brownish, straight, rarely curved, frequently bifurcated with abruptly rounded ends, slightly broader in the middle. The average length in a range of 24.7 to 152.0 $\mu$ was 78.4 $\mu$. The breadth in a range of 13.4 to 20.9 $\mu$ was 16.9 $\mu$ and it had 2 to 12 septa (figure 2).

Pathogenicity test was carried out by atomizing conidial suspension on the young leaves of *E. geniculata* Orteg. Typical symptoms developed within a period of 5 to 7 days incubation (figure 3). Re-isolations from the induced lesions established the identity with the original isolate. Control plants remained healthy. Morphological and other diagnostic characters indicated identity of the pathogen as *Helminthosporium bicolor* Mitra[4]. A culture of this fungus has been deposited at the Indian Agricultural Research Institute, New Delhi.

The authors thank the DST, Government of India, New Delhi for financial assistance.

28 December 1984; Revised 2 April 1985

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## APIGENIN 5-O-GALACTOSIDE FROM THE ROOTS OF *MELIA AZEDARACH*, LINN

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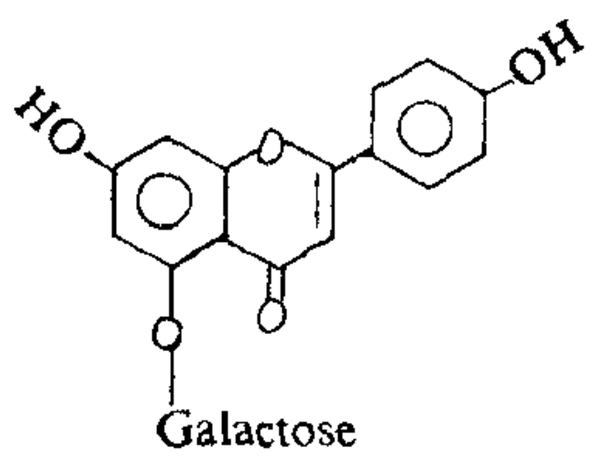
THE plant *Melia azedarach* Linn (N.O. Meliaceae) has been used in oriental medicine since ancient times, as a very important component in prescriptions for de-obstruent, resolvent, alexipharmic, nervous headache, anthelmic, antilithic, diuretic, rheumatism, leprosy, scrofulla, antiseptic, skin diseases and antimicrobial[1–4]. The isolation and characterization of a new flavone glycoside from the ethanolic extract of the roots of *M. azedarach* is reported here. The glycoside has been assigned the structure apigenin-5-O-$\beta$-D-galactopyranoside on the basis of spectral and chemical evidence.

The air dried and powdered roots of *M. azedarach* (5 kg) were extracted five times with rectified spirit (40 l) and the extract concentrated under reduced pressure to 400 ml and then poured into 800 ml of distilled water. The water insoluble fraction was filtered and the filtrate was concentrated and then extracted with organic solvents in the increasing order of their polarities. Ethyl acetate extract gave a glycoside which after purification by chromatography ($SiO_2$) yielded 1.5 g of a reddish yellow crystalline product (EtOH: pet.ether), [m.p. 148–50°] which was found to be a single entity (PC; $R_f$ 0.92, BAW 4:1:5 and TLC; $R_f$ 0.85, MeOH: $CHCl_3$, 5:5 and 0.77, MeOH: $CHCl_3$ 4:6); IR $\nu_{max}^{KBr}$ 825, 1020, 1120, 1170, 1280, 1350, 1465, 1510, 1640, 1610 and 3440 (br)$cm^{-1}$; UV[5] $\lambda$ max; + MeOH, 268, 335; + $AlCl_3$, 270, 335; (Found; C, 58.28; H, 4.59; $C_{21}H_{20}O_{10}$ required C, 58.33; H, 4.62%).

