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28. The Structure of Discretamine, a Tetrahydroprotoberberine Alkaloid

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Summary. On the basis of mass spectrometric analysis, including comparison with closely related isomers, *discretamine* is proposed to have the structure of a 3,10-dihydroxy-2,9-dimethoxy-tetrahydroprotoberberine.

Discretamine, a tetrahydroprotoberberine alkaloid of only partially known structure, was isolated in 1959 by *Schmutz* [1] from *Xylopia discreta* (L. FIL.) SPRAGUE *et* HUTCHINS in too low a yield to permit the usual chemical determination of its exact substitution pattern by ethylation of phenolic hydroxyl groups and subsequent oxidative degradation [2] [3]. From the elemental analysis a $C_{19}H_{21}O_4N$ composition appeared likely, pointing towards the presence of two hydroxyl and two methoxyl groups at the cyclic moiety. The tetra-oxygenated pattern was shown to correspond to the 2,3,9,10 substitution type by conversion of the compound into (–)-*tetrahydropalmatine* ($R^1 = R^2 = R^3 = R^4 = CH_3$) through treatment with diazomethane [1].

[1]) To whom inquiries should be directed.

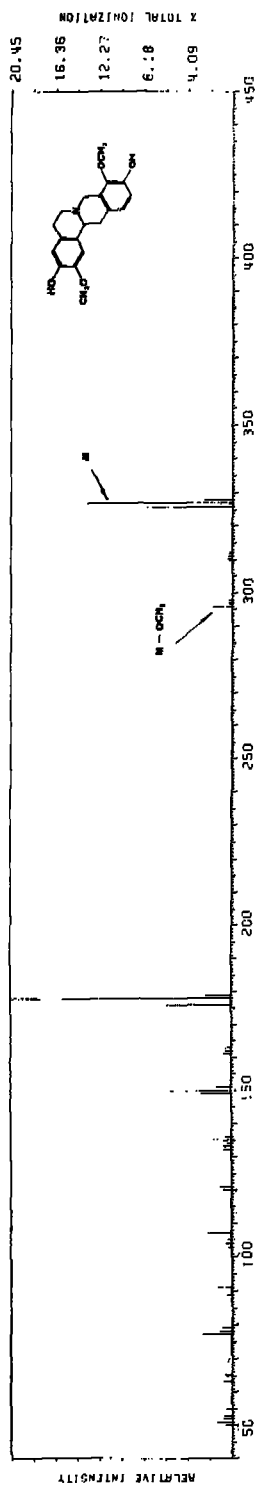
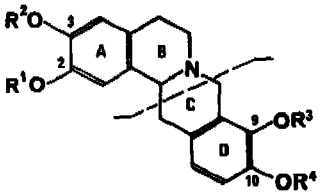


Fig. *Mass Spectrum of Discretamine*

This important finding left only the actual distribution of the HO- and CH_3O-substituents over the four positions undecided.



The mass spectrum of *discretamine* (Fig. 1) is in full agreement with these earlier results inasmuch as it exhibits a correct molecular ion peak *m/e* 327, which shifts to 329 upon H/D-exchange of the two hydroxyl groups with CH_3OD. In addition, characteristic fragments due to the pronounced cyclic collapse of ring **C** with and without hydrogen transfer [4], *m/e* 178/177/176 (rings **A**/**B**) and *m/e* 150/149 (ring **D** and two carbon atoms of ring **C**), indicate that one pair of –OH and $-OCH_3$ substituents is positioned at each of ring **A** and ring **D**. According to more recent observations, the presence of a 9-methoxy substituent can, moreover, be deduced from the significant relative intensity (9% of base peak, *i.e.* 13% of *M*) of an $(M - OCH_3)$ peak (*m/e* 296, Fig.), empirically found to be characteristic of such substitution at this very position [5]. This suggests a 9-methoxy-10-hydroxy pattern of ring **D**, identical with that of the known alkaloid (–)-*stepholidine* ($R^1 = R^4 = H$, $R^2 = R^3 = CH_3$) [3] [6], yet opposite to that of (–)-*scoulerine* ($R^1 = R^3 = H$, $R^2 = R^4 = CH_3$)[2]) [7]. Since discretamine is different from stepholidine (major quantitative differences in *m/e* 178/177/176 intensity ratios) its substitution of ring **A** ought to be the reverse, thus establishing its complete structure as that of a *2,9-dimethoxy-3,10-dihydroxy-tetrahydroprotoberberine* ($R^1 = R^3 = CH_3$, $R^2 = R^4 = H$).

[2]) Isolation of another 2,3,9,10-dihydroxy-dimethoxy-tetrahydroprotoberberine, similarly containing one methoxyl group in each of ring **A** and **D**, yet quite different from discretamine, was reported by *Slavikova & Slavik* [8]. Since neither a sample nor a mass spectrum of this compound was available we could not explore the interesting possibility as to whether it represents the so far unknown ring-**A** isomer of scoulerine.

Experimental Part. – The mass spectrum of discretamine was determined with a *CEC* 21-110 B mass spectrometer (70 eV ionizing energy, 180° source temperature, direct sample insertion). The authors wish to thank Dr. *J. Schmutz*, Forschungsinstitut Dr. *A. Wander AG*, Bern, Switzerland, for the generous gift of the remainder of his discretamine sample.

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29. Über Umwandlungen der *Iboga*-Alkaloide Voacangin und Conopharyngin

154. Mitteilung über Alkaloide[1])

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(18. XI. 74)

Summary. The reduction products voacanginol (**3**) and conopharynginol (**4**), obtained from the indole alkaloids voacangine (**1**) and conopharyngine (**2**) respectively, gave, by the treatment of their tosylates **5** und **6** with triethylamine, two fragmentation products, voaenamine (**7**) (70–80%) and conoenamine (**8**) (25–45%) respectively (*Scheme 1*). The structures of **7** and **8** were derived from spectroscopic evidence and some chemical transformations.

Conopharynginol tosylate (**6**) gave with tertiary base, besides **8**, the quaternary aziridinium salt **12** (58%) (*Scheme 3*). This salt could undergo nucleophilic attack, giving compounds of the A-series with a C-homo-conopharyngine skeleton (due to attack at C(18) and compounds of the B-series with a spiro-centre (due to attack at carbon(5)) (*Scheme 3*). The structures of these compounds were elucidated using D-incorporation experiments, ^{1}H- and ^{13}C-NMR. and mass spectra. On heating to 230°, acetylated spiroalcohol **22** was converted, probably *via* the ion pair **23**, into the base **16**, which on catalytic reduction gave **13**, a member of the A-series.

The reactions mentioned above constitute interesting skeletal isomerisations of the conopharyngine skeleton.

Die Indolalkaloide Voacangin (**1**) und Conopharyngin (**2**) (vgl. [2]) lassen sich leicht mit Lithiumaluminiumhydrid in Voacanginol (**3**) [3] bzw. Conopharynginol (**4**) und anschliessend in die entsprechenden Tosylate **5** bzw. **6** [4] überführen. Die kri-

[1]) 153. Mitt. s. [1].