

8-Hydroxy-1,2,3,7-tetraethoxyxanthone (Ib). Ia was methylated with CH_2N_2 in Et_2O , yielding Ib as yellow crystals, m.p. 116–118°. $\nu_{\text{KBr}}^{\text{max}}$ (cm^{-1}): 1658, 1608, 1593. $\lambda_{\text{max}}^{\text{EtOH}}$ (nm): 236, 255, 280, 305, 368 (ϵ resp. 26,400, 34,900, 28,600, 19,700, 8600); no alteration upon addition of NaOAc and of H_3BO_3 + NaOAc; $\lambda_{\text{max}}^{\text{EtOH}+\text{NaOH}}$ (nm): 238, 277, 305 sh (ϵ resp. 43,500, 34,500, 12,800) acidification restored the spectrum in EtOH; $\lambda_{\text{max}}^{\text{EtOH}+\text{AlCl}_3}$ (nm): 234, 266, 280, 295 sh, 320, 335 sh (ϵ resp. 35,700, 24,900, 26,600, 22,000, 18,300, 14,900); $\lambda_{\text{max}}^{\text{EtOH}+\text{AlCl}_3+\text{HCl}}$ (nm): 225 sh, 233, 255 sh, 279, 295 sh, 335 sh, 394 (ϵ resp. 32,500, 34,600, 22,900, 29,700, 17,600, 11,600, 7400). Gibbs test⁸ λ_{max} (nm): 465, 685 (Absorbance resp. 0.35, 0.71); MS: M 332 (100%), m/e (%) 317 (93), 302 (36), 299 (15), 287 (17), 274 (7), 259 (19).

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LEGUMINOSAE

ALIPHATIC ALCOHOLS, β -SITOSTEROLS AND ALKALOIDS IN *CASSIA JAHNII*

A. MORALES MENDEZ*

Instituto de Investigaciones Químicas. Facultad de Farmacia, Universidad de Los Andes, Mérida, Venezuela

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Plant. *Cassia jahnii* Britton & Rose. Leguminosae, known as Urumaco.

Source. Venezuelan Andes, at an altitude between 1500 and 3000 mts., near Mérida.

Use. Flowers used as purgative.

Previous work. Investigation of its anthraquinones.¹

Flowers. Alcoholic extract of flowers hydrolysed with aq. NaOH. The unsaponifiable material extracted with benzene and chromatographed on alumina with heptane. Initial fraction afforded a colourless solid m.p. 70–73°; TLC (Silica gel G, benzene) R_f 0.8; IR bands (KBr) ν_{max} 3400, 2940, 2860, 1475, 1065, 725 cm^{-1} ; NMR 6.4 τ (1 H, OH), 8.79 τ (50 H, CH_2) and 9.02 τ (3 H, CH_3); thus, the product has the properties of an aliphatic straight chain, primary alcohol. The mass spectrum has a base peak at m/e 83 with other major peaks at m/e 97, 111, 139, 182, 196, 250, 294, 308, 336, 364 and 392. The four latter peaks have a relative abundance of 27, 50, 22 and 1% respectively. Since both the IR and NMR show the presence of a hydroxy group, these four peaks, in the above proportions, cannot be due to any one compound but rather to a mixture of four compounds having molecular ions of m/e 308, 336, 364 and 392. The absence of a M^+-18 peaks suggests that

* Present address. Departamento de Química. Universidad Metropolitana. Avda. Gamboa San Bernardino, Caracas.

¹ C. SEELKOF and L. RUIZ TERÁN. *Rev. Fac. Farm. Universidad de Los Andes* 1, 7 (1958).

the latter four peaks are due to olefins, formed by elimination² of water from four primary alcohols of molecular weights 326 (C₂₂H₄₆O, docosyl alcohol), 356 (C₂₄H₅₀O, carnaubyl alcohol), 382 (C₂₆H₅₄O, ceryl alcohol) and 420 (C₂₈H₅₈O, 1-octocosanol) respectively. The isolation of ceryl alcohol from the flowers of *C. fistula*³ and myricyl alcohol (C₃₀H₅₀O) from *C. tora*⁴ has also been reported.

Later fractions afforded a second white solid, m.p. 138–139°; $[\alpha]_D^{20}$ –46.5°; IR bands (KBr) ν_{\max} 3450, 1645, 900, 810 cm⁻¹; NMR-(CDCl₃) 4.7 τ , 5.52 τ , 9.00 τ , 9.05 τ , 9.42 τ , 9.23 τ , 9.32 τ . This material was identical with an authentic sample of β -sitosterol. (Found: C, 80.09; H, 11.02. Calc. for C₂₉H₅₀O·H₂O; C, 80.19; H, –11.62%.) This was further confirmed by preparation of the acetate, m.p. 124–125°; $[\alpha]_D^{20}$ –40.6°; IR (KBr) ν_{\max} 1730, 1650, 1250, 905 cm⁻¹; NMR (CDCl₃) 4.60 τ , 5.30 τ , 7.80 τ , 8.90 τ , 9.02 τ , 9.20 τ , 9.30 τ . (Found: C, 81.02; H, 11.1. Calc. for C₃₁H₅₂O₂; C, 81.58; H, 11.40%.)

Leaves. The dried leaves were extracted after manner of Highet⁵ and yielded a small amount of a brown oil which on TLC silica gel (CHCl₃–Et₂NH, 9:1) and on alumina (CHCl₃–MeOH, 9:1) showed two spots R_f s 0.72, 0.69 and R_f s 0.52, 0.47 in the two systems respectively. Authentic samples of cassine and dihydrocassine showed identical behaviour both when run alongside and when co-chromatographed. β -Sitosterol was also isolated, using the same extraction procedure as in the case of the flowers.

² R. A. FRIEDEL, J. L. SHULTZ and A. G. SHARKEY. *Anal. Chem.* **28**, 926 (1956)

³ A. KUMAR, C. S. PANDE and R. K. KAND. *Indian J. Chem.* **4**, 460 (1966).

⁴ M. S. SASTRY. *Current Sci. India* **34**, 481 (1965).

⁵ R. J. HIGHET. *J. Org. Chem.* **29**, 471 (1964).

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THE FLAVONOIDS OF *CASSIA JAVANICA* FLOWERS

R. D. TIWARI and O. P. YADAVA

Department of Chemistry, University of Allahabad, Allahabad, India

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Abstract—From the ethanolic extract of the flowers of *Cassia javanica* Linn. four flavonoid glycosides have been isolated and characterised by normal methods. The compounds have been found to be, leucocyanidin-4'-O-methyl ether-3-O- β -D-galactopyranoside; dihydropinnetin-3-O- β -D-glucopyranoside; quercetin-3',4',7-trimethyl ether-3-O- α -L-rhamnopyranoside; kaempferol-3-rhamnoglucoside. Quercetin was also obtained.

INTRODUCTION

PLANTS of the *Cassia* genus (Leguminosae; subfamily, Caesalpionoidae) are known to be a rich source of polyphenol and anthraquinone derivatives.¹ *Cassia javanica* Linn. is extensively used as a medicinal substitute of *Cassia fistula*.² With a view to study the nature of the constituents the chemical examination of the flowers was undertaken.

¹ O. P. YADAVA, Doctoral Thesis, University of Allahabad (1969)

² K. R. KIRTIKAR and B. D. BASU, *Indian Medicinal Plants*, Vol. II, p. 877, Leader Press, India (1935).