

Isolation of 1,3,6,7-tetrahydroxyxanthone and an O-glucoside. The remainder of the crude tar from the CHCl_3 extraction was dissolved in the minimum of MeOH. Addition of H_2O dropwise, pptd a brown solid which separated into 2 bands by PLC (C_6H_6 -EtOAc, 3:2). From the band at R_f 0.4 a yellow solid was isolated which crystallised from EtOAc-light petrol as a yellow amorphous solid, mp $245-8^\circ$ (ch.). The MS of the metabolite resembled 1,3,6,7-tetrahydroxyxanthone and NMR spectrum suggested an O-glycoside of this xanthone. Xanthone glycoside was hydrolysed with dil. HCl and the sugar identified as glucose by PC (BuOH-EtOH- H_2O :4:1:5). From the band R_f 0.2, 1,3,6,7-tetrahydroxyxanthone was isolated as a pale yellow solid, mp 290° decomp (lit. 300° [1]) identical with an authentic sample (mmp, UV, IR). (Found: M^+ , 260.192 Calc. for $\text{C}_{13}\text{H}_8\text{O}_6$, 260.203). Structure of the metabolite was confirmed by methylation (CH_2N_2) which gave 1-hydroxy-3,6,7-trimethoxyxanthone, mp $222-224^\circ$, identical with an authentic sample (mmp, UV, IR, NMR) (Found: M^+ 302.280. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_6$, 302.282).

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HYDROQUINONE DIACETATE FROM *RHYNCHOSIA MINIMA*

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Key Word Index—*Rhynchosis minima*; Leguminosae; seed germination; seed; pericarp; hydroquinone diacetate.

In the leguminous weed *Rhynchosis minima* DC., Rangaswamy *et al.* [1] observed a prominent brown-black halo around seeds sown for germination on moist filter paper. The halo formation was attributed to the leaching of known phenolic substances from the seed coats. Further chemical examination has shown that the pericarp and seeds of *R. minima* contain hydroquinone diacetate.

The ether-soluble fraction of the alcoholic extract of the pericarp yielded, besides sitosterol, gallic acid, and protocatechuic acid. A fourth component **R** crystallized from petroleum as needles, mp $123-24^\circ$. **R** is a neutral compound; its IR spectrum indicated it to be an acetate ($\nu_{\text{max}}^{\text{KBr}}$ 1770 cm^{-1} and 1212 cm^{-1}) and aromatic ($\nu_{\text{max}}^{\text{KBr}}$ 1504 cm^{-1} and 855 cm^{-1}); its NMR spectrum (CDCl_3) contains 2 singlets, one at 7.05δ (aromatic protons) and the other at 2.2δ ($-\text{O}-\text{CO}-\text{Me}$) in the ratio 2:3. These data showed that **R** could be hydroquinone diacetate and its identity with an authentic sample was confirmed by co-TLC, mmp (undepressed), and superimposable IR and NMR spectra. On acid hydrolysis **R** gave hydroquinone.

To our knowledge this is the first report of occurrence of hydroquinone diacetate in a plant species, and it constituted as much as 1% of dry wt. of pericarp of *Rhynchosis minima*. The only other hydroquinone derivative reported in the Leguminosae is arbutin in *Lathyrus clymenum* var. *articulatus* [2]. Besides the well-known gallotannins and lichen depsides [3], the only other aryl esters known to occur naturally are the rare fungal metabolites, protoleucomelone and aurantia-cin leucodibenzoate [4].

Hydroquinone diacetate was not found in the seed kernel nor was hydroquinone detected in either seeds or pericarp. Hydroquinone is known to occur free [5-7], as monoglucoside [2,5,7] and as monomethyl, dimethyl and diethyl ethers [8] in many taxa. Whether or not hydroquinone diacetate is involved in halo formation during seed germination of *R. minima* is being investigated. Our voucher specimen of *Rhynchosis minima* tallies with the type specimen no. 321 (J. K. Maheshwari) of the Herbarium of the University of Delhi.

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LA DESACETYLRETULINE EXTRAITE DU *STRYCHNOS VARIABILIS*

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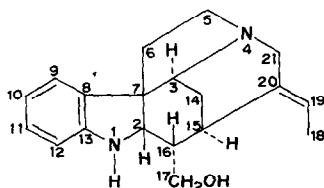
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Plante: *Strychnos variabilis* De Wild. (specimen voucher Evrard 6592-Herbarium du Jardin Botanique de Belgique à Meise). **Source.** écorces de racines récoltées par l'un d'entre nous (M.F.) dans la province de Kinshasa au Zaïre. **Usage.** l'écorce des racines est un poison violent [1]. **Travaux antérieurs.** différents screenings ont décelé la présence d'alcaloïdes dans les racines [2–4].

Partie examinée. l'Ecorce des racines. L'échantillon (1 Kg) a été soumis aux méthodes classiques d'isolement des alcaloïdes: percolation initiale par le MeOH; concentrat repris par HAc à 2% et extrait par CHCl₃ successivement à pH 5 (B₁), pH 8 (B₂) et pH 11 (B₃); enfin précipitation des alcaloïdes quaternaires (peu abondants) par l'acide picrique (B₄). Les extraits B₁ et B₂ contiennent plusieurs alcaloïdes dimères bis-indoliques de PM supérieur à 600 et dont l'étude structurale est en cours.



(1) Desacetylretuline C₁₉H₂₄ON₂

L'extrait B₃ ne contenait qu'un seul alcaloïde; il a été purifié par CCM sur S gel, suivie d'une

cristallisation dans le mélange MeOH-Et₂O. P.F. 165° SM m/e (abondance relative) = 296 1465, 1256, 1030 et 745 cm⁻¹—RMN (CDCl₃) δ [M⁺—C₁₉H₂₄N₂O (40)], 279 (6), 265 (5), 238 (13), 166 (100), 154 (4), 144 (14), 143 (10), 136 (6), 130 (8), 122 (8)—UV λ_{nm}^{max} (log ε), 212 (4,52), 247 (4,19) et 300 (3,81)—IR (KBr) ν 3350, 2930, 1605, 1488, 7,12-6,66 (4 H aromatiques)—5,32 (q., H₁₉)—1,62 (d. Me)—ORD (MeOH) [Φ] = +15000 à 255 nm. Effet Cotton positif qui indique une configuration 2β, 7β-acylindoline [5]. Ces données spectrales sont en accord avec la structure de la désacétylrétuline (1). Cette hypothèse semble corroborée par la similitude du comportement chromatographique et des spectres IR de l'alcaloïde B₃ acétylé à chaud (O et N acétylations) et de la rétuline acétylée à froid (O-acétylation).

C'est la première fois que la désacétylrétuline est signalée à l'état naturel; cependant ce produit avait été décrit dans les synthèses de la rétuline [6, 7]. De plus, il entre probablement dans la biosynthèse d'alcaloïdes plus complexes dont l'étude se poursuit.

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