Exudate Flavonoids in Asteraceae from Arizona, California and Mexico*

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A series of Asteraceae, belonging to the tribes Astereae, Eupatorieae, Helenieae and Heliantheae, have been analyzed for the presence of flavonoid aglycones accumulated on leaf and stem surfaces. Methyl ethers of apigenin, luteolin, kaempferol, and quercetin as well as methyl ethers of their relevant 6-hydroxy derivatives were abundant, whereas 8-O-substituted derivatives and flavanones were encountered only occasionally; 6,8-di-O-substituted flavonols were found in only one species.

Introduction

In the course of continuing studies on the occurrence of exudate flavonoids on plant surfaces, a number of Asteraceae from Arizona, California and northern Mexico have been analyzed. They comprise nineteen species, belonging to four different tribes (*sensu* Bremer, 1994). In the following we report our results with these plant exudates and contrast them with previous studies whenever they were available. The ^{13}C-NMR data of several rare flavonoid aglycones are published here for the first time.

Material and Methods

In most species, aerial parts including inflorescences were collected in the field and air-dried. The collection data are as follows.

Ageratina espinosara : NE of Cd. Oaxaca, Edo. Oaxaca, Mexico, 7 May 1983 (G. Yatskievych 83–146, E. Wollenweber).

Ambrosia ambrosiodes : grown in a greenhouse in Darmstadt. Seed origin: lower Mt. Lemmon, Pima Co., AZ, 6 May 1990 (G. Yatskievych, E. Wollenweber, s.n.).

Baccharis halimifolia : cultivated in the Botanical Garden at Darmstadt.

Baccharis pilularis var. *consanguinea* : E. base of Black Mountain, Marin Co., CA, 18 Aug 1988. (G. Yatskievych 88–148, K. Yatskievych)

Baccharis viminea : W of Cleveland Nat'l. Forest, Orange Co., CA, 2 May 1990 (G. Yatskievych 90–48, E. Wollenweber)

Brickellia californica : Trinity Nat'l. Forest, Trinity Co., CA, 24 Aug 1988 (G. Yatskievych 88.182, K. Yatskievych).

Chrysothamnus nauseosus ssp. *albicaulis* : On State Highway 299, near boarder of Whiskeytown-Shasta-Trinity Nat'l. Recreation Area, Shasta Co., CA, 24 Aug 1988 (G. Yatskievych 88–188, K. Yatskievych).

Ericameria bloomeri : S. slopes of Mt. Shasta, Siskiyou Co., CA, 25 Aug 1988 (G. Yatskievych 88–200, K. Yatskievych).

Ericameria linearifolia : San Bernardino Nat'l. Forest, San Bernardino Co., CA, 2 May 1990 (G. Yatskievych 90–59. E. Wollenweber).

Eriophyllum confertifolium var. *confertifolium* : Cleveland Nat'l. Forest, San Diego Co., CA, 1 May 1990 (G. Yatskievych 90–37, E. Wollenweber).

Eriophyllum staechadifolium : Sonoma Co., CA, 20 Aug 88 (G. Yatskievych 88–161, K. Yatskievych).

* Part III in the series "Exudate Flavonoids in Miscellaneous Asteraceae". For Part Part I see Wollenweber *et al.* (1989), for Part II see Wollenweber *et al.* (1997).

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Gaillardia arizonica : Santa Cruz Co., AZ, 5 June 1990 (G. Yatskievych 90–79, E. Wollenweber)

Grindelia nana var. *integrifolia* : cultivated at Kew Gardens, coll. July 1994.

Gymnosperma glutinosum : Northern outskirts of Tehuacan, Edo Puebla, Mexico, 29 Sept 1986 (G. Yatskievych 86–335, G. J. Gastony).

Hemizonia lutescens : Sonoma Co., CA, 20 Aug 1988 (G. Yatskievych 88–160, K. Yatskievych).

Madia elegans ssp. *densifolia* : Sonoma Co., CA, 20 Aug 1988 (G. Yatskievych 88–159, K. Yatskievych).

