FLAVONE GLYCOSIDES FROM LAWSONIA INNERMIS

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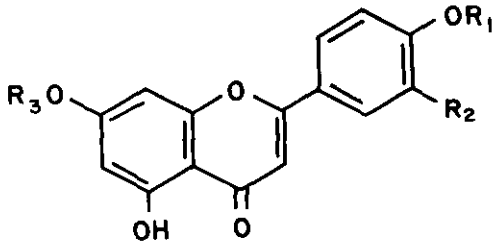
Four flavone glycosides representing 5,7,4' and 5,7,3',4'-substitution have been isolated from Lawsonia innermis

Lawsonia innermis (syn. L. alba), commonly known as henna, is an ancient plant popularly used for staining hands and hair due to the presence of a red colouring matter, lawsone, (2-hydroxy-1,4-naphthoquinone). A paste of the powdered leaves of this plant is used both as cosmetic and as a remedy for boils, wounds and some mycotic infections in the Middle East and Asia. The antibacterial activity of an aqueous extract of henna leaf has been demonstrated by Malekzadeh[1]. Recently Bhardwaj et-al[2] have reported the isolation of laxanthone-I; (1,3-dihydroxy-6,7-dimethoxyxanthone) and laxanthone-II; (1-hydroxy-3,6-diacetoxy-7-methoxyxanthone) from Lawsonia innermis but so far no reports have been mentioned for the identification of flavone glycosides from this plant. This is the concern of the present studies.

The dried powdered plant leaves (1 kg) were exhaustively extracted into light petroleum and then into methanol. The methanolic extract gave a dark thick syrup (120 g) after concentration under vaccum. This was chromatographed on silica gel columns followed by elution with light petroleum ether and then with ethyl acetate-methanol mixtures. Final purification of different components was achieved on a series of columns yielding flavone glycosides.

Apigenin-7-glucoside (1) crystallised from ethyl acetate-methanol mixtures, m.p. 230-233° C (lit.[3,4] m.p. 227-230° C). The absorption spectrum was characteristic of hydroxyflavones and showed typical shifts in the presence of additives such as aluminium chloride, sodium acetate and sodium hydroxide. The molecular ion (E.I. source) appeared at m/z 270 indicating the knocking off of the glucoside residue. The major breakdown pattern was as expected for apigenin m/z 242 (19%), 153 (22%), 152 (16%), 124 (18%), 123 (10%), 121 (6%), 118 (14%), The



(1) : $R_1 = R_2 = H$; R_3 = Glucosyl

(2) : $R_2 = R_3 = H$; R_1 = Glucosyl

(3) : $R_1 = H$; R_2 = OH; R_3 = Glucosyl

(4) : $R_1 = R_3 = H$; R_2 = O-Glucosyl

natural product gave a hexaacetate derivative m.p. 215-217°, consistent with the *i.r. and u.v. spectra.* τ($CDCl_3$) (hexaacetate): 2.1 (s, 1H, C_8Ar-H); 2.2 (s, 1H, C_6Ar-H), 2.7t, 3.0d, 3.35d, (4H, 4Ar-H); 3.43, (s,1H, C_3-H); 4.7 (m, 5H, glucosidic-H); 5.8 (b, 2H, -CH_2OAc); 7.55 (s, 3H, PhOCOCH_3); 7.7 (s, 3H, PhOCOCH_3); 7.9 (s, 12H, 4 x OCOCH_3).

Apigenin-4'-glucoside (2) crystallised as pale yellow needles m.p. 342-45° (lit.[5] m.p. 347° C). The absorption spectrum and the molecular breakdown pattern in its MS were identical with that of apigenin-7-glucoside. Its acid hydrolysis gave apigenin (5,7,4'-trihydroxyflavone) and glucose, identical with authentic samples[15]. The natural product gave a hexaacetate derivative m.p. 310-12°. τ($CDCl_3$): 2.10 (s, 1H, C_8Ar-H); 2.28 (s, 1H, C_6Ar-H); 2.7t, 3.1d, 3.4d, (4H, 4Ar-H); 3.5, (s,1H, C_3-H); 4.7 (m, 5H, glucosidic-H); 5.8 (b, 2H, -CH_2-OAc); 7.60 (s, 3H, Ph-OCOCH_3): 7.7 (s, 3H, pH.OCOCH_3); 7.9 (s, 12H, 4x-OCOCH_3).

Luteolin-7-glucoside (3) crystallised as pale yellow amorphous powder m.p. 245-47° C decomp. (lit.[6-12] m.p. 249-250° C decomp.). Its absorption spectrum was similar to apigenin glucoside except that it showed a red shift in the presence of boric acid indicating an ortho-dihydroxy group system in the molecule. In its mass spectrum the glucosidic moiety also knocked off and the molecular ion appeared at m/z 286 and its breakdown pattern was identical with luterolin (m/z

285, 258, 153, 152, 137, 134, 124, 123).

The parent compound gave a heptaacetate derivative m.p. 230-232°. τ ($CDCl_3$); 2.32 (d, 2H, C_6 & C_8 Ar-H); 2.7s, 3.0d, 3.28m. (3H, 3 Ar-H); 3.4, (s, 1H, C_3-H); 4.7 (m, 5H, glucosidic-H); 5.77 (b, 2H, $-CH_2OAc$); 7.55 (s, 3H, $Ph.OCOCH_3$); 7.63 (s, 6H, $Ph.OCOCH_3$); 7.9 (s, 12H, $4x\text{-}OCOCH_3$). Luteolin-7-glucoside is known to have low toxicity with mild influence on capillary resistance and diuretic and choleretic properties[13].

Luteolin-3'-glucoside (4) crystallised as pale yellow needles m.p. 245-247° C (lit.[14] m.p. 243-45° C). The fact that it showed no red shift in the presence of boric acid indicated that the catechol nucleus was not present in this compound. However, its mass spectral breakdown pattern was identical with that of luteolin-7-glucoside (3). Acid hydrolysis of the compound gave luteolin and glucose, identical with authentic samples[15]. The natural product gave a heptaacetate derivative m.p. 108-110°. ($CDCl_3$); 2.30 (s, 1H, C_8 Ar-H); 2.50 (s, 1H, C_6 Ar-H); 2.70d, 2.90d, 3.0d, 3.2d, (3H, 3 Ar-H); 3.5, (s,1H, C_3-H); 4.7 (b, 5H, glusidic-H); 5.8 (b, 2H, $-CH_2$-OAc): 7.6 (s, 6H, $Ph.OCOCH_3$); 7.7 (s, 3H, $PH.OCOCH_3$); 8.0 (s, 12H, $4x\text{-}OCOCH_3$).

The position of glycosidic link in all the four compounds (1-4) was established by observing a red shift in their absorption spectra in the presence of different additives such as sodium acetate, aluminium chloride or boric acid. Further confirmation came from the reported melting points of these compounds.

The alcoholic and petroleum ether extracts of Lawsonia innermis were thoroughly investigated for the presence of laxanthone-I and laxanthone-II but we were unable to detect these xanthones in these extracts. The presence of these xanthones in this plant has been reported by Bhardawaj and co-workers[2].

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