Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

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Strychnorubigine, strychnohirsutine, tetradehydro-strychnohirsutine and II-methoxystrychnofendlerine: new alkaloids of American Strychnos

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **65** (1978), n.6, p. 293–296.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1978_8_65_6_293_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1978.

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Strychnorubigine, strychnohirsutine, tetradehydrostrychnohirsutine and 11-methoxystrychnofendlerine: new alkaloids of* American Strychnos. Nota di GIOVANNI BATTISTA MARINI-BETTÒLO (*), CORRADO GALEFFI (**), MARCELLO NICOLETTI (*) e IRENE MESSANA (*), presentata (***) dal Corrisp. G. B. MARINI-BETTÒLO.

RIASSUNTO. — Nel quadro delle ricerche su alcaloidi di *Strychnos* sudamericane sono stati isolati quattro nuovi alcaloidi ed in particolare la stricnorubigina da *S. rubiginosa* de Candolle, la stricnoirsutina e la tetradeidrostricnoirsutina da *S. hirsuta* Spruce ex Bentham e la 11-metossistricnofendlerina da *S. fendleri* Sprague & Sandwith. Sono state anche studiate *S. erichsonii* Richard Schomburgk, *S. solimoesana* Krukoff e *S. glabra* Sagot ex Progel, dalle quali sono stati isolati alcaloidi già noti.

In previous papers we have described the isolation and the structure of alkaloids from a number of *Strychnos* species from tropical America [1], responsible for the curarizing and toxic properties of the extracts from these plants.

We now report the isolation and the structure determination of four new alkaloids from three *Strychnos* species, i.e. *S. rubiginosa* de Cand., *S. hirsuta* Spr. ex Benth. and *S. fendleri* Sprag. & Sand. Their structures suggest new pathways in the rather complicated biogenetical pattern of indole alkaloids.

Strychnorubigine I (Fig. 1) was isolated from the bark of roots of *S. rubiginosa*, sample collected in the state of Bahia, Brasil (Harley 19142).

I : m.p. 126-7° C (with decomp.), $C_{22}H_{28}N_2O_4$, MS m/e (%) : 384 (M^+, 83), 383 (80), 354 (65), 353 (80), 281 (100), 279 (60), 200 (41), 199 (37), 170 (37); UV_{EtOH} λ_{nm} (log ε) 227 (4.68). 274 (3.91, shoulder), 284 (3.84, shoulder), 293 (3.84); IR_{CHCl_3} 3400 and 1720 cm^{-1}.

The ^1H-NMR spectra ($CDCl_3$) of strychnorubigine and its O-acetyl-derivative II are in agreement with the proposed structure I. This is also confirmed by comparison of the MS spectrum of I with that of isositzirikine III [2]. The configuration of the chiral centre at C-3 was assigned on the basis of the ORD curve, whereas the configuration at C-15 was deduced from biogenetic considerations. Two already known alkaloids, 11-methoxydiaboline IV [3] (Fig. 2) and normacusine B, V [4] (Fig. 1), were also isolated from stem and root barks of the same plant.

