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TAXIFOLIN 3,5-DIRHAMNOSIDE FROM THE SEEDS OF *CORDIA OBLIQUA*

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Key Word Index—*Cordia obliqua*; Boraginaceae; taxifolin 3, 5-dirhamnoside; flavanonol glycoside.

Cordia obliqua is a medicinal plant [1, 2], but little work has been reported on the seeds [3] and roots [4–6]. We now report the identification of taxifolin 3,5-dirhamnoside.

The glycoside gave the characteristic reactions of flavanone, while acid hydrolysis gave 2 mol of rhamnose and taxifolin (dihydroquercetin). This aglycone was identified by analysis, spectral procedures, alkaline degradation and finally by co-chromatography with an authentic specimen [7].

Preparation of the nonamethyl ether of the glycoside by the Kuhn method [8] followed by its methanolysis [9] and then hydrolysis with aq. HCl gave 2,3,4-tri-*O*-methyl-L-rhamnose (2 mol) and taxifolin 7,3′,4′-trimethyl ether, which on demethylation with HBr–HOAc gave taxifolin (mp, mmp, co-IR and co-TLC). The observed consumption of 4.01 mol of periodate with the liberation of 1.01 mol of HCOOH together with methylation studies indicated that the L-rhamnose is present as two monosaccharide units in the pyranose form (if it was present as a disaccharide, the glycoside would have consumed *ca* 3 mol of periodate instead of *ca* 4 mol).

The position of the sugars in the glycoside was determined by the comparison of the spectral shifts of the glycoside with those of the aglycone. The glycoside was methylated, followed by acidic hydrolysis to afford an aglycone which displayed signal in the NMR (τ-2.40 (1H at C-5); 6.00 (9H, OMe at C-7, C-3′ and C-4′), −5.5 (2H at C-3)) which was identified as taxifolin 7,3′,4′-trimethyl ether (confirmed by UV, IR and KOH degradation), further confirming the rhamnose unit at C-3 and C-5. The fact that glycoside could not be hydrolysed with almond emulsin indicated the presence of α-linkages. Hence the glycoside is taxifolin 3,5-*O*-α-L-dirhamnopyranoside.

EXPERIMENTAL

Isolation and purification. The air-dried and powdered seeds of *Cordia obliqua* were extracted with $CHCl_3$ under reflux. The extract was filtered and concd. It deposited a yellow amorphous compound. It was purified over a Si gel column and eluted with MeOH–EtOAc. It was crystallized as yellow needles from EtOH, mp 148°(d). The homogeneity of the glycoside was checked by TLC (R_f 0.54 in MeOH–$CHCl_3$, 3:7) and PC (R_f 0.89 in BAW, 4:1:5). (Found: C, 54.35; H, 5.37. $C_{27}H_{32}O_{15}$ requires: C, 54.36; H, 5.37%.) ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1680, 1604, 1536, 1455, 1285, 1125, 822 and 725. λ_{max} nm: 288 (MeOH); 290 (+$AlCl_3$); 323 (+NaOAc).

Acidic hydrolysis. The glycoside (500 mg) was hydrolysed with 50 ml 7% ethanolic H_2SO_4 for 4 hr under reflux. It was poured into distilled H_2O (500 ml). On cooling a solid precipitated which was filtered off. The aq. hydrolysate, after neutralization with $BaCO_3$, was identified as L-rhamnose (co-PC and osazones). The solid was purified over a Si gel column and crystallized as golden needles from aq. EtOH. It was homogeneous by TLC (R_f 0.44 in $CHCl_3$–MeOH, 8:2) and PC (R_f 0.90 in BAW, 4:1:5), mp 237–38°, M^+ 304, $C_{15}H_{12}O_7$. (Found: C, 59.20; H, 3.94. $C_{15}H_{12}O_7$ requires: C, 59.19; H, 3.95%.) ν_{max}^{KBr} cm^{-1}: 3350, 2910, 1685, 1602, 1535, 1450, 1278, 1130, and 1030. λ_{max} nm: 290 (MeOH); 314 (+$AlCl_3$); 325 (+NaOAc). NMR (100 MHz, $(CD_3)_2CO$, −60°): τ 7.20 (3H, d, J_{gem} = 17 Hz), 6.70 (3H, *q*, J = 2 Hz), 2.90 (*s*, 6- and 8-H), 3.21 (5′-H), 2.2 (2′- and 6′-H), −2.40 (*s*, 5-OH), −4.04 (*s*, C_6- or C_8-H), 4.02 (1H, *d* centred at 4.75, C_2-H). The aglycone formed a penta-acetate (Ac_2O–Py), mp 150–51°, M^+ 514. (Found: C, 58.35; H, 4.25; acetate, 41.80. $C_{25}H_{22}O_{12}$ requires: C, 58.36; H, 4.28; 5 × acetate. 41.82%.) NMR at τ 7.90 (acetate group).

