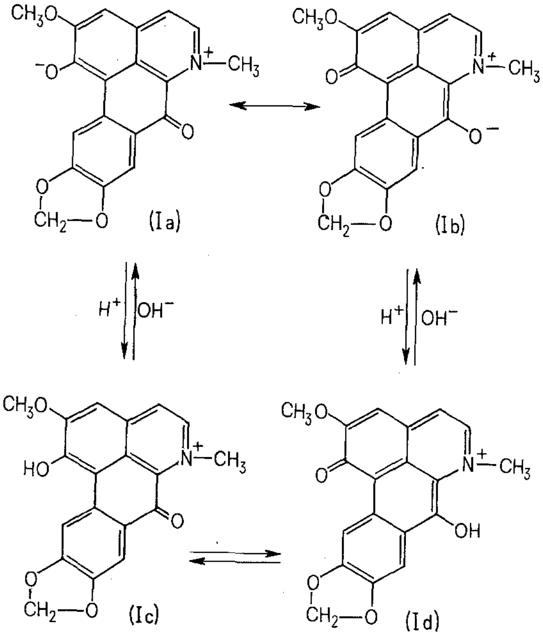
Nandazurine, a green colored alkaloid, was first isolated in 1925 from the bark of *Nandina domestica* Thumb. (Berberidaceae) by Kitazato[1], however its structure has long been unknown. Recently, we isolated nandazurine from the same plant along with several other alkaloids. In this communication we wish to present a report on the structure elucidation of nandazurine.

Nandazurine (I), amorphous dark green powder showing a single spot on TLC, $C_{19}H_{13}O_5N$ (elemental analyses, molecular ion peak at m/e 335), $[\alpha]_D$ ±0° ($C_5H_5N$). It is sparingly soluble in common organic solvents and insoluble in aqueous alkali, and gives a positive ferric chloride test. The IR-spectrum (KBr) of nandazurine (I) showed absorptions at 1625 (weak) and 1575 cm$^{-1}$ (medium) (conjugated $>C{=}O$ and $-\overset{|}{C}{=}\overset{|}{N}^{+}-$). Its NMR-spectrum (in trifluoroacetic acid) revealed an N-methyl group (at $4.98\delta$), a methoxyl group (at $4.43\delta$), a methylenedioxy group (at $6.22\delta$), 3 aromatic protons (at 7.62, 7.89, $8.85\delta$) and one AB quartet (J = 7 Hz, at 8.43, $8.67\delta$). Its UV-spectrum in ethanol or aqueous ethanolic alkali exhibited $\lambda_{max}$ 221, 230(sh), 260, 324, 394, 426, 450(sh) and 606 nm (log $\varepsilon$; 4.41, 4.43, 4.38, 4.58, 3.84, 3.78, 3.73 and 3.53), which showed a hypsochromic shift on addition of acid solution.

Treatment of nandazurine (I) with sodium borohydride in aqueous methanol gave hexahydronandazurine (II), light green needles, mp 230 ~234°, $C_{19}H_{19}O_5N$, $[\alpha]_D$ ± 0° ($CHCl_3$); NMR ($\delta$, $C_5D_5N$): 2.58 (3H, s., N–$CH_3$), 3.67 (3H, s., $OCH_3$), 5.00 (2H, broad s., 2×OH), 5.92, 6.01 (2H, 2×d., J = 1.5Hz, –$OCH_2O$–), 6.61, 7.17, 7.29 (each 1H, s., aromatic proton), 5.10 (1H, d., J=2.5Hz, $-\overset{|}{C}H(OH)$). Its UV-spectrum showed [$\lambda_{max}$ 221 nm (log $\varepsilon$, 4.86), 239 (sh., 4.11), 288 (4.08) and 310 (4.16)] which is characteristic to 1,2,9,10-tetrasubstituted phenolic aporphine alkaloids and exhibits a bathochromic shift on addition of alkali ethanolic solution[2]. These spectral data suggested that hexahydronandazurine (II) should have a 7-hydroxy-1,2,9,10-tetrasubstituted aporphine structure as in II.