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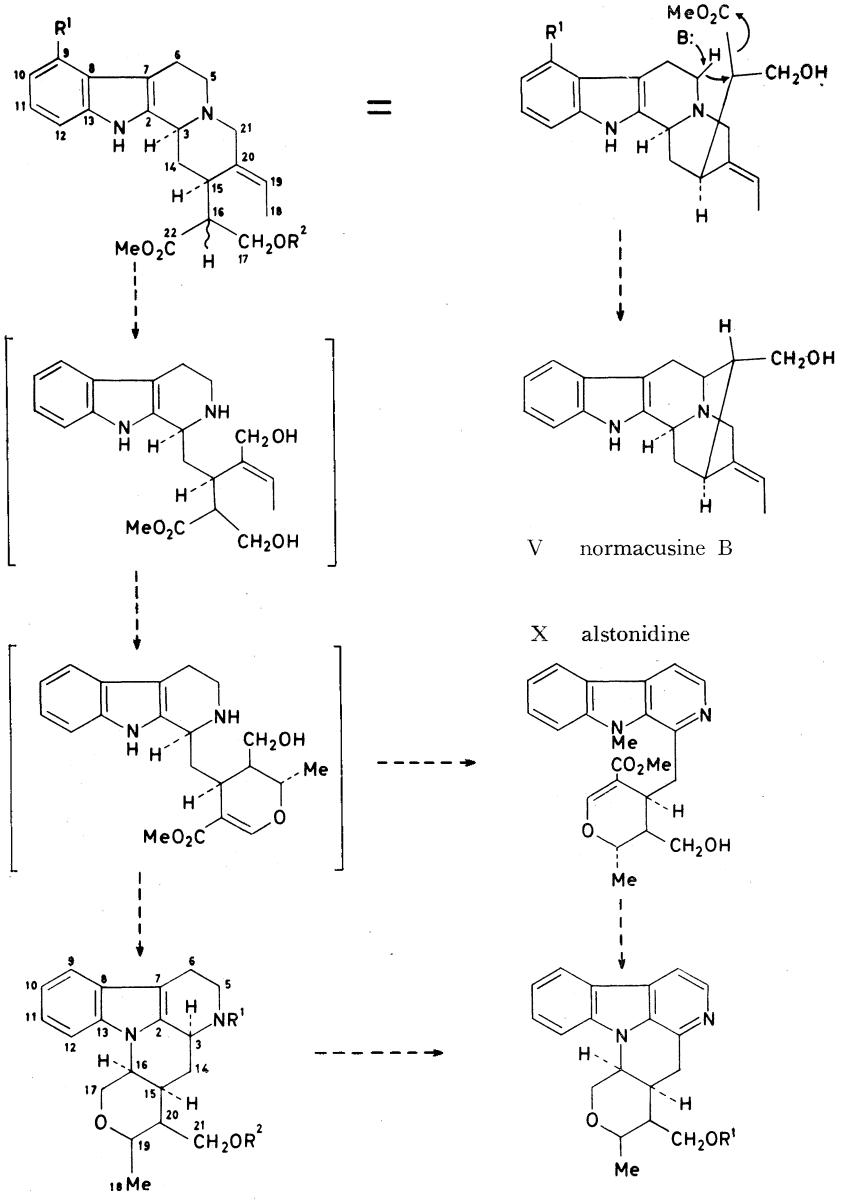
	R^1	R^2	
I	OMe	H	strychnorubigine
II	OMe	Ac	O-acetylstrychnorubigine
III	H	H	isositzirikine

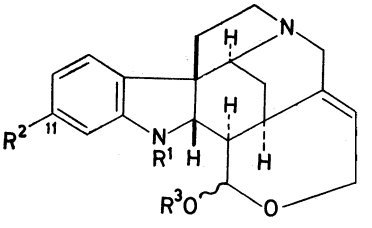


	R^1	R^2			R^1	
VI	H	H	strychnohirsutine	VII	H	tetradehydrostrychnohirsutine
VIII	Ac	Ac	N , O-diacetylstrychnohirsutine	IX	Ac	O-acetyltetradehydrostrychnohirsutine

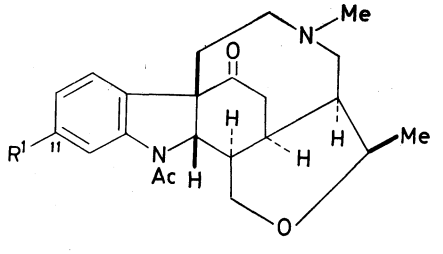
Fig. 1.

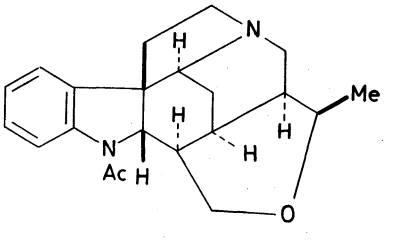
Strychnorubigine has the same aromatic substitution as that found in many alkaloids of the corynantheane group. Moreover, I is closely related to normacusine B , V: the co-occurrence of both substances in the same plant supports a biogenetic correlation.

Strychnohirsutine VI and tetradehydrostrychnohirsutine VII are both β-carboline derivatives isolated from the bark of roots of *S. hirsuta*, collected in Amazonas, Rio Maues (Prance 22104).



