

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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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–H₂O (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 com-

parison 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 Jawaharlal 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 $\times 2$ 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°), Et₂O 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–H₂O (63:12:9) showed 6 bands of which the 4 main ones were selected (R_f 0.44, 0.53, 0.64, 0.93).

Compound 1. TLC Si gel R_f 0.41 (EtOAc-Py-H₂O-MeOH, 80:12:10:5); cellulose 0.33 (15% HOAc). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 271, 330; + NaOAc 277, 350; + NaOAc + H₃BO₃ 273, 330; + AlCl₃ 279, 305, 348, 381; + AlCl₃ + HCl 280, 304, 344, 381; + NaOH N/10 281, 332, 397. Permethyl ether: MS (m/e) 660 (M^+ , 17%), 645 ($M-15$, 24%), 629 ($M-31$, 100%), 541 ($M-119$, 20%), 529 ($M-131$, 21%), 515 ($M-145$, 12%); TLC Si gel R_f 0.21 (CHCl₃-EtOH-Me₂CO, 5:4:1), PM 6,8-di-C- α -L-arabino-pyranosylapigenin 0.11, PM 6,8-di-C- β -D-xylopyranosylapigenin 0.30.

Compound 2. TLC Si gel R_f 0.49 (EtOAc-Py-H₂O-MeOH, 80:12:10:5); cellulose 0.31 (15% HOAc). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 273, 331; + NaOAc 275, 302 (i), 341; + NaOAc + H₃BO₃ 273, 333; + AlCl₃ 279, 306, 348, 384; + AlCl₃ + HCl 277, 305, 344, 378; + NaOH N/10 280, 332, 396. Permethyl ether: MS (m/e) 660 (M^+ , 16%), 645 ($M-15$, 26%), 629 ($M-31$, 100%), 541 ($M-119$, 20%), 529 ($M-131$, 28%), 515 ($M-145$, 14%); TLC Si gel R_f 0.26 (CHCl₃-EtOAc-Me₂CO, 5:4:1).

Compound 3. TLC Si gel R_f 0.58 (EtOAc-Py-H₂O-MeOH, 80:12:10:5); cellulose 0.15 (15% HOAc). Permethyl ether: MS (m/e) 660 (M^+ , 24%), 645 ($M-15$, 25%), 629 ($M-31$, 100%), 541 ($M-119$, 30%), 529 ($M-131$, 58%), 515 ($M-145$, 26%); TLC Si gel R_f 0.21 (CHCl₃-EtOAc-Me₂CO, 5:4:1).

Compound 4. TLC Si gel R_f 0.78 (EtOAc-Py-H₂O-MeOH, 80:12:10:5), 0.65 (EtOAc-MeOH-H₂O, 63:12:9); cellulose 0.11 (15% HOAc). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 269, 331; + NaOAc 274, 295, 354; + AlCl₃ 276, 304, 346, 384; + AlCl₃ + HCl 276, 302, 342,

382; + NaOH N/10 277, 330, 392. Permethyl ether: MS (m/e) 486 (M^+ , 91%), 355 ($M-131$ 100%), 341 ($M-145$, 69%), 325 ($M-161$, 13%), 311 ($M-175$, 12%); TLC Si gel R_f 0.23 (CHCl₃-EtOAc-Me₂CO, 5:1:4).

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FLAVONOIDS FROM THE LEAVES OF *CASSIA LAEVIGATA*

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Key Word Index—*Cassia laevigata*; Leguminosae; ombuin; quercetin 7,4'-dimethyl ether; ombuin 3-O-(2-rhamnosylglucoside).

Ombuin (3,5,3'-trihydroxy-7,4'-dimethoxyflavone) and a new glycoside, 3-O-(2-rhamnosylglucosyl)-ombuin, have been isolated from the leaves of *Cassia laevigata*. The flavonol was identified by mp, mmp, colour reactions, derivatization, UV, IR, NMR and MS. It has been reported earlier from many plant sources [1–3].

The glycoside gave the characteristic reactions of a flavonol glycoside [4] and the acid hydrolysate showed the presence of ombuin, glucose and rhamnose. Methylation and hydrolysis gave quercetin 5,7,3',4'-tetra-O-methyl ether (mp, mmp, co-chromatography, UV and IR spectra) showing that the sugars were linked at position 3 of the aglycone. The NMR spectrum of the glycoside had a doublet at δ 1.32 which is typical of the rhamnose methyl group. The broad signal at δ 3.82, which overlapped with the methoxyl singlet at δ 4.00, was also due to the sugar protons. The nature of the sugar linkage was deduced by comparison of the rhamnose methyl signal with corresponding signals of neohesperidoside, δ 1.20 (*d*) and rutinoside, δ 0.80–0.95 (*br*) [5–7] to be of the

neohesperidoside type. Thus it is identified as ombuin-3-O-neohesperidoside.

EXPERIMENTAL

The leaves of *Cassia laevigata* were obtained from United Chemicals and Allied Products, Calcutta-1, India. Dried ground leaves were extracted with EtOH and the conc extract diluted with H₂O to give a coloured ppt. which after column chromatography of the EtOAc-soluble fraction on Si gel gave ombuin, mp 229°.

The EtOAc extract of the original aq. soln gave three compounds (Si gel TLC; EtOAc-MeOH, 1:1) which were separated by column chromatography. The EtOAc eluate contained a single entity on TLC (Si gel, EtOAc), a yellow glycoside, mp 310° (*d*). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3370, 2920, 2860, 1625, 1530, 1485, 1180, 1160, 1140, 850, 830, 800, 760 and 690. UV λ_{max} nm: EtOH 255, 355; AlCl₃ 275, 419; AlCl₃-HCl 270, 415; NaOAc 256, 385; NaOAc-H₃BO₃ 260, 365; NaOEt 275, 418. ¹H NMR (90 Hz, (CD₃)₂SO₄): δ 1.32 (3H, *d*, *J* = 12 Hz, rhamnose-Me), 4.00 (*s*, 6H, OMe), 4.90 (1H, *s*, H-1" rhamnosyl); 5.20 (1H, *br*, H-1"