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7,2″-DI-*O*-GLYCOSYL-6-*C*-GLYCOSYLFLAVONES FROM *CERASTIUM ARVENSE*

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Key Word Index—*Cerastium arvense*; Caryophyllaceae; *C*-glycosylflavonoids; isovitexin 7-*O*-glucoside-2″-*O*-arabinoside; isomollupentin 7,2″-di-*O*-glucoside; isomollupentin 7-*O*-glucoside-2″-*O*-xyloside; isomollupentin 7-*O*-glucoside-2″-*O*-arabinoside.

Abstract—Four 7,2″-di-*O*-glycosyl-6-*C*-glycosylflavones were isolated from *Cerastium arvense*, including two new compounds: isomollupentin 7-*O*-glucoside-2″-*O*-arabinoside and isomollupentin 7-*O*-glucoside-2″-*O*-xyloside. The known compounds are isovitexin 7-*O*-glucoside-2″-*O*-arabinoside and isomollupentin 7,2″-di-*O*-glucoside.

INTRODUCTION

We have previously reported the isolation of several new *C*-glycosylflavones from *Cerastium arvense* L. [1, 2]. One of them was identified on the basis of UV, acid hydrolysis and mass spectrometry of the permethylated (PM) derivatives as isovitexin 7,2″-di-*O*-glucoside [3, 4]. In this paper we report the isolation and characterization of four other 7,2″-di-*O*-glycosyl-6-*C*-glycosylflavones, two of which are new compounds, from the whole plant of *C. arvense*.

RESULTS AND DISCUSSION

Fresh plant material of *C. arvense* was extracted with 95% ethanol. After elimination of the lipophilic pigments the water-soluble fraction yielded the known compounds isomollupentin 7,2″-di-*O*-glucoside, previously isolated from *Spergularia rubra* [5], and isovitexin 7-*O*-glucoside-2″-*O*-arabinoside, previously isolated from *Melandrium album* [6], and two new ones, **1** and **2**.

Compound **1** showed the UV spectrum and diagnostic shifts of a 7-*O*-substituted apigenin [7]and the chromatographic properties of a triglycoside. Acid hydrolysis with 4 N HCl–MeOH (1:1) or 0.1% HCl yielded isomollupentin (6-*C*-arabinosylapigenin) (UV, mass spectrometry of PM ether and TLC comparison with standard free and permethylated samples) accompanied by its Wessely–Moser isomer and equal amounts of arabinose and glucose (TLC). The mass spectrum of PM **1** showed the characteristic fragmentation pattern of a PM 5,7-dihydroxy-6-*C*-glycosylflavone 7,2″-di-*O*-glycoside [5]: $[M]^+$ (*m/z* 850), absence of $[M-15]^+$ and $[M-31]^+$ peaks (showing the absence of a 2″-OMe [8] owing to the presence of a 2″-*O*-glycosyl residue) replaced by the ions $[SO]^+$ (*m/z* 675) and $[S]^+$ (*m/z* 659) by loss of the PM 2″-*O*-glycosyl residue, respectively without and with the oxygen atom of the glycosidic bond (the pentose nature of the 2″-*O*-glycosyl group is given by the difference $[M-SO] = 175$; the homologous peaks $[SO(AH)]^+$ (*m/z* 457) and $[S(AH)]^+$ (*m/z* 441), derived from $[SO]^+$ and $[S]^+$ by loss of the PM 7-*O*-glycosyl group with hydrogen transfer, showed the hexose nature of this group by the difference $[S-S(AH)] = 218$. Finally, the important peak $[j(AH)]^+$ (*m/z* 327) agreed with the apigenin nature of the flavone moiety and the difference $S(AH)-j(AH) = 114$ with the pentose nature of the 6-*C*-glycosyl residue. Compound **1** is thus identified as isomollupentin 7-*O*-glucoside-2″-*O*-arabinoside.

Compound **2** again showed the UV spectrum and diagnostic shifts of a 7-*O*-substituted apigenin and the chromatographic properties of a triglycoside. Acid hydrolysis with 4 N HCl–MeOH (1:1) or 0.1% HCl led to equal amounts of xylose and glucose (TLC) and to isomollupentin (identified as above). The mass spectrum of PM **2** also showed the characteristic fragmentation pattern of a PM 5,7-dihydroxy-6-*C*-glycosylflavone 7,2″-di-*O*-glycoside and all peaks were found at the same *m/z* values as in the mass spectrum of PM **1**. These data proved **2** to be isomollupentin 7-*O*-glucoside-2″-*O*-xyloside. A number of 7,2″-di-*O*-glycosyl-6-*C*-glycosylflavones have been previously identified in *Melandrium album*: isovitexin 7-*O*-glucoside-2″-*O*-arabinoside [4] and -2″-*O*-rhamnoside [9], isovitexin 7-*O*-galactoside-2″-*O*-glucoside and -2″-*O*-rhamnoside [10], isovitexin 7-*O*-xyloside-2″-*O*-glucoside [4], -2″-*O*-arabinoside and -2″-*O*-rhamnoside [6], and isovitexin 7,2″-di-*O*-glucoside [4]. But isomollupentin 7-*O*-glucoside-2″-*O*-xyloside and -2″-*O*-arabinoside are characterized for the first time.

EXPERIMENTAL

Plant material. Cerastium arvense L. subsp. *arvense* was collected on the roadside at Chamboeuf (Côte d'Or), France. A voucher specimen, No. 116, has been deposited at the Herbarium, Faculté de Pharmacie, Université de Dijon.

