bitter ones, despite the bulky *N*-substituent. The absence of sweetness may be related with some validity to the *N*-substitution, in terms of a recent hypothesis[6] that the system AH,B (where AH is a proton donor and B is a proton acceptor, of a certain proximity) is a prerequisite for sweetness. In saccharin, the AH group is the imide NH– missing from I.

This theory assumes that sweetness can be related to a particular structural feature (e.g. the AH,B system), rather than to overall properties of the molecule. If *N*-substitution made the saccharin moiety tasteless, one might expect a mild, sugar-like sweetness with I, since the AH,B group of the glucose moiety (C·1–OH, C·2–OH) remains intact. Apparently, any such effect of the sugar is overwhelmed by the much greater bitterness of I. The intensity suggests the bitterness is that inherent[7] in the saccharin structure, and only the sweetness of saccharin has been removed by *N*-substitution.

Résumé. La saccharine a été fixée par son azote imidique sur le C_6 du glucose, par l'action de la saccharine sodée sur un dérivé protégé du *p*-toluénesulfonyl-6-*O*-D-glucose, et élimination des groupes protecteurs pour former un composé hydrosoluble. La saveur amère peut être attribuée à l'élimination du proton imidique de la saccharine.

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Life Sciences Research, Stanford Research Institute, Menlo Park (California 94025, USA), 17 June 1968.

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Studies in Medicinal Plants. Part III. Protoberberine Alkaloids from the Roots of *Cissampelos pareira* Linn.[1]

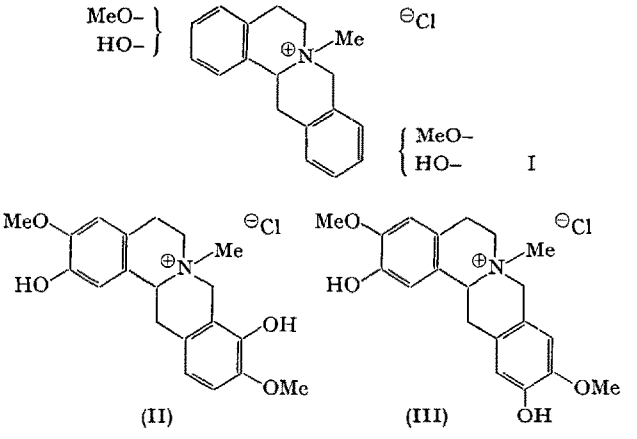
Our interest in the alkaloids from the roots of *Cissampelos pareira* Linn.[2–5] led us to the examination of its water-soluble quaternary bases previously isolated by two of us[5]. In the present communication only the essential data required to establish the constitution of Cissamine – the major quaternary alkaloid present in the roots of the plant – are reported.

Cissamine chloride has m.p. 215–220°, $[\alpha]_D^{26}$ – 129° (c = 1.00; MeOH). Its mass-spectrum revealed that the previous formula[5] was untenable; this has now been revised to $C_{20}H_{24}NO_4Cl$. Its UV-absorption at λ_{max}^{EtOH} 212, 235 and 285 nm (log ε 4.51, 4.10 and 3.94 respectively) corresponds to a tetrahydroberberine structure and the phenolic nature was shown by the spectral change in alkali to 218 nm (log ε 4.52) 253 nm (log ε 4.15) and 302 nm (log ε 4.04). The IR-spectrum supported the presence of phenolic hydroxyl group(s) (3509^{-1} cm).

The NMR-spectrum taken in D_2O on a Varian A-60 machine showed signals for 4 aromatic protons (3.02 to 3.15 τ), 1 $\overset{\oplus}{\text{N}}$-*Me* (6.75 τ) and 2 aromatic OMe groups (6.18 τ, 6.24 τ). There were 6 protons in the region 6.4–7.0 τ and 3 at τ 5.45.

A clue to the structure of cissamine chloride was provided by degradation studies. A double Hofmann degradation of the base chloride yielded a compound, m.p. 152–153° which contained 1 NMe_2 and 2 OMe groups. This, in conjunction with the foregoing data indicated that the N in this compound was in an environment as in tetrahydropalmatine and the partial structure of cissamine chloride could thus be written as (I). This was confirmed by the mass-spectrum of the quaternary base which showed the base peak at m/e 341 corresponding to the fragment M-HX (X = Cl)[6]. This narrowed the assignment of the structure of cissamine chloride to (II) and (III). The fixation of the positions of the 2 hydroxyls and 2 methoxyls in the 2 aromatic rings in these structures follows mainly biogenetic grounds.

A compound with the structure (II), named cyclanoline had recently been isolated from *Stephania tetrandra* by Tomita et al.[7]. A comparison of cissamine chloride with cyclanoline chloride (m.p., thin-layer chromatography, optical rotation and IR-spectrum) showed that the 2 compounds were, indeed, identical[8]. Structure II for cissamine chloride is thus confirmed.



Zusammenfassung. Cissaminechlorid aus den Wurzeln von *Cissampelos pareira* Linn. ist als Protoberberin-Alkaloid erkannt und mit Cyclanolinechlorid aus *Stephania terandra* identifiziert worden.

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Central Drug Research Institute, and University, Lucknow (India), 11 June 1968.

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