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A NEW FLAVANONE GLYCOSIDE FROM THE FLOWERS OF *ALTHAEA ROSEA*.

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ALTHAEA ROSEA (N.O. Malvaceae) is reputed for its medicinal importance[1] in our indigenous system of medicines. Seeds are used as demulcent, diuretic and febrifuge. Roots and flowers are applied in rheumatism. The earlier work on the flowers of *A. rosea* was reported by Jain *et al*[2]. In the present paper the authors report the isolation and characterization of a new flavanone glycoside, eriodictyol-4'-0-rhamnosyl-xylopyranoside (I) by physico-chemical techniques.

The glycoside (I) had m.p. 129–30° and analysed for $C_{26}H_{30}O_{14}$. It gave colour reactions specific for a flavanone glycoside.[3] The IR spectrum (KBr, cm^{-1}) of (I) showed the absorptions at 3400 (broad OH), 1685, 1610, 1570, 1420, 1360, 1260, 1210, 1200, 1130, 1025, 985, 945, 885, 825 and 722 and λ max 288, 330 (sh) nm (in methanol).

The glycoside when hydrolysed for 4 hr with 7% H_2SO_4 gave an aglycone (II) and aqueous hydrolysate after neutralization ($BaCO_3$) revealed the presence of D-xylose and L-rhamnose (R_f values and co-paper chromatographies). The aglycone (II), $C_{15}H_{12}O_6$, m.p. 267–68°, analysed for four hydroxyl groups [(acetate), ν max 3350 (broad, OH)]. PMR spectrum (DMSO-d_6, 90 MHz, TMS, δ) of the (II) displayed signals at 2.60–2.90 (m, 2H, H-3), 4.95–5.20 (dd, 1H, J = 4 and 12 Hz, H-2), 5.90 (d, 1H, J = 2.5 Hz, H-8), 5.75 (d, 1H, J = 2.5 Hz, H-6), 6.90–6.80 (m, 3H, H-2',5' and 6') and 13.40 (s, OH, exchangeable on D_2O shake). The UV spectrum of (II) showed maxima at 290, 335 (sh) nm in methanol. It gave positive bathochromic shifts with $AlCl_3$ [λ max 315, 335 (sh)] and NaOAc [λ max 325, 330 (sh)] respectively indicating the presence of free hydroxyls at C-5 and C-7 positions respectively. The $KMnO_4$ oxidation of the aglycone (II) and its methyl ether (prepared by using Me_2SO and K_2CO_3) yielded protocatechuic acid, m.p. 197–98° (m.m p. and Co-TLC) and veratric acid, m p. 178–80° (m.m.p. and Co-TLC) respectively as one of their oxidation products. The aglycone on alkaline degradation[4] gave phloroglucinol, m.p. 216–17° (m.m p. and Co-TLC) and protocatechuic acid (m.m.p. and Co-TLC) respectively. Thus the aglycone was assigned the structure of eriodictyol which was further supported by its mass spectral data [288 (M^+), 287 ($M^+ - 1$), 270 ($M^+ - H_2O$), 260 ($M^+ - CO$), 178 ($M^+ - C_6H_6O_2$), 152 ($M^+ - C_8H_8O_2$), 136 ($M^+ - C_7H_4O_4$), 135 ($M^+ - C_7H_5O_4$) and 109 ($M^+ - C_9H_7O_4$)]. The aglycone as eriodictyol was finally confirmed with the authentic sample (m.m.p. and Co-TLC)[5].

The glycoside was oxidised with $NaIO_4$[6] at room temperature. Results (after 60 hr) showed the consumption of 3.00 mol of periodate with the liberation of 2.00 mol of formic acid per mol of glycoside indicating the presence of disaccharide in the pyranose form.

