

THE OCCURRENCE OF NOR-DIHYDROTOXIFERINE IN STRYCHNOS PSEUDOQUINA

A. ST. HIL.

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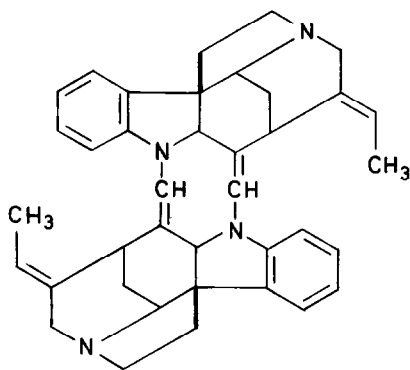
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Nor-dihydrotoxiferine,  $C_{38}H_{40}N_4$ , is a bistertiary Strychnos alkaloid, first isolated by Asmis et al. (1) from the bark of *S. toxifera*, in very small amounts.

Its structure was established in 1968 by Bernauer et al. (2) and later confirmed by synthesis (3).

On the course of our investigations on the alkaloids of Strychnos species (4) we have isolated in large amounts and of high purity nor-dihydrotoxiferine from *S. pseudoquina* St. Hil where it occurs as the 6% of the crude bark.

The sample was collected by Romeu P. Belém, near Brasilia in 1968, and determined by Murça Pires of Instituto Agronomico do Norte (Belém).



(I)

Nor-dihydrotoxiferine was extracted in Soxhlet from the plant material (bark of branches, inner bark of the trunk, corky bark of root, bark of root, bark of branches) successively with cyclohexane and chloroform.

The cyclohexane extract was fractionated on a Florisil column using as eluant  $CHCl_3-CH_3OH$  and yields pure nor-dihydrotoxiferine (58% of the total extract),  $\beta$ -sitosterol (15%) and two unidentified alkaloids (10%).

Nor-dihydrotoxiferine was identified through its analytical data, UV and IR spectra. MS gives a molecular weight 552 in accordance with the proposed formula. NMR spectra confirm the structure (I);  $[\alpha]_D^{28} = -820$  (c = 1, 2;  $\text{CHCl}_3$ ).

Its picrate decomposes at  $220^\circ\text{C}$ ; iodometylate crystals (do not melt before  $340^\circ$ )  $[\alpha]_D^{24} = -494$  (c = 1; in MeOH).

Sitosterol was identified through its m.p., IR, UV and NMR spectra in comparison with an authentic specimen.

The occurrence of nor-dihydrotoxiferine in large amount and rather pure form is significant for the biogenesis of Strychnos alkaloids.

So far very small amounts of both nor-dihydrotoxiferine and its precursors, i. e. 18 desoxy-W.G. -aldehyde, was found only in S. toxifera.

This is the first time that a large amount of bistertiary Strychnos alkaloid is found in a plant. Owing to its very high chemical instability we may speculate that, as diaboline in S. ignatii, dihydrotoxiferine may represent not only the chemical intermediate, as anticipated by Bernauer et al. (2), of C-dihydrotoxiferine, but also the precursor in the biogenetic pathway of bisquaternary alkaloids of the C-curarine group.

#### References.

1. H. Asmis, P. Waser, H. Schmid, P. Karrer, *Helvetica Chimica Acta*, **38**, 1661 (1965).
2. K. Bernauer, F. Berlage, W. von Philipsborn, H. Schmid, P. Karrer, *Helvetica Chimica Acta* **41**, 2293 (1958).
3. *Swiss Appl. Jan.* 30 (1959); *U.S.* 3·073·832 (Cl. 260-93, Jan. 15 (1963); *C.A.* 58, 9160(1963).
4. The previous paper on this subject is: "Research on the alkaloids of Strychnos. XVII. The alkaloids of Strychnos Jobertiana Baill. and Strychnos rondeletoides Spruce: the occurrence of a new alkaloid, Jobertine (O-acetyl-diaboline B) in Strychnos Jobertiana." *Delle Monache F.*, Corio E. and Marini Bettòlo G.B., *Ann. Ist. Super. Sanità* (1967) **3**, 564.