Madia sativa : Marin Co., CA, 19 Aug 1988 (G. Yatskievych 88–151, K. Yatskievych).

Perityle lemmonii : Sta.Catalina Mts., Pima Co., AZ, 6 May 1990 (G. Yatskievych 90–86, E. Wollenweber).

Zinnia acerosa : Pima Co., AZ, 5 May 1990 (G. Yatskievych 90–81, E. Wollenweber).

Vouchers are accessioned at the Missouri Botanical Garden Herbarium (MO). Vouchers of *Baccharis halimifolia* and of *Ambrosia ambrosioides* are kept at the Botanischer Garten der TH Darmstadt.

Air-dried plant material was rinsed with acetone and the concentrated solutions were subjected to column chromatography and analyzed by thin-layer chromatography as reported in the previous paper (Wollenweber *et al.*, 1997).

Spectral data are not reported where they agreed with literature data. In the following we present only such ^{13}C-NMR data which to our knowledge have not yet been published. The spectra were recorded in DMSO-d_6 at 50 MHz. Values marked with * or with # may be interchanged.

Scutellarein-7-Me (from *Ambrosia ambrosioides*). ^{13}C-NMR δ (ppm): 163.7 (C-2), 102.5 (C-3), 182.1 (C-4), 146.2 (C-5), 129.9 (C-6), 154.3 (C-7), 91.1 (C-8), 149.6 (C-9), 105.0 (C-10), 121.3 (C-1'), 128.3 (C-2'), 115.9 (C-3'), 161.1 (C-4'), 115.9 (C-5'), 128.3 (C-6'), 56.2 (7-OMe).

Isoscutellarein-8,4'-diMe (from *Madia sativa*). 13C-NMR δ (ppm): 163.0 (C-2), 103.3 (C-3), 181.8 (C-4), 156.1 (C-5), 99.0 (C-6), 157.1 (C-7), 127.7 (C-8), 149.4 (C-9), 103.5 (C-10), 122.90 (C-1'), 128.1* (C-2'), 114.7# (C-3'), 162.3 (C-4'), 114.7# (C-5'), 128.1* (C-6'), 60.9 (8-OMe), 55.5 (4'-OMe).

Hypolaetin-8,3'-diMe (from *Hemizonia lutescens*). *13C-NMR δ (ppm): 163.5 (C-2), 103.1** (C-3), 182.0 (C-4), 156.2 (C-5), 99.0 (C-6), 157.1 (C-7), 127.7 (C-8), 149.5 (C-9), 103.5* (C-10), 121.6 (C-1'), 109.9 (C-2'), 148.1 (C-3'), 150.8 (C-4'), 115.9 (C-5'), 120.2 (C-6'), 61.1 (8-OMe), 55.8 (3'-OMe).

5,7,3',5'-tetraOH-3,6,8,4'-tetraOMe flavone (from *Gymno*-sperma glutinosum). ^{13}C-NMR δ (ppm): 154.8 (C-2), 138.03* (C-3), 178.3 (C-4), 147.8 (C-5), 131.5 (C-6), 1451.5 (C-7), 127.9 (C-8), 144.5 (C-9), 103.2 (C-10), 124.9 (C-1'), 107.6 (C-2'/6'), 150.7 (C-3'/5'), 138.02* (C-4'), 59.8# (3-OMe), 60.0# (6-OMe), 61.1 (8-OMe), 59.7# (4'-OMe).

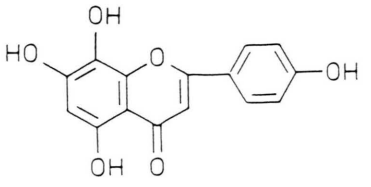
Results and Discussion

The analysis of lipophilic exudate flavonoids in the present study revealed the existence of quite different flavonoid patterns. It seems unreasonable, therefore, to present the results in tabulated form; instead they are reported for each species sequentially and grouped according to their tribal affiliation within the Asteraceae (Bremer, 1994). Core structures of most of the flavones, flavonols and flavanones cited here have been presented in the previous paper (Wollenweber *et al.*, 1997). In Fig. 1 we therefore only depict the structures of three additional flavonoids, derivatives of which have been isolated during our own studies. In the text, abbreviations -OH = hydroxy- and -OMe = methyl ether are used throughout.