The glycoside was methylated by Hakomori's method[7] followed by acid hydrolysis gave 2,3-di-O-methyl-D-xylose (R_G value and co-paper chromatography)[8], 2,3,4-tri-O-methyl-L-rhamnose (R_G value and co-paper chromatography)[8] and (III). The (III) on alkali degradation[4] yielded vanillic acid, m.p. 206–7° (lit. m.p. 207°, m.m.p. and Co-TLC) and phloroglucinol dimethyl ether (m.m.p. and Co-TLC) which confirmed the attachment of the sugars at 4' position in the aglycone.[9]

Partial hydrolysis of the glycoside (7% H_2SO_4) at room temperature showed the liberation of L-rhamnose first after 72 hr followed by D-xylose after 120 hr indicating the presence of L-rhamnose as the terminal sugar.

The glycoside on treatment with tokadiastase solution afforded L-rhamnose (co-paper chromatography) and (IV), m.p. 122–24° (dec). (IV) was treated with almond enzyme solution which yielded (II) (m.p., m.m.p. and Co-TLC) and D-xylose (co-paper chromatography). The above facts clearly indicated the presence of α-linkage between L-rhamnose and D-xylose and β-linkage between D-xylose and aglycone. Thus the glycoside was assigned a structure (I).

The flowers of *A. rosea* was collected from the local city Sagar and authenticated by the botanical survey of India, Allahabad circle (U.P.), India.

Isolation and purification: The air dried and powdered flowers of *A. rosea* (1 kg) were exhaustively extracted with methanol under reflux for 20 days. The total

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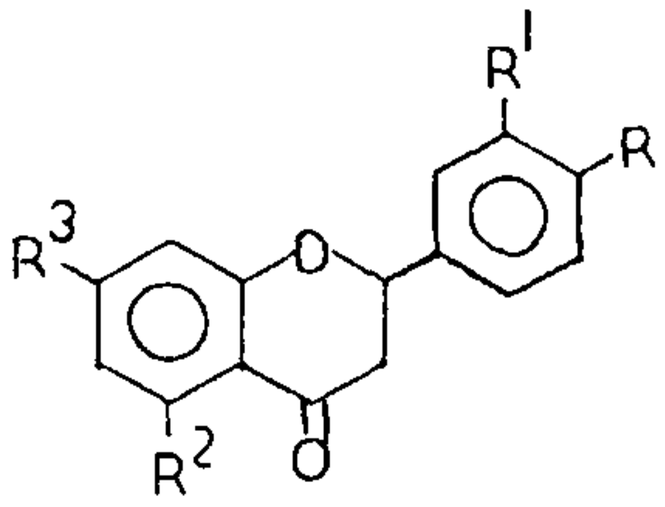

(I) $-R^1 = R^2 = R^3 = OH$; R = O-rhamnosylxyloside.
(II) $-R = R^1 = R^2 = R^3 = OH$
(III) $-R = OH$; $R^1 = R^2 = R^3 = OMe$
(IV) $-R^1 = R^2 = R^3 = OH$; R = D-xylose.

extract (20 l) was concentrated under reduced pressure to give a dark reddish amorphous substance (yield 4 g). It was passed through silica column and eluted with benzene*, chloroform*, EtOAc chloroform* (5:5), ethyl acetate* and methanol respectively. The methanolic fraction was further rechromatographed on silica column and eluted with methanol: acetone (8:2) which yielded the reported glycoside. The glycoside was crystallized from methanol as yellow needles (yield 1.400 g). The homogeneity of the glycoside was checked by TLC [Si gel, 28°, R_f: 0.81 ($CHCl_3$: MeOH, 6:4) and R_f: 0.62 (Me_2CO: MeOH, 5:5)] and PC [Whatman No. 1, descending, 28°, R_f: 0.61 (n-BuOH: OHAc: H_2O, 4:1:5) and R_f: 0.59 (15% gl. OHAc)]; (Found; C, 55.02; H, 5.33; required for $C_{26}H_{30}O_{14}$; C, 55.12; H, 5.30%).

