Exudate Flavonoids in Several Asteroideae and Cichorioideae (Asteraceae)*

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Introduction

In the course of continuing studies on the occurrence and distribution of exudate flavonoids on higher plants (Wollenweber, 1990; 1996), many Asteraceae have been found to produce and accumulate flavonoid aglycones externally on leaves, stems, and inflorescences. The Asteroideae in particular are a rich source of flavonoid aglycones which accumulate externally on the plant surfaces (Wollenweber and Valant-Vetschera, 1996). The species dealt with in the present paper belong to eight different tribes, some of them placed in the subfamily Cichorioideae (according to Bremer, 1994).

Material and Methods

Aerial parts including inflorescences were collected either in the field or in Botanical Gardens and air-dried. The collection data are as follows.

Achillea eriophora: Iran, coll. A. Rustaiyan, July 1993.

Achillea millefolium ssp. *lanulosa*. 3 miles North of Mindenmines, Barton Co., Minnesota, coll. G. & K. Yatskievych 20/05/88 (G. Yatskievych 88–33, K. Yatskievych).

Arctotis venusta: Botanical Garden, Vienna; coll. K. M. Valant-Vetschera, September 1989; Botanical Garden Darmstadt; coll. K. Mann, August 1990.

Artemisia diffusa: Iran, coll. A. Rustayian, 1992.

Asteriscus sericeus: Botanical Garden, Darmstadt; coll. H. Groh, September, 1991.

Helichrysum aureum: Katberg pass, Seymor District, Republic of Ciskei, coll. by E. H. Graven, 13.03.91 .

Helichrysum bracteatum: Botanical Garden Darmstadt (seeds from Australia; J. G. West 5142); coll. E. Wollenweber, June 1989.

Hieracium amplexicaule: Metnitztal, Nord-Kärnten, Austria; coll. 23.08.1989 (Leute & Kniely, 8951/3).

Inula brittanica: Iran, coll. A. Rustaiyan, June 1993.

Inula ensifolia: Quarry near Lindabrunn, Niederösterreich, Austria; coll. K. M. Valant-Vetschera, 16.09.95.

Inula germanica : Seeben, near Halle/Saale, Germany; coll. K. M. Valant-Vetschera, 16.09.95

Inula germanica: Mettenheim, near Worms, Germany; coll. Th. Andreef, 20.09.96.

Inula helenium: Botanical Garden Darmstadt; coll. Th. Andreef, 25.08.96.

Inula salicina: Botanical Garden, Vienna; coll. K. M. Valant-Vetschera, August '96.

Oncosiphon grandiflorum: Botanical Garden, Darmstadt (seeds from Vienna, ST 181); coll. M. Dörr, August 1996.

Pulicaria dysenterica: Bessunger Forsthaus, near Darmstadt; coll. E. Wollenweber, August 1987.

Senecio viscosus: Darmstadt, growing as a garden weed; coll. E. Wollenweber, July 1992.

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Tanacetum balsamita: Botanical Garden, Vienna; coll. K. M. Valant-Vetschera, October 1993.

Tragopogon pratensis: Darmstadt, weed among railway lines at freight depot; coll. K. D. Jung, August 1995.

Xanthium strumarium: Botanical Garden, Darmstadt; coll. K. Polin, September 1991.

Vouchers are kept at the Herbaria of the Botanischer Garten der TH Darmstadt, Institut für Botanik der Universität Wien (WU), Department of Botany at Shahid Beheshty University in Teheran, Missouri Botanical Garden (MO), and in the Kärntner Landesherbar (KL) at Klagenfurt, Austria.

Air-dried plant material was briefly rinsed with acetone to dissolve the lipophilic exudates. Concentrated solutions were defatted (MeOH, -10 °C; centrifugation) and passed over Sephadex LH-20, eluted with methanol, to separate the flavonoids from the prevailing terpenoids. Flavonoid portions were subjected to column chromatography on silica and/or polyamide SC-6, eluted with toluene and increasing amounts of methylethyl ketone and methanol (cf. Wollenweber *et al.*, 1996). Fractions were monitored and comparisons with markers were made by TLC on polyamide DC-11 with the solvents petrol$_{100-140}$ – toluene – methylethyl ketone – methanol 12:6:1:1, toluene – petrol$_{100-140}$ – MeCOEt – methanol 12:6:2:1, toluene – dioxane-methanol 8:1:1 and toluene – methylethylketone – methanol 12:5:3 and on silica with the solvents toluene – methylethylketone 9:1 and toluene – dioxane – glacial acetic acid 18:5:1. Chromatograms were viewed under UV before and after spraying with Naturstoffreagenz A (NA). Unless otherwise stated, identifications were made by direct comparisons on TLC and in some cases confirmed by UV-spectra and by mass spectra (recorded at 70 eV).