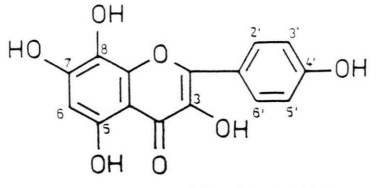
A) Astereae

1. *Baccharis halimifolia* L.. The presence of luteolin, 6-hydroxyluteolin-6-Me, 6-hydroxyluteolin-6,3'-diMe and quercetin-3-Me in the exudate of this species (material obtained from the Botanical Garden in Saarbrücken) has been reported earlier from our lab (Wollenweber *et al.*, 1989). In the material now analyzed we found quercetagetin-3,6-dimethyl ether as an additional minor constituent.

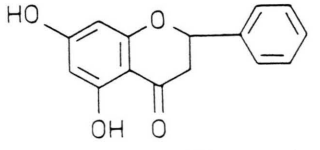
2. *Baccharis pilularis* DC var. *consanguinea* (DC.) Kuntze. This species produces a rich array of flavonoid aglycones. These comprise kaempferol and five of its methyl derivatives (3-Me, 7-Me, 4'-Me, 3,7-diMe, 3,4'-diMe), two methyl ethers of 6-hydroxykaempferol (6,7-diMe and 6,7,4'-triMe), herbacetin-3-methyl ether, two quercetin-methyl



Isoscutellarein



Herbacetin



Pinocembrin

Fig. 1. Structures of the flavone isoscutellarein (8-OH-apigenin), the flavonol herbacetin (8-OH-kaempferol), and the flavanone pinocembrin.

ethers (7-Me and 3,7-diMe), apigenin-7-methyl ether, three methyl derivatives of scutellarein (6,7-diMe, 6,4'-diMe, 6,7,4'-triMe), isoscutellarein and 6-hydroxyluteolin-6-methyl ether. Herbacetin-3-methyl ether and isoscutellarein are only trace constituents in the leaf resin of *B. pilularis*. However, due to the characteristic color reaction of their TLC-spots (bluish-violet in daylight after spraying with NA (= Naturstoffreagenz A), typical of 5,7,8-OH-substituted flavones and flavonols; cf. Wollenweber and Roitman, 1991) they can be identified unambiguously.

3. *Baccharis viminea* DC.. This species exhibits galangin and galangin-7-Me, kaempferol-4'-Me and kae-3,4'-diMe, quercetin and qu-3'-Me, chrysin and its 7-Me, apigenin and ap-4'-Me, pinocembrin, and naringenin-7,4'-diMe.

A good number of *Baccharis* species have been studied for flavonoid aglycones, some of them in our lab (Wollenweber *et al.*, 1986). There is a general tendency, in this genus, for the accumulation of "normal" as well as 6-O-substituted flavones and flavonols, some of them also exhibiting 8-O- and/or 6,8-di-O-substitution. However, it should be kept in mind that according to Bremer (1994) the genus *Baccharis* includes some 400 species; hence the members studied so far are too few to be representative of the genus. Since *Baccharis* shrubs and subshrubs are described as "usually viscid" (Bremer, 1994), it is assumed that most of the other species also produce flavonoid aglycones; a comprehensive study is hence desirable.

4. *Chrysothamnus nauseosus* (Pallas) Britton ssp. *albicaulis* (Nutt.) Hall & Clements. In the exudate of this plant we identified kaempferol, kae-3-Me, kae-4'-Me, kae-3,4'-diMe, quercetin, qu-3'-Me, qu-7-Me, apigenin, and ap-4'-Me. Two or three minor flavonoids remain unidentified. The unconspicuous flavonoid pattern of this species does not permit any conclusions regarding the flavonoid patterns of the 14 additional members of this genus, nor does the earlier finding of three flavanones in *C. nauseosus* (Bohlmann *et al.*, 1979).