Acid hydrolysis: The glycoside (500 mg) was refluxed with 7% H_2SO_4 (50 ml) for 4 hr. The reaction mixture was cooled and poured into distilled water. The precipitated aglycone was separated by filtration. The aqueous hydrolysate was neutralized ($BaCO_3$), filtered and evaporated under reduced pressure to a syrup which was found to contain D-xylose (R_f: 0.28, n-BuOH: OHAc: H_2O, 4:1:5) and L-rhamnose (R_f: 0.38, n-BuOH: OHAc: H_2O, 4:1:5).

The aglycone was purified on magnesol column, eluted with Me_2CO: MeOH (1:1) and crystallized from methanol: water (9.5:0.5) as yellow needles. The homogeneity was checked by TLC [Si gel, 28°, R_f: 0.85 ($CHCl_3$: MeOH; 6:4) and R_f: 0.66 (Me_2CO: MeOH, 1:1)] and PC [Whatman No. 1, descending, 28°, R_f: 0.64 (n-BuOH: OHAc: H_2O, 4:1:5), R_f: 0.64 (n-BuOH: OHAc: H_2O, 4:1:5) and R_f: 0.60 (15% gl. OHAc)]; ν_{max}^{KBr} 3350, 2910, 1680, 1604, 1510, 1460, 1275 and 1030 cm^{-1}. (Found; C, 62.52; H, 4.18; calculated for $C_{15}H_{12}O_6$; C, 62.50; H, 4.16%). Acetyl derivative prepared by Ac_2O/Py method (100 mg II + 6 ml Ac_2O + 5 ml C_5H_5N) and the product was crystallized from Me_2CO: MeOH as pale yellow needles, m.p. 135–36° (lit. m.p. 137°)[10] (Found; C, 60.53, H, 4.37; acetyl, 37.72; calculated for $C_{23}H_{20}O_{10}$; C, 60.52; H, 4.38; 4 × acetyl, 37.71%).

Methylation and hydrolysis of the glycoside: The glycoside (500 mg) was methylated by Hakomori's method. The methylated product was crystallized from MeOH: Me_2CO (5:5), m.p. 120–23°. The methylated glycoside (300 mg) was hydrolysed with 7% H_2SO_4 (30 ml) for 5 hr. The resulting mixture was poured into ice cold water (100 ml). The precipitated aglycone (III) was filtered. The aqueous hydrolysate after neutralization ($BaCO_3$) gave 2,3 di-O-methyl-D-xylose (R_G, 0.74, n-BuOH: EtOH: H_2O, 5:1:4) and 2,3,4-tri-O-methyl-L-rhamnose (R_G, 1.01, n-BuOH: EtOH: H_2O, 5:1:4). The aglycone (III) was crystallized as yellow needles from Me_2CO: Et_2O (5:5), m.p. 140–45° (d) (Found; C, 65.40; H, 5.42; calculated for $C_{18}H_{18}O_6$; C, 65.45; H, 5.45%).

Hydrolysis with tokadiastase and enzymatic solutions: The glycoside (200 mg) in ethanol (30 ml) was suspended with tokadiastase solution. The reaction mixture was left at room temperature for 50 hr. The reaction mixture was then shaken with ether. The hydrolysate was found to contain only L-rhamnose (co-paper chromatography). The etherial solution was concentrated and crystallized as microcrystalline yellow needles. (MeOH: Me_2CO) (IV) (Found; C, 57.09; H, 4.77; calculated for $C_{20}H_{20}O_{10}$; C, 57.14; H, 4.76%). To (IV) (50 mg) in ethanol (20 ml) almond enzyme solution was added and kept at room temperature for 48 hr. The reaction mixture was then shaken with ether which yielded eriodictyol (m.m.p. and Co-TLC). The hydrolysate showed the presence of D-xylose (co-paper chromatography).

