

ON THE CONTENTS OF SCHUMANNIOPHYTON PROBLEMATICUM (RUBIACEAE)

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(Received in UK 1 June 1978; accepted for publication 12 June 1978)

Bark of "faux Schumanniohytum" (name never published) was left to us by the late Dr. Raymond-Hamet of Paris. This material, according to PC ¹⁾ and strong antiinflammatory activity of crude extracts and pure yohimbine, turned out to be derived from *Pausinystalia yohimbe* (Rub.).

During the time these investigations were carried out, we became interested in "vrai Schumanniohytum". With the help of M. Aké Assi Laurent, Centre floristique, Université d'Abidjan (Ivory Coast), we were able to secure genuine root bark of *Schumanniohytum problematicum* (A. Chev.) Aubrév. ²⁾. The basionym of this binominal is *Assidora problematica* A. Chev. ³⁾, named after a well-known botanist on the Ivory Coast who had originally discovered this plant.

The *Schumanniohytum problematicum* (6 kg of dried root bark) was collected on June 19, 1974, in the forest of Amitiora. A voucher-specimen has been deposited in the Botanical Institute of Abidjan under "L. Aké Assi, 12.540".

Shortly after the beginning of our work it was found ⁴⁾ that the stem and leaf of this plant appeared to contain an alkaloid (positive Mayer- and Dragendorff-reactions), whereas long ago ⁵⁾ M. Raymond-Hamet indicated that the plant was alkaloid-free.

Our dried root bark (2 kg) was extracted with MeOH containing 2% acetic acid. The soluble material (21 g) was dissolved in little methylene chloride and on standing at 5-10°C for a few days a crystalline mixture (A) (3,5 g) separated. Its mother liquor (B) was chromatographed on silica gel.

(A) contained scopoletin (1) and a new pyridine derivative (3), for which we propose the name "Schumanniohytine".

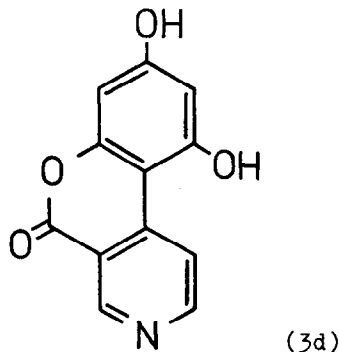
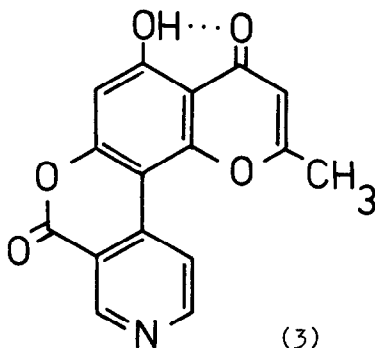
From (B) scopoletin (1), nor-eugenin (2), a little (3) and two new piperidine-2-ones, (4) and (5) were separated.

The empirical formulae, the m.wt., the m.p. and the yields of the unknown substances were:

- (3) $C_{16}H_9NO_5$ m.wt. (MS): 295.0481 m.p. 284-6°C (600 mg)
 (4) $C_{15}H_{15}NO_5$ m.wt. (MS): 289.0950 m.p. 300-3°C (35 mg)
 (5) $C_{16}H_{17}NO_5$ m.wt. (MS): 303.1102 m.p. 309-13°C (7 mg)

(3) was recrystallised from glacial acetic acid. It gave a dark violet ferric chloride colour and yielded a methiodide ($C_{17}H_{12}NO_5I \cdot H_2O$, m.p. 286°C, (3a)) and an O-acetyl derivative ($C_{18}H_{11}NO_6$, m.p. 243-5°C, (3b)) which gave no colour with ferric chloride.

Compound (3) was identified from its spectra and those of its derivatives (3a) and (3b), along with the results of degradative experiments. Oxidation of (3) with conc. HNO_3 ⁶⁾ gave cinchomeric acid ($C_7H_5NO_4$, m.p. 262°C, (3c)), while treatment with strong alkali ⁷⁾ gave 4,6-dihydroxy-benzo-(1',2'-2,3)-pyrano(5,4-c)-pyridine-9-one ($C_{12}H_7NO_4$, m.p. >350°C, (3d)).



