A FLAVONOL NEOHESPERIDOSIDE FROM *JACARANDA ACUTIFOLIA*[1]

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ABSTRACT.—From the bark of *Jacaranda acutifolia* Humb. et Bonpl. (Bignoniaceae) has been isolated a new flavonol, 3-O-neohesperidoside, (7,2',3',4' tetrahydroxy flavone 3-O-neohesperiodoside).

Jacaranda acutifolia is widely distributed throughout Central America where it is used as an ornamental tree. Other closely related genera such as *Tabebuia*, *Tecoma*, *Tecomaria*, and *Catalpa* are found in abundance in central and southern Brazil. Although the leaves of many of the species of these genera have been investigated (1, 2, 3), no definitive studies have been found concerning flavanoid constituents in the bark of species of these genera.

EXPERIMENTAL[2]

PLANT MATERIAL.—The bark of the plant was collected in the area surrounding Guadalajara, Jalisco, Mexico. A voucher specimen is deposited in the herbarium of the Botany Department of the University of Guadalajara.

EXTRACTION AND ISOLATION.—The bark was stripped from trees eight to ten years old and immediately chopped into small pieces for air drying. The dry material was then milled, dried further in air and, finally, pulverized. The powdered bark (150 g) was extracted exhaustively in a Soxhlet extractor with dichlormethane. The marc was then removed from the thimble and air dried after which it was returned to the thimble, and the glycosides were completely extracted with methanol. The methanol solution was filtered and evaporated in a Roto-Vaporator to a syrupy consistency and then completely dried; a high vacuum oil pump was used to remove the last traces of methanol.

The dry crystalline mass was then dissolved in deionized water, warmed slightly and filtered; the clear filtrate was treated with successive small amounts of a 20% aqueous solution of normal lead acetate until precipitation was complete. The yellow precipitate was then filtered off and washed with water to remove the excess of lead acetate. It was again removed by filtration and suspended, while still moist, in warm methanol. The lead salt was then precipitated with hydrogen sulfide and the solution filtered to remove the lead sulfide. The filtrate was boiled to remove hydrogen sulfide and evaporated to dryness in the Roto-Vaporator. A small amount of the material was chromatographed on a polyamide-celite column (1:2) (3.5 x 70 cm) with methanol-water mixtures starting with water. The methanol-water (75:25) fraction yielded golden crystals on evaporation of the methanol and lyophyllization of the remaining aqueous solution. The physical data which follow were developed by the methods of Mabry *et al.* (4) See fig. 1.

IDENTIFICATION OF 7,2',3',4'-TETRAHYDROXY FLAVONE 3-O-NEOHESPERIDOSIDE.—The uv spectra established: a substituted C_3 and a free C_4' hydroxyl group resulting from a Band I bathochromic shift of 46 nm (MeOH to NaOMe); an increase in intensity ($\Delta=20$) and decomposition; an orthodihydroxy grouping in the "B" ring resulting from a 27 nm hypsochromic shift with $AlCl_3$/HCl relative to $AlCl_3$; the absence of a C_5-hydroxyl group since the MeOH spectrum is regenerated on acidification (HCl) of the $AlCl_3$ solution; a free C_7-hydroxyl group resulting from a Band II bathochromic shift of 10 nm (MeOH to NaOAc); also further proof of an orthodihydroxy group in the "B" ring, a Band I bathochromic shift of 21 nm (NaOMe to NaOAc/H_3BO_3). The uv spectral data are as follows: λ max MeOH, 242, 290, 332; NaOMe 254, 310, 378; $AlCl_3$ 263, 300, 359; $AlCl_3$/HCl 248, 290, 332; NaOAc 252, 290, 336; NaOAc/H_3BO_3 257, 293, 353; pmr (as TMSi ethers in CCl_4)[3] δ 1.2–1.6 (rhamnose methyl of neohesperiodse) (5), δ 3.35–3.95 (10-H's br.m. glucose and rhamnose), δ 5.1 (1 H, rhamnose-H_1) δ 6.0 (1 H, glucose-H_1), δ 6.75 (C_6-H), δ 6.8 (C_8-H), δ 7.0 (C_5'-H), δ 6.7 (C_6'-H), δ 8.01–8.05 (C_5-H). The coupling constants for the ortho aromatic protons are $J_{5,6}=8$ cps and $J_{5',6'}=7$ cps, while the meta-proton value is $J_{6,8}=2$ cps. These values are in agreement with literature values (6).