(II) Y=OH
(III) Y=H



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When reduced with zinc and hydrochloric acid, nandazurine (I) afforded colorless needles, mp 150 $\sim$153°, $C_{19}H_{19}O_4N$, which was proved to be completely identical with an authentic sample of dl-domesticine (III)[3] by IR ($CHCl_3$), NMR ($CDCl_3$) and TLC-comparisons. Therefore, it is proved that the hexahydronandazurine has structure II, and consequently nandazurine must have structure I.

Since it has been known[4,5] that 7-oxo-dibenzo[de, g]quinoline derivatives possessing a phenol group on C-1 or C-11 exhibit green color when they can assume a zwitterionic structure, the foregoing observations suggest that nandazurine possesses a mesomeric and zwitterionic structure (Ia) ↔ (Ib).

*Zusammenfassung.* Strukturaufklärung des grünen Farbstoffs Nandazurin, aus Rinden von *Nandina domestica* Thumb. extrahiert. Chemische Reaktion und Spektren weisen auf eine Zwitterstruktur hin (Formel Ia ↔ Ib).

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[8] The authors are grateful to President M. Tomita, Kyoto College of Pharmacy, for his encouragement in this work.

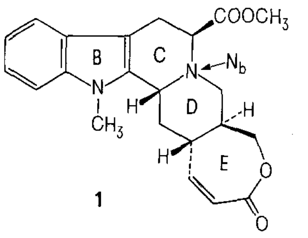
## Alkaloids of Cranberries

Alkaloids separated up to date from cranberries are derivatives of two major chemical families, these being the indolic – cannagunine series – and the azatricyclic – cannivonine series – families[1–4]. All the alkaloids, each having a N-methyl function, probably participate as active ingredients in the physiologically active extracts of this plant. The study of 2 basic products isolated from cranberry extracts is now reported (Formulae).

*Results and discussion.* The identification of the first alkaloid – Cannagunine B (**1**) was relatively easy because of the similarity in structure with the known product[1], the only difference being the carbomethoxy group α to the $N_B$ atom. The NMR-spectra (Varian A-60, $CDCl_3$, TMS, δ, ppm) of Cannagunine[1] and Harmene type alkaloids[5] give the following results: $N-CH_3$ proton signal at 2.7 ppm, $COOCH_3$ proton signal at 3.6 ppm, 4 aromatic protons' signal at 2.2–2.6 ppm. The IR-spectrum showed an α, β-unsaturated, 7 membered, lactone ring system at 1718 $cm^{-1}$.

The first problem was determining the posision of substitution by the $COOCH_3$ group. The particular $N-CH-COOCH_3$ proton, its signal appearing at 3.70 ppm, having a common coupling constant with the protons of the tryptophane part of the skeleton[6], permitted the localisation of the carbomethoxy group in the indicated position. The exact mass measurement of the molecular weight peak gives 380.1740, which corresponds to $C_{22}H_{24}N_2O_4$. The base peak at 379 ($M^+-1$) corersponds to a loss of hydrogen and an intense $M^+-15$ fragment confirms our suppositions. The structure of the E ring is supported by two fragments, at $M^+-44$ and $M^+-70$ ($-CO_2$, $-C_2H_4$). Details of the fragmentation process were previously discussed[1].

The structure of the second alkaloid-Cannagunine C (**2**), exact mass measurement–398.1847–($C_{22}H_{26}N_2O_5$), was established through spectral analysis and basic hydrolysis of **1**. The possibility that **2** was formed during the isolation of **1** is improbable because the hydrolysis condi-



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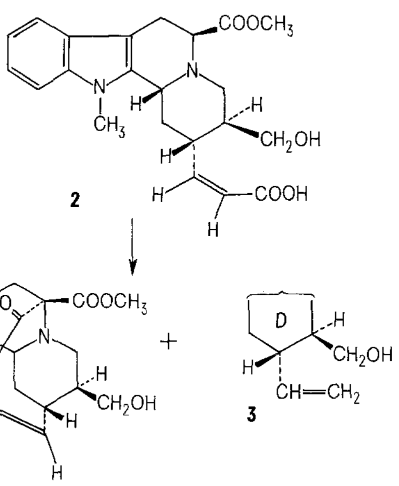

2

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3

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