The glycoside (500 mg) on hydrolysis with $H_2SO_4$ (50 ml, 7%) gave D-galactose ($R_f$ 0.16, BAW, 4:1:5 and Co-PC) and an aglycone which was recovered as usual and crystallized from ethanol: pet. ether as yellow needles, m.p. 347–48°. This product gave positive test for Shinoda reaction; produced red colour with Mg-HCl; IR $\nu_{max}^{KBr}$, 1020, 1120, 1280, 1360, 1460, 1500, 1600, 1640, 1615 and 3440 (br) $cm^{-1}$; UV $\lambda$ max; + MeOH, 268, 336; + NaOMe, 275, 324, 392; + $AlCl_3$, 276, 345, 380 and + $H_3BO_3$-NaOMe, 260, 335 nm; MS[6] at m/e270 ($M^+$), 242 ($M^+$-CO), 118 ($M^+$-$C_7H_4O_4$), 90 ($M^+$-$C_7H_4O_4$ + CO), 149 ($M^+$-$C_7H_5O_2$) and 152 $M^+$-$C_8H_6O$), (Found; C, 66.59; H, 3.69; $C_{15}H_{10}O_5$ required; C, 66.66; H, 3.70%). It formed a tri-acetate ($Ac_2O$/py)[7], m.p. 181–82° (lit. m.p. 181–82°), (Found; C, 63.10; H, 4.00; 3 × OAc, 32.60; $C_{21}H_{16}O_8$ required; C, 63.63; H, 4.04; 3 × OAc, 32.57%) and trimethyl ether ($Me_2SO_4$/$K_2CO_3$)[7], m.p. 155–56° (lit. m.p. 156°), (Found; C, 69.19; H, 5.09; 3 × OMe, 29.75; $C_{18}H_{16}O_5$ required; C, 69.23; H, 5.12; 3 × OMe, 29.80%). 50% KOH degradation[8] of the aglycone (100 mg) yielded phloroglucinol, m.p. 212–13° (lit. m p. 214°; mmp and Co-TLC) and *p*-hydroxy benzoic acid, m.p. 216–17° (lit. m.p. 217°, mmp and Co-TLC) while $KMnO_4$ oxidation afforded *p*-hydroxy benzoic acid (mmp and Co-TLC) as one of oxidation products. Hence the aglycone was assigned as apigenin[6] which was finally confirmed with an authentic sample of apigenin (lit. m.p. 347–48°, mmp and Co-TLC).

Periodate oxidation[9] showed the consumption of 2.00 moles of periodate with the liberation of 1.00 mol of formic acid per mol of the glycoside suggesting the presence of only one moiety of galactose in pyranose form. Since there are three OH groups in aglycone, the sugar can be linked to any one of them. Assignment of

sugar linkage was deduced by comparing the properties of the aglycone with those of the glycoside. The glycoside neither gave a positive reaction with Dimorth reagent[10] nor produced any positive test with boric acid and citric acid in acetone[11, 12]. In addition to this, ethanolic solution of the glycoside in $AlCl_3$[13, 14] or $ZrOCl_2$[15] gave no specific observations under UV light, indicating that 5-OH group was not free in the glycoside. The completely methylated glycoside (Hakomori method[16]) on hydrolysis with acid (7% $H_2SO_4$) afforded dimethyl ether of apigenin, which responded to all the colour reactions characteristic of 5-hydroxy flavone and 2,3,4-tri-O-methyl-D-galactose ($R_G$ value and Co-PC). The UV spectra of glycoside as well as aglycone further confirmed the galactosidation at C-5 OH ($\lambda_{max}^{MeOH}$ nm, glycoside, 268, 335; + $AlCl_3$, 270, 335; aglycone; 268, 336; + $AlCl_3$, 276, 345, 380). The glycoside was hydrolysed with almond enzyme emulsin to yield apigenin (m.p., m.m.p. and Co-TLC) and D-galactose (Co-PC) indicating the presence of $\beta$-linkage.




The authors thank the Director, CDRI, Lucknow for the micro-analysis and spectral data of the glycoside and Dr J. S. Chauhan, Chemistry Department, Allahabad University for providing the authentic sample of apigenin. HOG thanks the Ministry of Health and Family Welfare, New Delhi for a fellowship.

5 August 1983; Revised 4 August 1984

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## REACTIONS OF BENZYLPYRIDINIUM BROMIDE AND 4-NITROBENZYL-PYRIDINIUM BROMIDE WITH $\alpha,\beta$-UNSATURATED KETONES: SYNTHESIS OF SOME NEW 1,3-DISUBSTITUTED NAPHTHALENES

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THE pyridinium salts and their ylides have been utilized in the synthesis of a wide variety of heterocyclic compound[1-12]. But little attention has been paid towards the synthesis of carbocyclic system especially leading to the naphthalene nucleus by the interaction of pyridinium ylides and $\alpha,\beta$-unsaturated ketones[13]. With a view of exploring the domain of such a reaction, we have studied the reaction of substituted benzylpyridinium salts with different $\alpha,\beta$-unsaturated ketones, in the presence of anhydrous $AlCl_3$ or $ZnCl_2$ in a mixture of glacial acetic acid of sodium acetate.

The experimental techniques were the same as reported earlier[2-4]. Both the pyridinium salts (2a, b) were prepared by heating benzyl bromides (1a, b) with pyridine in dry benzene[13, 14].