5. *Grindelia nana* Nutt. var. *integrifolia* Nutt. Only flavonols have been detected in the exudate: kaempferol-3-Me, kae-3,7-diMe, kae-3,4'-diMe, kae-3,7,4'-triMe and quercetin-3'-Me, qu-3,3'-diMe, qu-7,3'-diMe, qu-3,7,4'-triMe, and qu-3,7,3',4'-tetraMe. Earlier studies had revealed the presence of kaempferol and quercetin methyl ethers in the twelve *Grindelia* species (out of ca 55) so far analyzed (cf. Wollenweber *et al.*, 1993 and refs. therein; Timmermann *et al.*, 1994). Methyl derivatives of 6-hydroxykaempferol and of quercetagetin were also encountered frequently.

6. *Gymnosperma glutinosum* (Spreng.) Less. From material collected in Nuevo Leon, México, a total of 18 highly O-substituted flavonols has been reported earlier (Yu *et al.*, 1988). Most of them exhibit 6- and/or 8-O-substitution, and many of them 2'-O- or 5'-O-substitution also. In our material from Puebla, México, we encountered only five of these flavonols, namely 5,7,4'-triOH-3,6,8-triOMe, 5,7,3',4'-tetraOH-3,6,8-triOMe, 3,5,7,3',4'-pentaOH-6,8-diOMe, 5,7,3',5'-tetraOH-3,6,8,4'-tetraOMe, 5,7-diOH-3,6,8,2',4',5'-hexaOMe. In addition, however, we identified 8-OH-galangin-3,8-diMe, 5,7-diOH-3,6,8-triOMe and 5,7-diOH-3,6,8,3',4',5'-hexa-OMe and the trivial compounds

kaempferol, quercetagetin-3,6-diMe, scut-6-Me, luteolin, 6-OH-lut-6-Me, and 6-OH-lut-6,3'-diMe. Obviously the two populations also represent two different chemotypes of *G. glutinosum*. It is noteworthy to state that in this species flavonols clearly prevail over flavones, both in number and quantity, and that no other class of flavonoids is encountered. Most of the flavonols exhibit 6,8-diO-substitution. The ^{13}C NMR spectrum of 5,7,3',5'-tetraOH-3,6,8,4'-tetraOMe flavone, not previously reported, is presented in the Experimental section. – Note that *Gymnosperma* is a monotypic genus.

From the generic assemblage around *Haplopappus*, some species of *Ericameria* were now studied for the first time.

7. *Ericameria bloomeri* (A. Gray) J. F. Macbr. (= *Haplopappus bloomeri* A. Gray). Only two flavonoids have been identified from the exudate of this species: kaempferol-3,4'-diMe and apigenin-4'-Me. Traces of two or three further flavonoids remained unidentified.

8. *Ericameria linearifolia* (DC.) Urb. & J. Wussow (= *Haplopappus linearifolius* DC.). This species exhibits seven trivial flavonols: kaempferol with two of its methyl ethers (kaempferol-3-Me and kae-3,4'-diMe) and quercetin with three methyl ethers (qu-3-Me, qu-3'-Me, qu-3,3'-diMe).

Two further species of *Ericameria* have been studied so far. Thus, *E. diffusa* and *E. laricifolia* were found to produce methyl ethers of apigenin, kaempferol and quercetin and only one 6-O-substituted flavone (Clark and Wollenweber, 1984 and ref. therein). This relatively simple flavonoid profile is in accordance with our findings in *E. bloomeri* and *E. linearifolius*.