Results

As in the previous paper (Wollenweber *et al.*, 1996), the results are reported for each species sequentially, since presentation in tabulated form did not appear feasable. The species are grouped according to their tribal affiliation within the Asteraceae (Bremer, 1994). Abbreviations OH = hydroxy- and Me = methyl ether are used throughout. In most cases, references to chemotaxonomy were kept to a minimum since this seems premature at this stage. For more detailed information on this subject, see Wollenweber and Valant-Vetschera (1996).

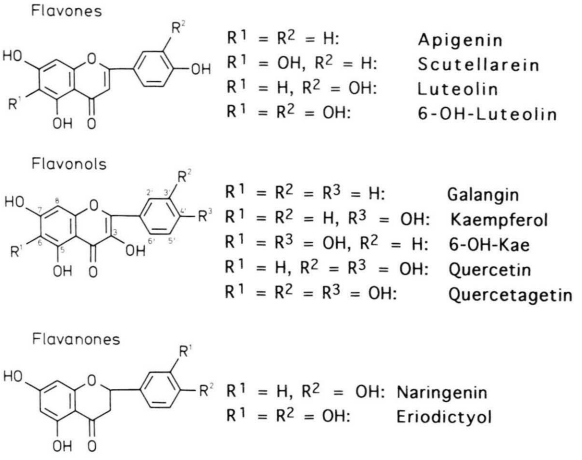

Fig. 1. Core structures of flavones, flavonols and flavanones found in the present study.

Subfamily Asteroideae

Anthemideae

Achillea eriophora DC. Aerial parts of this plant yielded apigenin-4'-Me and ap-7,4'-diMe, scutellarein-6,7,4'-triMe, 6-OH-luteolin-6,7,4'-triMe and 6-OH-lut-6,7,3',4'-tetraMe,6-OH-kaempferol-6,7,4'-triMe and 6-OH-kae-3,6,7,4'-tetraMe, quercetagetin-3,6-diMe and quercetagetin-3,6,7-triMe. By and large this pattern fits the "usual" flavonoid pattern in *Achillea* sect. *Achillea* (Valant-Vetschera and Wollenweber, 1994), to which this species belongs. However, apigenin-4'-Me, ap-7,4'-diMe and quercetagetin-3,6-diMe are new compounds for species of this section.

Achillea millefolium L. ssp. *lanulosa* (Nutt.) Piper. This species exhibited luteolin, four methyl ethers of 6-OH-kaempferol (3,6-diMe, 3,6,7-triMe, 3,6,4'-triMe and 3,6,7,4'-tetraMe), and the 3,6-diMe and 3,6,7-triMe of quercetagetin. The present analysis is in good agreement with an earlier study including species of the North American *A. millefolium* complex (Valant-Vetschera and Wollenweber, 1988). However, the earlier studies yielded less complex profiles for collections from the same taxon.

Artemisia diffusa Krasch. ex Poljak. The flavonoid pattern of this species was reported earlier (Valant-Vetschera and Wollenweber, 1995). In that paper, the presence of a phloracetophenone was mentioned. It should be added here that its structure corresponds to the 4,6-dimethyl ether of phloracetophenone. Its NMR data agree with those measured previously for the same product, isolated from *Artemisia aucheri* (Wollenweber *et al.,* 1992). Phloracetophenone-4,6-dimethyl ether (xanthoxylin) has also been found in *Artemisia brevifolia* (called brevifolin). *p*-Hydroxyacetophenone was reported from *A. scoparia* (Liu and Ye, 1991), and several acetophenone derivatives were reported for *Artemisia campestris* subsp. *glutinosa* (de Pascual-Teresa *et al.,* 1984). Those species accumulating this groups of compounds belong either to sect. *Seriphidium* (*A. diffusa, A. aucheri, A. brevifolia*) or to sect. *Dracunculus* (A. *campestris, A. scoparia*). Its further distribution among *Artemisia* might prove to be of systematic value.