$KMnO_4$ *oxidation of the aglycone.* The aglycone (50 mg) was dissolved in 20 ml Me_2CO and 10% aq. $KMnO_4$ soln was added until its colour persisted. The reaction mixture was refluxed on a water bath for 4 hr. It was cooled, $NaHSO_3$ was added to remove excess MnO_2, it was made acidic (conc HCl), and then extracted with Et_2O. The ethereal layer was washed with H_2O to remove mineral acid. It was dried and concd to 1 ml. The

product was identified as protocatechuic acid by mp 198° (lit. mp 199°), mmp and co-chromatography with an authentic sample. Aglycone methyl ether on similar oxidation, veratric acid, mp 180° (lit. mp 181°) was obtained as one of the oxidation products.

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NEW C-GLYCOSYLFLAVONES FROM *MOLLUGO PENTAPHYLLA*

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Key Word Index—*Mollugo pentaphylla*; Aizoaceae; *C*-glycosylflavones; 8-*C*-α-L-arabinopyranosylapigenin; mollupentin; 6,8-di-*C*-pentosylapigenins.

In continuation of our work on the anthocyanin-producing genus *Mollugo* [1], we report in this paper the isolation and characterization of new *C*-glycosylflavones from *Mollugo pentaphylla*.

Four chromatographically distinct compounds were isolated from the aerial parts of the plant. They were designated 1 to 4 in the order of increasing R_f on Si gel PTLC in EtOAc–MeOH–H_2O (63:12:9). Compounds 1, 2 and 4 showed UV spectra and diagnostic shifts [2] characteristic of unsubstituted apigenins and the chromatographic properties of all compounds indicated a glycosidic structure which was confirmed as *C*-glycosidic by the MS of the permethyl (PM) derivatives. PM compound 4 gave the MS of a PM 8-*C*-pentosylapigenin: *m/e* 486 (M^+, 91%), 355 (M−131, 100%) [3]. Direct chromatographic comparison showed PM compound 4 to be identical with PM 8-*C*-α-L-arabinopyranosylapigenin [4] and different from PM 8-*C*-β-D-xylopyranosylapigenin [5], the identity of compound 4 with synthetic 8-*C*-α-L-arabinopyranosylapigenin [4] being confirmed by direct comparison of the free compounds.

This is the first report of this compound in nature and we therefore suggest for it the name mollupentin by analogy with molludistin, its 7-*O*-methyl ether isolated from *Mollugo distica*. The PM derivatives of compounds 1, 2 and 3 all gave MS of PM 6,8-di-*C*-pentosylapigenins: *m/e* 660 (M^+, 16–25%), 645 (M−15), 629 (M−31, 100%), 529 (M−131, 21–58%), with arabinose in 6 (M−131 > M−119 > M−145) [3]. Direct chromatographic comparison showed none of them to be identical with PM 6,8-di-*C*-α-L-arabinopyranosylapigenin [6] or PM 6,8-di-*C*-β-D-xylopyranosylapigenin [5]. However, PM compounds 1 and 3 could not be distinguished on TLC; thus compound 3 may be an *O*-methyl derivative of compound 1. The available amounts did not allow further investigation. From the UV and MS data, it can be concluded that compounds 1 and 2 are 6-*C*-arabinosyl-8-*C*-pentosylapigenins of a type already found in the genus *Hymenophyton* [7].

EXPERIMENTAL

Plant. Mollugo pentaphylla L. syn. *M. stricta* L., Aizoaceae (voucher specimen No. 10/76 deposited at Jahawarlal Institute); eaten as pot herb and recorded to contain carotene, vitamin C and a saponin [8].

Isolation. Fresh aerial parts of *M. pentaphylla* (1.5 kg) were extracted × 2 with hot rectified spirit under reflux; the combined extracts (15 l.) were concd under red. pres. to *ca* 600 ml and successively extracted with petrol (60–80°), Et_2O and EtOAc (*ca* 2 l. each). The EtOAc concentrate yielded a mixture of 3 saponins as the major constituents; after the removal of the saponins the mother liquor was found to be rich in water-soluble flavonoids. More was present in the aq. mother liquor which was extracted with MeCOEt and combined with the EtOAc extract. PPC in 30% HOAc led to 4 bands (R_f 0.29, 0.41, 0.55 and 0.67) which were still complex mixtures. PTLC of the first band on Si gel H in EtOAc–MeOH–H_2O (63:12:9) showed 6 bands of which the 4 main ones were selected (R_f 0.44, 0.53, 0.64, 0.93).