Some of the thus far studied *Haplopappus* spp. such as *H. scrobiculatus* and *H. sericeus* accumulate mainly flavones (refs. see Wollenweber and Jay, 1988). The most interesting flavonoid encountered in *Haplopappus* s. l. is haplopappin, a methylbenzyl derivative of kaempferol-3,4'-diMe from *H. foliosus* (Tschesche *et al.*, 1985), but methyl ethers of quercetagetin (*H. rengifoanus*) and of myricetin (*H. integerrimus* var. *punctatus*) are also worth mentioning (refs. see Wollenweber and Jay, 1988). The taxonomy of *Haplopappus* has undergone a number of changes in recent years, with the old concept of the genus *Haplopappus* becoming divided into a number of smaller genera such as *Ericameria* (Lane and Hartmann, 1996). Some of the other groups, especially those from South America, still await taxonomic revision. The accumulation trends observed thus far do not provide chemical characters in the species studied. It is noteworthy, however, that flavanones, dihydroflavonols, chalcones and dihydrochalcones have not yet *been detected in Haplopappus* or its various segregates. More and detailed botanical and phytochemical studies are needed to clarify the complex taxonomic situation in this generic assemblage.

B) Eupatoriae

1. *Ageratina espinosa* (Gray) King & Robinson: Numerous flavonoid aglycones are present in the exudate of this plant. We found apigenin and ap-7-methyl ether, luteolin and lut-3'-methyl ether, kaempferol, the 6-Me, 3,6-diMe, 3,6,7-and 3,6,4'-triMe and the 3,6,7,4'-tetraMe of 6-hydroxy-kaempferol, quercetin and its 3-Me, the 3,6,3'-triMe, the 3,6,4'-triMe and the 3,6,3',4'-tetraMe of quercetagetin. Four flavanones were also present, namely naringenin-7-Me, eriodictyol and its 7-Me and 7,3'-diMe.

Flavonoid aglycones have been reported for only three species of *Ageratina: A. saltillensis* (Yu *et al.*, 1986), *A. stevioides* (Méndez and Rosquette, 1988) and *A. tomentella* (Fang and Mabry, 1986). They were found to produce methyl ethers of apigenin, scutellarein and 6-hydroxyluteolin as well as of kaempferol, 6-hydroxykaempferol, quercetin and quercetagetin. Flavanones, dihydroflavonols, chalcones and dihydrochalcones are absent from these species. However, the genus includes some 290 species with "usually glandular leaves" (Bremer, 1994), and it would be presumptuous to speak of any trend in its exudate flavonoid pattern.

2. *Brickellia californica* (Torrey & Gray) A. Gray: In this material we found four methyl ethers of scutellarein (6-Me, 6,7-diMe, 6,4'-diMe, 6,7,4'-triMe) along with the 6-Me and the 6,7-diMe of 6-hydroxyluteolin. Mues *et al.* (1979) have studied this species previously and found a total of eight flavonoid aglycones. They did not find scutellarein-6,7,4'-Me, but they did isolate 6-OH-luteolin-6,4'-diMe, quercetagetin-6,3'-diMe and queg-6,7,4'-triMe in addition to the aglycones we de-

tected. It may be assumed that this difference is due to the existence of chemical races in *B. california*. To our knowledge flavonoid aglycones have been reported for 13 of 110 species composing the genus *Brickellia*. Most of these are flavonols, but there are also some flavones and a few flavanones (naringenin-7-Me and eriodictyol methyl ethers). Among the flavonols, a variety of methyl ethers of 6-hydroxykaempferol and of quercetagetin is prevailing, and almost all the flavones are methyl ethers of scutellarein and of 6-hydroxyluteolin. Thus 6-O-substitution seems to be important in this genus. The most interesting product, so far found only twice in other genera, is brickellin, 5,2'-diOH-3,6,7,4',5'-pentaOMe flavone.

C) Helenieae

1. *Eriophyllum confertifolium* (DC.) A. Gray var. *confertifolium*: This species exhibits four methyl ethers of quercetagetin (6-Me, 3,6-diMe, 6,3'-diMe, and 3,6,4'-triMe), all of them being present in very small amounts only.

2. *Eriophyllum staechadifolium* Lag. In this species the flavonoid excretion also is not important. Quercetin and three of its methyl ethers (3-Me, 3'-Me and 3,3'-diMe) as well as quercetagetin-3,6-diMe and queg-3,6,3'-triMe occur in low amounts only.

To the best of our knowledge this is the first report of flavonoid aglycones in any species of this genus. Nine further species remain to be examined for exudate flavonoids.