Oncosiphon grandiflorum (Thunb.) Källersjö. (syn. *Pentzia grandiflora* Thunb.). The lipophilic exudate of this species contained scutellarein 6-Me, scut-6,7-diMe and scut-6,4'-diMe, the 6-Me, 6,7-diMe and 6,7,3'-triMe of 6-OH-luteolin, the 3,6-diMe and 3,6,7-triMe of 6-OH-kaempferol, a trace of quercetin-3-Me, and the 3,6-diMe and 3,6,7-triMe of quercetagetin. The identification of further flavonoids will require work-up of additional plant material. The pattern of this species coincides largely with those of other genera of the Anthemideae. However, the taxonomic position within the tribe as well as the generic delimitation have not yet been clarified (Bremer and Humphries, 1993). The exudate profile of one species from the genus *Eriocephalus*, which is positioned near *Oncosiphon*, was quite different (Wollenweber and Mann, 1989).

Tanacetum balsamita L. Scutellarein-6-Me and scut-6,4'-diMe, luteolin, 6-OH-lut-6-Me and 6-OH-lut-6,3'-diMe, and quercetagetin-3,6-diMe were identified from the acetone wash of aerial parts. This flavonoid pattern resembles very closely those previously reported for *T. santolinoides* (Seif El-Din *et al.,* 1985),*T. chiliophyllum, T. vulgare* (Wollenweber *et al.,* 1989b), and *T. polycephalum* (Wollenweber and Rustaiyan, 1991). The earlier reported aglycones from *T. ferulaceum* (apigenin, 6-OH-kaempferol-3,6-diMe and quercetagetin-3,6-diMe) (Gonzalez *et al.,* 1990) and from *T. albipannosum* (scutellarein-6,7,4'-triMe, 6-OH-luteolin-6,7,3',4'-tetraMe) (Gören and Jakupovic, 1990) are in good agreement with the general substitution trends observed in *Tanacetum*. Only two aglycones (quercetagetin-3,6,4'-triMe and quercetagetin-4'-Me-7-acetate) were reported for *T. microphyllum* (Abad *et al.,* 1993), which might be due, however, to the activity-orientated nature of that publication. The 3,7-dimethyl ethers of 6-hydroxykaempferol and of quercetagetin as well as 6-OH-kae-3,7,4'-triMe and queg-3,7,3'-triMe have recently been reported from the exudate of *T. parthenium* (Williams *et al.,* 1995). None of these four compounds (queg-3,7,3'-triMe is very rare and 6-OH-kae-3,7,4'-triMe is a novel compound) has so far been reported for any other species of *Tanacetum*. Several 6-methoxyylated flavanones have been isolated from *Tanacetum sibiricum* (Stepanova *et al.,* 1982), differing markedly from the other known flavonoid structures so far known from *Tanacetum* spp. However, this species was segregated from *Tanacetum* as genus *Filifolium* which is claimed to be related to *Artemisia* (Bremer and Humphries, 1993).

Gnaphalieae

Helichrysum aureum (Houtt.) Merrill was found to excrete the flavone luteolin-3'-Me and several flavonols: galangin, gal-3-Me, gal-7-Me, kaempferol, 8-OH-galangin-8-Me, 8-OH-gal-3,8-diMe, quercetin-3-Me, and qu-3,3'-diMe. Due to the presence of galangin and its derivatives as well as of 8-O-substituted flavonols the flavonoid pattern of this species is similar to those observed in *Gnaphalium* species, in *Cassinia quinquefaria* and in *Anaphalis margaritacea* (Wollenweber *et al.,* 1993a, b).

Helichrysum bracteatum (Vent.) Andr. exhibited a quite different flavonoid pattern, lacking flavonols, with flavanones dominating: apigenin-7-Me, ap-7,4'-diMe, luteolin, lut-3'-Me, lut-7,3'-diMe, naringenin-7-Me, nar-7,4'-diMe, eriodictyol, eriod-7-Me, eriod-7,3'-diMe. Interestingly enough, the flavonoid pattern of cultivated colourful garden plants (everlastings) was found to be quite similar to that of wild plants, thus indicating taxon specifity.

In both *Helichrysum* species, several flavonoids remained unidentified. In *H. bracteatum*, two of

these might be 6-O- and 8-O-prenylated flavanones.

About half of the known *Helichrysum* species have thus far been analyzed. In general they produce a rich array of exudate flavonoids, with 6-substituted and 6,8-disubstituted flavones and flavonols dominating. Flavanones, chalcones and derivatives of both groups, in particular O-prenylated compounds, also play an important rôle and appear to be an important feature of the genus (cf. Wollenweber and Valant-Vetschera, 1996).

