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FLAVONE GLYCOSIDES OF SOME *LAUNAEA* SPECIES

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Key Word Index—*Launaea*; Compositae; apigenin and luteolin glycosides; chemosystematics.

Abstract—Eight flavone glycosides were isolated from *Launaea nudicaulis* and identified as apigenin 7-glucoside and 7-gentiobioside, luteolin 7-glucoside, 7-gentiobioside, 7-rutinoside, 7,3′-diglucoside, 7,4′-diglucoside and 7-gentiobioside-4′-glucoside. All eight glycosides were detected in five other *Launaea* species; the 7-glucosides being the major glycosides in all species studied.

The genus *Launaea* Cass. belongs to the tribe Lactuceae (Cichorieae) of the Compositae and contains about 40 species [1]. *Launaea* species are characterized by their heteromorphous beakless achenes which distinguishes them from the closely related genera: *Sonchus*, *Lactuca* and *Crepis* [2]. There have been no previous reports on the flavonoids of *Launaea* species. In the present study the major flavonoid glycosides were apigenin and luteolin 7-glucosides (Table 1). The six other glycosides detected were only present in very small amounts, and their glycosylation patterns were elucidated through chemical and physical methods (see Experimental) as luteolin and apigenin 7-gentiobiosides and luteolin 7-rutinoside, 7,3′-diglucoside, 7,4′-diglucoside and 7-gentiobioside-4′-glucoside. Apigenin and luteolin 7-glucoside are of common occurrence within the Lactuceae [3]. The present report of the 7-gentiobiosides of luteolin and apigenin and luteolin 7-rutinoside is not surprising since small quantities of a luteolin 7-diglucoside were detected in *Hieracium murorum* L. subsp. *grandidens* (Dahlst) by Zahn [4]. 7-Diglucosides of apignenin and luteolin have been reported in *Pyrrhopappus* species [5] and the 7-rutinosides of both luteolin and apigenin were detected in *Sonchus* species [6]. All these species belong to the tribe Lactuceae. The nature of the diglucoside linkage in [4] and [5] was not studied. Luteolin 7,3′-diglucoside, luteolin 7,4′-diglucoside and luteolin 7-gentiobioside-4′-glucoside are uncommon glycosides, not only in the Compositae, but also in nature. Luteolin 7,3′-diglucoside was first reported from *Reseda luteola* (Resedaceae) [7]. The only luteolin 7,4′-diglycoside previously isolated is luteolin 7,4′-diglucuronide from *Marchantia polymorpha* (Hepaticae) [8]. Luteolin 7-gentiobioside-4′-glucoside is also reported here for the first time.

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EXPERIMENTAL

Plant material. A fresh sample of *Launaea nudicaulis* (L.) Hook. f. was collected from the suburbs of Cairo and identified by Professor Dr M. N. El-Hadidi, Cairo University. Herbarium samples of the remaining species were used for the identification of their flavonoids.

Isolation of flavonoids. Plant material (leaves and stems) was extracted with 70% EtOH. The extract was dried under vacuum, and subjected to CC (polyamide) using H_2O followed by increasing concns of EtOH as solvent. Fractions were further separated into single components using elution techniques. For

Table 1. Distribution of flavonoid glycosides in some *Launaea* species

	Apigenin		Luteolin					
Launaea species	7Glc	7Gent	7Glc	7Gent	7RG	73′Glc	74′Glc	7Gent 4′Glc
L. capitata (Sprent.) Dandy	t	t	+++	t	t	t	t	t
L. cassiniana (Jaub. & Sp.) Burkill	+++	t	+++	t	t	t	?	t
L. nudicaulis (L.) Hook. f.	t	t	+++	t	t	t	t	t
L. resedifolia (L.) Kuntze	+++	?	+++	t	?	t	?	t
L. spinosa (Forssk.) Sch. Bip.	+++	t	+++	t	t	t	?	t
L. tenuiloba (Boiss.) Kuntze	+++	t	+++	t	t	t	t	t

Key: 7Glc = 7-glucoside, 7Gent = 7-gentiobioside, 7RG = 7-rutinoside, 73′Glc = 7,3′-diglucoside, 74′Glc = 7,4′-diglucoside, 7Gent 4′Glc = 7-gentiobioside-4′-glucoside, +++ = major constituent, t = trace.

ies of the other *Launaea* species, small columns rate and conc the glycosides. This was followed raphy with those isolated from *L. nudicaulis*. *f flavonoids*. Standard methods of identification . The glycosides were subjected to strong acid acid hydrolysis and enzymic hydrolysis (β- :y all gave the corresponding aglycones and the expected intermediates. H_2O_2 oxidation of des and 7-rutinosides gave small amounts of rutinose, respectively, which co-chromato- hentic disaccharides. R_G values of gentiobiose e: BAW 44,72; PhOH 60, 98 and BBPW 23,77. ıside co-chromatographed with a sample from 5]. The UV data of glycosides occupied in either ons showed an increase in intensity (free 4′) or sity (occupied 4′) of Band I in the presence of s (× 100), colour changes with NH_3 under UV, r the six most frequent glycosides are shown

tiobioside. R_fs (apigenin 7-glucoside as refer- ıes). BAW 27 (46); H_2O 10 (4); 15% HOAc 31 4). (brown → light yellow) UV data: λ_{max}^{MeOH} nm: Me 274, 298 sh, 394; + $AlCl_3$ 275, 298, 345, 382; 275, 299, 343, 382; + NaOAc 266, 345 sh, 390. *ıoside*. R_fs (luteolin 7-glucoside for reference in N 25 (33); H_2O 5 (2); 15% HOAc 24 (11); PhOH → yellow). UV λ_{max}^{MeOH} nm: 253, 266, 345; 300 sh, 398; + $AlCl_3$ 271, 300, 327, 422;), 298, 352, 390; + NaOAc 260, 402; + H_3BO_3

iobioside. R_fs: BAW 19; H_2O 5; 15% HOAc 21; vn → yellow). UV λ_{max}^{MeOH} nm: 256, 267, 345; 298 sh, 407; + $AlCl_3$ 270, 300, 324, 420;), 298, 350, 390: + NaOAc 261, 280 sh, 372, 400 0, 370.

Luteolin 7,3′-*diglucoside*. R_fs: BAW 14; H_2O 3; 15% HOAc 16; PhOH 34 (brown → lemon yellow). UV λ_{max}^{MeOH} nm: 270, 280 sh, 332; + NaOMe 277, 395 sh, 387; + $AlCl_3$ 274, 300 sh, 344, 384; + $AlCl_3$–HCl 270, 300 sh, 343, 384; + NaOAc 268, 282 sh, 396; + H_3BO_3 270, 282 sh, 345.

Luteolin 7,4′-*diglucoside*. R_fs: BAW 14; H_2O 6; 15% HOAc 29; PhOH 40 (brown → brown) UV λ_{max}^{MeOH} nm: 269, 284 sh, 331; + NaOMe 269, 300 sh, 375; + $AlCl_3$ 275, 296 sh, 345, 383; + $AlCl_3$–HCl 276, 296 sh, 342, 383; + NaOAc 265, 325, 380 sh; + H_3BO_3 267, 336.

Luteolin 7-*gentiobioside*-4′-*glucoside*. R_fs: BAW 13; H_2O 15; 15% HOAc 40. (brown → brown). UV λ_{max}^{MeOH} nm: 270, 284, 328; + NaOMe 274, 297 sh, 376; + NaOAc 266, 325, 380 sh; + H_3BO_3 266, 334.

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