Extraction and isolation. Fresh leaves and flowers were extracted with 95% EtOH under reflux. After concn under red. pres., the residue was macerated with hot H_2O and filtered. The aq. soln was extracted with $CHCl_3$. The remaining aq. layer was fractionated first on a Lichrosorb RP 18 (25–40 μm) column eluted with a discontinuous gradient MeOH–H_2O–HOAc, 5:15:1, 6:13:1, 10:9:1 (pressure 10 bars, flow rate 10 ml/min),

then on a microcrystalline cellulose column (5 bars) eluted by isocratic 5% HOAc (flow rate 3.5 ml/min), and finally on a Lichrosorb RP 18 (10 μm) column (10 bars) eluted by isocratic MeOH–H_2O–HOAc, 35:65:2 (flow rate 6 ml/min.).

1: *Isomollupentin 7-O-glucoside-2″-O-arabinoside* (*apigenin* 6-C-[2-O-*arabinosylarabinoside*]-7-O-*glucoside*). UV λ_{max}^{MeOH} nm: 272, 334; + NaOAc 270, 298 sh, 394; + $AlCl_3$ 278, 302, 350, 388 sh; + $AlCl_3$ + HCl 280, 300, 350, 384 sh; + NaOMe 274, 306 sh, 352 sh, 396. TLC (polyamide) R_f 0.73 (H_2O–EtOH–MeCOEt–$AcCH_2COMe$, 12:4:3:1); (cellulose) 0.52 (5% HOAc), 0.69 (15% HOAc), 0.45 (BAW, 4:1:5); (silica gel) 0.19 (EtOAc–MeOH–H_2O, 21:4:3). Permethyl ether: EIMS 70 eV, *m/z* (rel. int.): 850 $[M]^+$ (7), 705 $[SOj]^+$ (20), 689 $[SOk]^+$ (7), 675 $[SO]^+$ (100), 659 $[S]^+$ (86), 487 $[SOj(AH)]^+$ (20), 471 $[SOk(AH)]^+$ (3), 457 $[SO(AH)]^+$ (79), 441 $[S(AH)]^+$ (51), 409 $[S-MeOH(AH)]^+$ (15), 341 $[i(AH)]^+$ (11), 327 $[j(AH)]^+$ (99), 311 $[k(AH)]^+$ (11). TLC (silica gel) R_f 0.03 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1), 0.23 ($CHCl_3$–EtOAc–Me_2CO, 5:1:4).

2: *Isomollupentin 7-O-glucoside-2″-O-xyloside* (*apigenin* 6-C-[2-O-*xylosylarabinoside*]-7-O-*glucoside*). UV λ_{max}^{MeOH} nm: 274, 332; + NaOAc 272, 348 sh, 392; + $AlCl_3$ 272, 308, 352, 394 sh; + $AlCl_3$ + HCl 300, 320 sh, 360, 396 sh; + NaOMe 270, 348 sh, 388. TLC (polyamide) R_f 0.73 (H_2O–EtOH–MeCOEt–$AcCH_2COMe$, 12:4:3:1); (cellulose) 0.50 (5% HOAc), 0.67 (15% HOAc), 0.40 (BAW, 4:1:5); (silica gel) 0.17 (EtOAc–MeOH–H_2O, 21:4:3). Permethyl ether: EIMS 70 eV, *m/z* (rel. int.): 850 $[M]^+$ (5), 719 $[SOi]^+$ (7), 705 $[SOj]^+$ (8), 689 $[SOk]^+$ (11), 675 $[SO]^+$ (80), 659 $[S]^+$ (77), 501 $[SOi(AH)]^+$ (3), 487 $[SOj(AH)]^+$ (7), 471 $[SOk(AH)]^+$ (4), 457 $[SO(AH)]^+$ (57), 441 $[S(AH)]^+$ (100), 409 $[S-MeOH(AH)]^+$ (20), 341 $[i(AH)]^+$ (11), 327 $[j(AH)]^+$ (95), 311 $[k(AH)]^+$ (11). TLC (silica gel) R_f 0.05 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1), 0.33 ($CHCl_3$–EtOAc–Me_2CO, 5:1:4).

Acid hydrolysis. The samples were dissolved in MeOH–4 N HCl (1:1) or in 0.1% HCl and heated at 100° for 1 hr in a sealed tube. After repeated evapns of the solvent, the residue was taken up in H_2O and extracted with *n*-BuOH. The aglycones were identified in the *n*-BuOH extracts by TLC (silica gel) in EtOAc MeOH–H_2O (21:4:3), 15% HOAc and BAW, 4:1:5. The sugars were identified by TLC (0.2 M Na_2HPO_4-impregnated silica gel plates) in Me_2CO–H_2O (9:1) against standard markers; flavones and sugars were respectively detected with bis-diazotized benzidine–Na_2CO_3 and aniline phthalate. The aglycones were permethylated and co-chromatographed on TLC (silica gel) with PM 6-*C*-arabinosylapigenin: R_f 0.16 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1), 0.54 ($CHCl_3$–EtOAc–Me_2CO, 5:1:4).

Isovitexin 7-*O*-glucoside-2″-*O*-arabinoside and isomollupentin, 7,2″-di-*O*-glucoside were identified by UV, acid hydrolysis, MS of PM ethers and comparison with standard samples.

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