Heliantheae

Xanthium strumarium L. Very small amounts of exudate were obtained from this species. It contained only the two flavonols 6-OH-kaempferol-6-Me and quercetagetin-3,6-diMe, thus yielding poor results in qualitative as well as in quantitative respect. Similar observations have been made in *Zinnia acerosa* (Wollenweber, unpubl.), whereas several other genera of this tribe are known for their complex exudate aglycone profiles (Wollenweber and Valant-Vetschera, 1996).

Inuleae

Asteriscus sericeus (L.f.) DC. exhibited quercetagetin-3,6-diMe, queg-3,6,3'-triMe and queg-3,7,3'-triMe. The latter compound has been found only three times before in nature. The flavonoid pattern of this plant is hence quite characteristic, but cannot be claimed to be specific at the generic or tribal level. Quercetagetin-3,6,3'-triMe has also been isolated from the aerial parts of *A. graveolens* (Ahmed *et al.*, 1991).

Inula brittanica L. accumulated apigenin, scutellarein-6-Me, scut-6,7-diMe, luteolin, lut-3'-Me; 6-OH-luteolin-6-Me, 6-OH-lut-6,7-diMe, 6-OH-lut-6,3',4'-triMe, quercetagetin-3,6,7-triMe, queg-3,6,3'-triMe, queg-3,6,7,3'-tetraMe, and queg-3,6,7,3',4'-pentaMe.

Inula germanica L.: Two different collections produced a series of exudate flavonoids. Major compounds were 6-OH-luteolin-6-Me and quercetagetin-3,6-diMe. Scutellarein 6-Me and 6-OH-lut 6,3'-diMe as well as queg 3,7-diMe and queg 3,6,7-triMe were identified as minor constituents from both collections. Thus, this aglycone profile can be regarded as being species specific. Earlier, Bohlmann *et al.* (1985) have isolated the stilbene pinosylvin from this species.

Inula salicina L. was found to accumulate only 6-OH-luteolin-6-Me in its exudate, which appears to be a much reduced pattern compared to other *Inula* spp. However, the genus also comprises species in which no exudate flavonoid production is detectable, such as *Inula ensifolia* L. and *I. helenium* L., which have been analyzed here for the first time. The rare flavonol quercetagetin-3'-Me has recently been reported (erroneously as a new compound) from the aerial parts of *Inula crithmoides*, along with a new compound (inucrithmin) to which the structure of 3,7,4',5'-tetraOH-6,3'-diOMe flavone has been ascribed (El-Lakany *et al.*, 1996). Whereas the first compound agrees with the substitution patterns so far known from *Inula* spp., the second structure is quite unusual. It is comparable, though, to structures reported from *I. grantioides* Boiss., which was found to produce 7-hydroxy-6,3',5'-trimethoxflavone, 5-hydroxy-3,6,7,2',5'-pentamethoxy- and 5-hydroxy-3,6,7,8,2',5'-hexamethoxyflavonol as typical compounds (Ahmad and Ismail, 1991a, b), along with scutellarein-6-Me and scut-6,7,4'-triMe (Ahmad and Ismail, 1993). In some respects, the observed aglycone profiles of *Inula* spp. are also similar to those reported for *Pulicaria* (see below). However, the exudate of *Inula viscosa* (L.) Aiton has been reported to contain a series of flavanones and dihydroflavonols along with flavones and flavonols (Grande *et al.*, 1985, Wollenweber *et al.*, 1991). It is noteworthy that the flavanones and dihydroflavonols have not been observed in exudates of other *Inula* species. These differences thus further support the suggested segregation as *Dittrichia viscosa* (L.) W. Greuter.

Pulicaria dysenterica. (L.) Bernh. In an earlier paper we have reported kaempferol and kae-3-Me, 6-OH-kae-3,7-diMe, quercetin, qu-7-Me, qu-3'-Me, qu-3,7-diMe, qu-3,7,4'-triMe from this species (Wollenweber *et al.*, 1989 a). From a remaining fraction we have now identified quercetagetin-3,7,3',4'-tetraMe. Queg-3,7-diMe and queg-3,7,4'-triMe had been found earlier in *P. dysenterica* (Schulte *et al.*, 1968; Pares *et al.*,1981), but the 3,7,3',4'-tetramethyl ether is reported here for the first time from this plant. Previously the isomeric queg-3,6,7,3'-tetramethylether was isolated from *P. gnaphalodes* (Wollenweber and Rustaiyan, 1991). Flavonoid aglycones have now been re-