3. *Hemizonia lutescens* (Greene) Keck. In this species we found quercetin-3-Me, quercetagetin-3,6,7-triMe, 5,7,4'-triOH-8,3'-diOMe flavone (hypolaetin-8,3'-diMe), and 5,7,3',4'-tetraOH-3,6,8-triOMe flavone. The identities of the two 8-O-substituted compounds have been confirmed by their MS and NMR spectra. We present here the ^{13}C-NMR data of hypolaetin-8,3'-diMe, which have not been published previously. Hypolaetin-8,3'-diMe is a very rare flavone that has so far been found only in three Asteraceae: *Ambrosia dumosa* (Seaman *et al.,* 1972), *Doronicum grandiflorum* (Reynaud *et al.,* 1983) and *Conyza* spp. (Urzua *et al.,* 1991). In the latter case its occurrence in resinous exudate was mentioned.

Two studies on flavonoid aglycones of *Hemizonia* dealing with some 20 species are known (Proksch *et al.,* 1984; Tanowitz *et al.,* 1987). In addition to rather trivial methyl ethers of kaempferol, quercetin and quercetagetin, the authors reported more interesting compounds, namely two gossypetin methyl ethers (3,8-diMe and 3,7,8-triMe), 5,7,8,3',4'-pentaOH-6-OMe-flavone, and 5,7,3',4'-tetraOH-3,6,8-triOMe-flavone. The flavanones naringenin, eriodictyol and erio-7-Me were also encountered. Some 10 species still need to be studied.

4. *Madia elegans* D. Don ssp. *densifolia* (Greene) Keck. In the leaf and stem exudate of this plant we identified luteolin, kaempferol-7-Me, kae-7,4'-diMe, quercetin-7-Me and qu-7,3'-diMe, eriodictyol and the rare dihydroflavonol, taxifolin-7-methyl ether. Some further components remain unidentified.

5. *Madia sativa* Mol. The material we analyzed exhibited luteolin and its 3'-Me and 7,3'-diMe, isoscutellarein-8,4'-diMe, 6-OH-luteolin-6-Me and -6,7-diMe, quercetin and qu-3-Me, quercetagetin-3,7-diMe and queg-3,6,7-triMe, gossypetin-3,8-diMe and eriodictyol and eriod-7-Me. This species has been studied previously by Bohm *et al.* (1992), also collected in California. These authors reported a rather different flavonoid pattern. Once more the possible existence of chemical races must be considered. The two 8-O-substituted flavonoids found in our material merit special mention. Gossypetin-3,8-diMe has so far been found only in some Asteraceae. Isoscutellarein-8,4'-diMe (bucegin) has been found only once as a natural product, namely in the liverwort *Bucegia romanica* (Markham and Mues, 1983). The identity of both products could be confirmed by direct comparisons with markers (Roitman and James, 1985; Nakayama *et al.,* 1983). The so far unpublished ^{13}C NMR spectrum of bucegin is reported in the Experimental section.

Sixteen additional species of the genus *Madia* remain to be studied.

6. *Perityle lemmonii* (A.Gray) McBride. Only two widespread flavonols were detected in the exudate of this plant: 6-OH-kaempferol-3,6-diMe and 6-OH-kae-3,6,4'-triMe. A second species of this genus, *P. vaseyi,* has been analyzed previously for non-polar flavonoids (Bohm *et al.,* 1986). It yielded two O-methylated derivatives of kaempferol, four of 6-OH-kaempferol, three of quercetagetin, and trace amounts of 7,4'-dimethyl nar-

ingenin. In total the genus includes 63 species (Bremer, 1994).

D) Heliantheae

1. *Ambrosia ambrosioides* (Cav.) Payne. In an earlier study on this plant's exudate flavonoids we had identified apigenin, scutellarein-6-Me, luteolin, 6-OH-luteolin-6-Me, kaempferol and quercetin from a limited amount of material. Analysis of bulk material has now permitted the identification of three additional products: scutellellarein-7-Me, 6-OH-luteolin-6,3'-diMe and quercetin-3'-Me. The exudate flavonoid patterns of other *Ambrosia* species have been discussed previously (see Wollenweber *et al.*, 1995), but a number of species remain to be studied.