Rf values by desc. chrom. TBA=0.51, HOAc (15%)=0.75, mp. (uncorr) 215–216°, colors; vis-yellow, uv-blue, NH_3-vis-yellow, NH_3-uv-blue. Anal. Calcd. for $C_{27}H_{36}O_{19}$:C,48.77; H, 5.46.

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[1]Presented at the APHA (Academy of Pharmaceutical Sciences) St. Louis meeting, March 1981.

[2]The Roto-Vaporator Model 5101 was an SMI, the Lyophyllizer was a Thermovac model FD-3, the polyamide used was (Macherey-Nagel-CC6), and the celite was Johns Manville (.535). The uv spectra were recorded on a Perkin-Elmer-Coleman 124 and the pmr spectra on a Hitachi Perkin-Elmer R-24-60.

[3]Trimethylsilyl.

Found: C.49.17; H.5.97; this is based on the presence of 3 moles of water of crystallization. The pmr spectrum of the TMSi ethers in CCl_4 shows that the relative intensities of H_4':H_5':H_6:H_5 is 1:1:1:1. This would rule out the possibility of having the hydroxyl groups at the 3', 4', 5' positions since this would give a ratio of H_2':H_6':H_3 of 2:1:1. This, therefore, provides strong evidence for the presence of hydroxyl groups at the 2', 3' and 4' positions.

PREPARATION OF THE AGLYCONE.—The glycoside (150 mg) was refluxed in a steam bath with 200 ml of 6% HCl for two hours, cooled and chromatographed on a polyamide: celite (1:2) column (2.5 x 25 cm). After application of the hydrolyzing reaction mixture, the column was washed with water until the eluate was neutral. This solution contrained the sugars rhamnose and glucose. Subsequent elution with methanol and evaporation afforded the pure aglycone.

IDENTIFICATION OF 3,7,2',3',4'-PENTAHYDROXY FLAVONE.—The uv spectra established: a free C_3,C_3' and C_4'-hydroxyl grouping as a result of the rapid decomposition in NaOMe; the absence of a C_5-hydroxyl group; the regeneration of the MeOH spectrum on acidification (HCl) of the $AlCl_3$ solution; a free C_7-hydroxyl group resulting from a 19 nm bathochromic shift in Band II (MeOH to NaOAc); and an orthodihydroxy group in the "B" ring resulting from a 21 nm bathochromic shift in Band I (MeOH to NaOAc/H_3BO_3). The uv spectral data follow: λ max MeOH 242, 290, 324; NaOMe 251, 290, 352; $AlCl_3$ 260, 292, 365; $AlCl_3$/HCl 251, 291, 328; NaOAc 259, 290, 343; NaOAc/H_3BO_3 260, 288, 345; pmr (as TMSi ethers in CCl_4) δ 6.6 (C_8-H), δ 6.67 (C_6-H), δ 6.95 (C_5'-H), δ 6.98 (C_6'-H), δ 7.75–7.95 (C_5-H). R_f values by desc. chrom. TBA=0.56, HOAc (15%)=0.60. colors vis.-colorless, vis.(NH_3) yellow, uv blue, uv (NH_3) blue.

The identity of the neohesperidose is proved by the fact that, on hydrolysis of the glycoside, both rhamnose and glucose are obtained and by the pmr value for the rhamnose methyl peak of δ 1.2–1.6 (5).

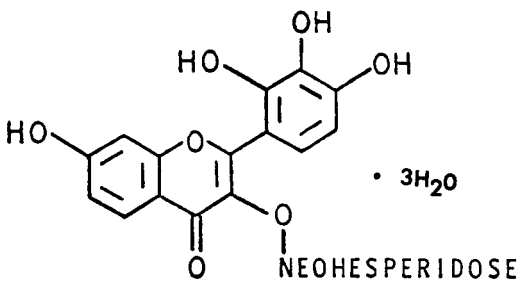

FIG. 1

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