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* These fractions yielded rutin, chrysin, kaempferol, robinetin, acacetin and phloretin respectively (see Reference 2).

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SYNTHESIS AND PYROLYSIS OF 1,3-DIBENZYL-2-ARYL-4-METHYL BENZIMIDAZOLINES

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WHILE extensive work was done on the synthesis and pyrolysis of 1,3-dibenzyl-2-arylbenzimidazolines and their 5-substituted derivaties[1-3], there is no report in literature regarding the formation and elimination reactions of the 1,3-dibenzyl-2-aryl-4-substituted benzimidazolines. Therefore, as a representative case the synthesis of 1,3-dibenzyl-2-aryl-4-methylbenzimidazolines(V) has been undertaken with a view to studying the effect of the substitutent on their formation and elimination reactions.

The condensation of 3-methyl-o-phenylenediamine with formic acid in dilute hydrochloric acid yielded 4 (or 7)-methylbenzimidazole[4](II). 1,3-dibenzyl-4-methylbenzimidazolium chloride (III) has been prepared by benzylation of this benzimidazole with excess of benzyl chloride. The quarternary salt (III) on hydrolysis with alcoholic potassium hydroxide afforded N^1, N^2-dibenzyl-3-methyl-o-phenylenediamine(IV). The diamine (IV) on condensation with equimolar quantity of benzaldehyde in alcohol-acetic acid medium yielded a colourless crystalline compound, m.p. 136°. This compound has shown no absorption due to N-H in the IR spectrum (KBr). Its PMR* spectrum has shown signals at 2.26 (s, 3H), at 4.4 (q, J = 10Hz, 4H) at 5.56 (s, 1H) and around 6.7 (m, 18H), assignable for a C–CH_3, two N–CH_2 groups, a methine and eighteen aromatic protons respectively. The foregoing data is in agreement with the expected, 1,3-dibenzyl-2-phenyl-4-methylbenzimidazoline structure (V Ar = ph) for the compound. The condensation with the diamine (IV) has been carried out with five other aromatic aldehydes and in all the cases, the corresponding benzimidazolines have been obtained in good yields (table 1).

Pyrolysis of 1,3-dibenzyl-2-phenyl-4-methylbenzimidazoline (V Ar = ph) at 200° for one hour yielded a single crystalline colourless compound, m p. 105°. The mass spectrum of the compound has shown the molecular ion at m/e 298. IR spectrum ($CHCl_3$) of the compound revealed the absence of NH and PMR spectrum (CS_2) [2.6 (3H, C–CH_3); 5.3 (s, 2H, N–CH_2-ph); around 7.2 (m, 13H, aromatic protons)] indicated the compound to be a 1,2-disubstituted benzimidazole and the structure was confirmed as 1-benzyl-2-phenyl-4-methylbenzimidazole (VI Ar = ph)[5] by comparison with the authentic sample. Compound (VI) was formed by the elimination of a benzyl radical from N^3 and a hydrogen atom from C^2. The formation of (VI Ar = ph) and not the isomeric benzimidazole (VII Ar = ph), which could be formed by the elimination of a benzyl radical from N^1 and a hydrogen atom from C^2, in this elimination reaction indicates that the methyl group at position 4 is exerting a strong steric effect in the benzimidazoline, facilitating exclusive elimination of N^3-benzyl group (scheme 1). The pyrolysis reaction has been extended to two more benzimidazolines *viz* 2-p-methylphenyl and 2-p-methoxyphenyl derivative (V Ar = p-methylphenyl, p-methoxyphenyl) and in both the cases the corresponding benzimidazoles (VI) have been obtained.

1,3-Dibenzyl-4-methylbenzimidazolium chloride (III).

4 (or 7)-Methylbenzimidazole (15 g) and freshly distilled benzyl chloride (30 ml) were thoroughly mixed in a round bottomed flask and heated in an oil

* PMR values are given in δ ppm.