Scutellarein-7-Me was first isolated from leaves of *Sorbaria stellipila* and called sorbifolin (Arisawa *et al.*, 1970). It was since reported from half a dozen of unrelated plant species. Although the methyl ethers of scutellarein are widely distributed in plant exudates, the 7-Me occurs only rarely. This is the first report of its occurrence in an exudate. Its thus far unreported ^{13}C NMR data are presented in the Experimental.

2. *Gaillardia arizonia* A. Gray. The exudate flavonoid pattern expressed by this plant is rather simple, consisting of only a few rather polar aglycones: scutellarein-6-Me, luteolin, 6-OH-luteolin-6-Me and a trace of eriodictyol. To our knowledge, exudate flavonoids have been mentioned for only two of the 28 species comprising this genus, namely scutellarein-6-Me and luteolin for *G. megapotamica* var. *radiata*, 6-OH-luteolin-6,3'-diMe and eriodictyol for *G. tontalensis* (Petenatti *et al.*, 1996).

3. *Zinnia acerosa* (DC) A. Gray. As in the preceding species, exudate production is very low. We have identified apigenin-7-Me, isoscutellarein-8-Me, and isoscut-8,4'-diMe. Isoscutellarein-8-Me is not very widespread, and isoscut-8,4'-diMe (bucegin) is an extremely rare flavone (see above, *Madia sativa*). Twenty-one additional species of this genus have yet to be studied for exudate flavonoids.

As compared with other plant families, a large proportion of Asteraceae species have been examined for exudate flavonoids (cf. Wollenweber and Valant-Vetschera, 1996; Wollenweber *et al.*, 1997). In view of the immense number of species, however, it still is only a small proportion in this large family. The taxonomic utility of the flavonoids in most genera can only be tested when sampling of species has become much more complete.

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Arisawa M., Takakuwa T. and Nakaoli T. (1970), Studies on unutilized resources, IV. Flavonoids in the leaves of *Sorbaria stellipila* (Rosacae). Chem. Pharm. Bull. **18**, 916–918.

Bohlmann F., Dutta L., Robinson H. and King R. M. (1979), Neue Labdan-Derivate aus *Chrysothamnus nauseosus*. Phytochemistry **18**, 1889–1892.

Bohm B. A., Averett J. E. and Powell A. M. (1986), Non-polar flavonoids of *Perityle vaseyi* (Asteraceae). Phytochemistry **25**, 2551–2553.

Bohm B. A., Fong C., Hiebert M., Jamal A. and Crins W. J. (1992), Non-polar flavonoids of *Calycadenia*, *Lagophylla* and *Madia*. Phytochemistry **31**, 12661–1263.

Bremer K. (1994), Asteraceae: Cladistics and Classification. Timber Press, Portland.

Clark W. D. and Wollenweber E. (1984), Flavonoids of *Ericameria laricifolia* (Ast.). Z. Naturforsch. **39c**, 1184–1185.

Fang N. and Mabry T. J. (1986), Flavonoid aglycones from *Ageratina tomentella*. J. Nat. Prod. **49**, 738–739.

Lane M. A. and Hartmann R. L. (1996), Reclassification of North American *Haplopappus* (Compositae, Astereae) completed: *Rayjacksonia* gen. nov. Amer. J. Bot. **83**, 356–370.

Markham K. R. and Mues R. (1983), Taxonomically significant 8-hydroxyflavone glucuronides from the Marchantialean liverwort, *Bucegia romanica*. Phytochemistry **22**, 143–146.

Méndez A. M. and Rosquette C. (1988), Flavonoides de la *Ageratina stevioides*. Rev. Latinoamer. Quím. **19**, 47–49.

Mues R., Timmermann B. N., Ohno N. and Mabry T. J. (1979), 6-Methoxyflavonoids from Brickellia californica. Phytochemistry **18**, 1379–1383.