ported for six out of 80 species forming the genus *Pulicaria*. Relatively simple flavonol methyl ethers and a dihydroflavonol without 6-O-substitution were reported for *P. incisa* (Mansour *et al.*, 1990). Biogenetically rather simple 6-O-substituted flavone- and flavonol-methyl ethers were described from *P. paludosa* (scutellarein-7,4'-diMe, 6-OH-kaempferol-3,6-diMe, 5,6,8-triOH-7,4'-diOMe flavone) (SanFeliciano *et al.*, 1989) and from *P. crispa* (queg-3,6-diMe only) (Al-Yaya *et al.*, 1988). By contrast, polymethylated derivatives were found in *P. arabica* (quercetagetin-3,6,7,3',4'-pentaMe, queg-3,5,6,7,3'-pentaMe, queg-3,5,6,7,3',4'-hexaMe) (Melek *et al.*, 1988). Quercetagetin-3,7-diMe, queg-3,5,7-triMe and queg-3,5,7,3'-tetraMe were reported earlier from the same species (El-Negoumy *et al.*, 1982), possibly from another chemotype. It should be added that in none of these references was mention made of the flavonoid localization; we assume, however, that they are exudate constituents in each case.

Senecioeae

Senecio viscosa L. The glandular exudate of this viscid plant contains ap-7-Me, lut-7,3'-Me, kae-3-Me, kae-3,7-diMe, kae-3,7,4'-triMe, and qu-3,7,3'-triMe. This seems to be the first report of flavonoid aglycones from a temperate *Senecio*. The genus comprises more than 1200 species and only very few have so far been screened for the presence of exudate flavonoids. From the wax-like epicuticular layer of three succulent species we have recently isolated a series of triterpenoids (Siems *et al.*, 1995). We would be most grateful for samples of further species producing leaf resins if such exist.

Subfam. Cichorioideae

Arctoteae

Arctotis venusta T. Norl. produces a series of flavonoid aglycones but only one of them could so far be identified, due to lack of material. By NMR-analysis it was found to be 6-OH-luteolin-7,3'-dimethyl ether, a very rare flavone. It was reported earlier as a constituent of three closely related Lamiaceae, *Thymbra spicata, Th. capitata* (Barberán *et al.*, 1986), and *Thymus satureioides* (Voirin *et al.*, 1985). To our knowledge its ^{13}C-NMR spectrum is reported here for the first time: ^{13}C-NMR δ (ppm): 167.0 (C-2), 103.0 (C-3), 182.4 (C-4), 176.3 (C-5), 130.1 (C-6), 154.5 (C-7), 91.4 (C-8), 149.9 (C-9), 105.2 (C-10), 121.9 (C-1'), 110.2 (C-2'), 148.2 (C-3'), 150.8 (C-4'), 116.0 (C-5'), 120.6 (C-6'), 56.5 (7-OMe), 56.2 (3'-OMe).

Lactuceae

Hieracium amplexicaule L. was found to accumulate naringenin-7-Me, nar-7,4'-diMe and apigenin-7,4'-diMe in its exudate. The aglycone composition is very similar to that of *H. intybaceum* (Wollenweber, 1984).

Tragopogon pratensis L. The solution obtained on rinsing of flower heads with acetone contains flavonoids, but surprisingly these were **not** aglycones. We found a trace of luteolin-7-glucoside and two quercetin glycosides, one of which was identified as quercetin-3-glucoside. Hydrolysis yielded quercetin as major product, and some luteolin.

These findings are of high interest for two reasons. Firstly, the occurrence of exudate flavonoids as such in members of the subfamily Cichorioideae is extremely rare. We have so far encountered them as aglycones in another alpine *Hieracium* (Wollenweber, 1984), in *Centaurea* and *Cirsium* species (Cardueae), and in one *Vernonia* spp. (Vernonieae) (Wollenweber *et al.*, 1989). Secondly, it is unusual that flavonoid glycosides occur in lipophilic plant excretions. This phenomenon has been observed only a few times before: quercetin-3-rhamnoglucoside was isolated from the leaf and stem exudate of *Lycopersicon lycopersicum* (Solanaceae); we have found eriodicytol-7-glucoside in *Cotoneaster microphyllum* (Rosaceae) (Wollenweber, 1990). Quercetin glycosides and the dihydrochalcone glucoside phloridzin had been reported earlier to occur in two species of *Kalmia* (Ericaceae) along with lipophilic C-methylated flavones. Recently flavonoid glycosides have been detected in leaf exudate of *Nothofagus antarctica* (Fagaceae), where they co-occur with lipophilic aglycones (Wollenweber *et al.*, in press).

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