	R^1	R^2	R^3	
IV	Ac	OMe	H (OH β)	11-methoxydiaboline
XIII	Ac	H	H (OH β)	diaboline
XIV	Ac	H	Ac (OAc β)	henningsamine
XVI	H	H	H (OH β)	N-desacetyldiaboline
XVII	Ac	H	Ac (OAc α)	jobertine





	R^1	
XI	OMe	11-methoxystrychnofendlerine
XII	H	strychnofendlerine

XV spermostrychnine

Fig. 2.

VI : m.p. 141–3° C, $C_{19}H_{24}N_2O_2$, $[\alpha]_D^{20} = -6.3$ (c. 0.5, $CHCl_3$); MS m/e (%) : 312 (M^+, 100), 283 (78), 240 (94), 180 (94); UV_{EtOH} λ_{nm} (log ε) 228 (4.51), 276 (3.84), 284 (3.86), 293 (3.75, shoulder).

The structure VI was deduced by ^1H-NMR spectroscopy of the N , O-diacetylderivative VIII, whereas the configuration to the chiral centre C–3 was inferred from the positive Cotton effect, and that of C–15 from biogenetic considerations. By catalytic dehydrogenation with Pd and maleic acid VI is converted into VII.

VII : m.p. 221–5° C , $C_{19}H_{20}N_2O_2$, MS m/e (%): 308 (M^+, 75) 249 (25), 205 (100); UV_{EtOH} λ_{nm} (log ε) 240 (4.68), 254 (4.38), 282 (3.99), 291 (4.22), 346 (3.77), 360 (3.82).

Assignation of ^{1}H– and ^{13}C–NMR chemical shifts of the O–acetylderivative IX confirms the proposed structure. On the basis of their structures these substances (VI and VII) may be considered biogenetically related to alstonidine X [5], isolated from *Alstonia constricta* (Apocynaceae). This correlation represents another link between the alkaloids of Loganiaceae and Apocynaceae.

11–methoxystrychnofendlerine XI (Fig. 2) was isolated from stem bark of *S. fendleri*, collected in Brasil, Roraima (Murça Pires 14687). We have previously reported the isolation from the same plant and the structure determination of four new alkaloids [6] related to XI. The structure of the latter was in effect determinated by direct comparison with strychnofendlerine XII [6], present in the same plant.

XI : m.p. 242–4° C , $C_{23}H_{30}N_2O_4$, $[\alpha]_D^{20} = +123$ (c. 0,5, $CHCl_3$); MS m/e (%) : 398 (M^+, 100), 339 (32), 327 (15), 297 (30), 285 (4), 259 (10), 215 (33), 202 (3), 174 (14); UV_{EtOH} λ_{nm}^{max} (log ε) 251 (4.03), 290 (3.72), 296 (3.69, shoulder), λ_{nm}^{min} 273 (3.47).

From the same plant three known alkaloids were also isolated: diaboline XIII, henningsamine (O–acetyldiaboline A) XIV and spermostrychnine XV.

Diaboline has been also isolated by us in the present research from root bark of *S. erichsonii* Richard Schomburgk, Mato Grosso, Rio Aripuana (Prance 18651) and from the root bark of two samples of *S. solimoesana* Krukoff, Amazonas, Rio Purus (Prance 21254 and Prance 13929). In the latter sample also two dimeric alkaloids were isolated, C–calebassine (0.5 %) and C–curarine (0.1 %). 11–Methoxydiaboline IV was isolated the first time by us from stem bark of *S. romeu belenii* Krukoff [3], Mareu, Bahia, Brazil (Romeu Belem 3504) and now from the roots of the same plant.

The present results confirm the ubiquity in the *Strychnos* genus of diaboline and its derivatives: N–desacetyldiaboline (= W.G. aldehyde) XVI, 11–methoxydiaboline IV and O–acetylderivatives, henningsamine XIV and jobertine XVII.

Experimental details will be reported elsewhere.

We are indebted to Dr. B. A. Krukoff (N.Y. Botanical Garden) for supplying and identifying the plants and for his suggestions and comments.

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