Spectral data for (3):

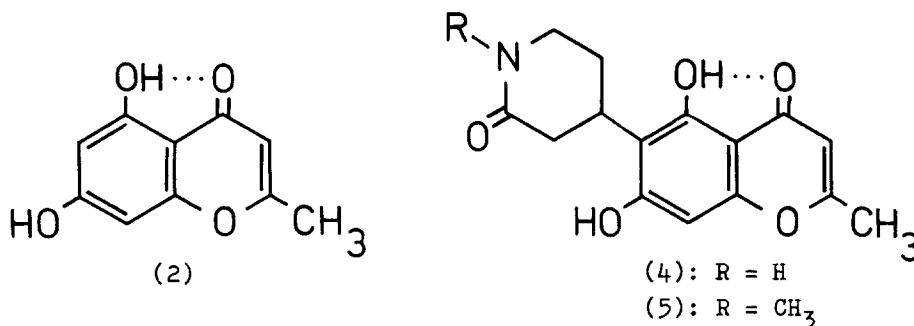
UV: λ_{max} (nm)(log ϵ)(MeOH): 225 (4.4), 237 (4.41), 251 (4.46), 256 (4.45), 292 (4.07), 318 (4.11).

IR: (KBr): 3200-2400 (OH), 3070 (aromat. C-H), 1750 ($>C=O$, lactone ring), 1660 ($>C=O$, δ -pyranone ring), 1620 ($>C=C<$), 1580 (aromat. $>C=C<$) cm^{-1} .

1H -NMR: δ (ppm)($CDCl_3$): 2.66 (allylic CH_3 -group, d, $J = 0.5$ Hz)
 6.34 (vinylic H, q, $J = 0.5$ Hz)
 6.82 (aromatic H, s)
 8.48 (pyridine H, q, $J_1 = 5.8$ Hz, $J_2 = 0.7$ Hz)
 8.97 (pyridine H, d, $J = 5.8$ Hz)
 9.58 (pyridine H, d, $J = 0.7$ Hz)
 13.47 (OH, s)

MS: m/e (rel. %): 295 (M^+ , 100), 267 (9), 255 (18), 227 (4).

The spectral data for (4) and (5) and the comparison with that of nor-eugenin (2) allowed us to propose the structures shown for (4) and (5). Lack of material prevented any degradative work.



The position of the amide group in the piperidine-2-one ring was deduced from NMR double-resonance experiments.

(4) was recrystallised from EtOH, (5) from EtOH/benzene, and both compounds gave a green ferric chloride colour.

(4) was methylated with diazomethane at the 7-hydroxyl group, whereas the hydrogen bonded OH-group at position 5 remained unchanged ($C_{16}H_{17}NO_5$, m.p. 262-3°C (4a)).

The spectral data for (4a) confirmed our conclusions.

Spectral data for (4) and (5):

UV: λ_{max} (nm)(log ϵ)(MeOH):

(4): 205(4.35), 225(4.18), 251(4.25), 257(4.27), 295(3.78), 318(3.68);

(5): 205(4.35), 225(4.16), 251(4.22), 257(4.23), 295(3.77), 318(3.66).

IR: (KBr): (4): 3370 (NH), 3300 - 2400 (OH), 1670 ($>C=O$, γ -pyranone ring and sec. amide), 1625 ($>C=C<$), 1600 (aromat. $>C=C<$) cm^{-1} ;

(5): 3400 - 2400 (OH), 2950 (N-CH₃), 1670 ($>C=O$, γ -pyranone ring and tert. amide), 1620 ($>C=C<$), 1600 (aromat. $>C=C<$) cm^{-1} .

1H -NMR: δ (ppm)(d_6 -DMSO):

	7 aliph. H	allyl. CH ₃	vinyl. H	arom. H	NH	N-CH ₃	7-OH	5-OH
(4):	1.6-3.8	2.38	6.16	6.3	7.53	-	10.88	12.9
(5):	1.6-3.8	2.36	6.14	6.26	-	2.84	10.89	12.9

MS: m/e (rel. %): (4): 289 (M^+ , 88), 272 (79), 245 (64), 244 (43), 231 (40), 229 (22), 219 (26), 218 (41), 217 (26), 216 (41), 205 (100), 193 (24), 192 (41), 189 (21);

(5): 303 (M^+ , 57), 272 (13), 245 (19), 244 (10), 231 (19), 218 (24), 217 (14), 216 (17), 205 (100), 193 (16), 192 (43).

Analytical data for (3), (4) and (5), as well as for their derivatives, agreed with the proposed structures.

One of the authors (U.S.) is grateful for financial assistance from Synthélabo-Paris.

The pharmacological experiments on "faux Schumanniohytum" and yohimbine were carried out by Synthélabo-Paris.

We thank M. Aké Assi Laurent, Centre floristique, Université d'Abidjan, most heartily for his collaboration.

For gifts of genuine material we are indebted to Dr. A. Lindemann (Sandoz AG, Basel), Prof. C.H. Eugster (University of Zürich), Dr. M.C.J. Ross (Chester-Beatty Res. Institution, London) and to Dr. F.J. Villani (Schering Corp., Bloomfield, USA).

We are also grateful to Dr. H. Heine, Laboratoire de Phanérogamie, Muséum National d'Histoire Naturelle, Paris, for his continuous help with botanical problems and to Prof. H. Becker, University of Heidelberg, for some pharmacognostical experiments.

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