Nakayama M., Horie T., Lin C.-N., Arisawa M., Shimizu M.M and Morita N. (1983), The synthesis of 5,7-dihydroxy-4',8-dimethoxyflavone: Revised structure for cirsitakaogenin and cirsitakaoside. Yakugaku Zasshi **103**, 675–678.

Petenatti E. M., Pestchanker M. J., del Vitto L. A. and Guerreiro E. (1996), Chemotaxonomy of the Argentinian species of *Gaillardia*. Phytochemistry **42**, 1367–1368.

Proksch P., Budzikievicz H., Tanowitz B. D. and Smith D. M. (1984), Flavonoids from the external leaf resins of four *Hemizonia* species (Asteraceae). Phytochemistry **23**, 679–680.

Reynaud J., Raynaud J. and Voirin B. (1983), Sur la présence de deux flavones méthoxylés rares chez *Doronicum grandiflorum* Lam. (Composées). Die Pharmazie **38**, 628.

Roitman J. N. and James L. F. (1985), Chemistry of toxic range plants. Highly oxygenated flavonol methyl ethers from *Gutierrezia microcephala*. Phytochemistry **24**, 835–848.

Seaman F., Rodriguez E., Carman N. J. and Mabry T. J. (1972), A new flavonoid from Ambrosia dumosa. Phytochemistry **11**, 2626–2627.

Tanowitz B. D, Leeder K., Ross P. N. and Proksch P. (1987), Foliar flavonoid exudates and sectional taxonomy of *Hemizonia*. Biochem. Syst. Ecol. **15**, 535–540.

Timmermann B., Wollenweber E., Dörr M., Armbruster S., Valant-Vetschera K. M. and Fuentes E. R. (1994), External flavonoids in two *Grindelia* species. Z. Naturforsch. **49c**, 395–397.

Tschesche R., Delhvi M. S., Sepúlveda-Boza S., Zilliken F., Kirfel A. and Will G. (1985), Haplopappin, ein 8-(α-Methylbenzyl) flavonoid aus *Haplopappus foliosus*. Liebigs Ann. Chem. **1985**, 2465–2471.

Urzua A., Cuadra P., Rodriguez R. and Mendoza I. (1991), Flavonoid aglycones in the resinous exudate of some Chilean plants. Fitoterapia **62**, 358.

Wollenweber E. and Jay M (1988) Flavones and flavonols. In: The Flavonoids – Advances in Research since 1980, 233–302 (Ed.: Harborne J. B.). Chapman and Hall, London-New York.

Wollenweber, E., K. Mann, S. Hochwart, G. Yatskievych (1989), Exudate flavonoids in miscellaneous Asteraceae. Phytochem. Bull. **21**, 19–23 (1989).

Wollenweber E. and Roitman J. N. (1991), New frond exudate flavonoids from Cheilanthoid ferns. Z. Naturforsch. **46c**, 325–330.

Wollenweber E. and Valant-Vetschera K. M. (1996), New results with exudate flavonoids in Compositae. In: D. J. N. Hind. Proceedings of the International Compositae Conference, Kew, 1994. Vol. **1**. Systematics (vol. eds. D. J. N. Hind, H. Beentje and G. V. Pope) Royal Botanic Gardens, Kew, pp.169–185.

Wollenweber E., Dörr M., Timmermann B. N., Strand J and Fuentes E. R. (1993), Exudate Flavonoids from *Grindelia tarapacana* of Chile. Z. Naturforsch. **48c**, 533–534. W 199

Wollenweber E., Schober I., Dostal P., Hradetzky D., F. J. Arriaga-Giner F. J. and Yatskievych G. (1986), Flavonoids and terpenoids from the exudates of some *Baccharis* species. Z. Naturforsch. **41c**, 87–93. W 109

Wollenweber E., Hradetzky D., Mann K., Roitman J. N., Yatskievych G, Proksch M. and Proksch P. (1987), Exudate flavonoids from aerial parts of five *Ambrosia* species. J. Plant Physiol. **131**, 37–43.

Wollenweber E., Mann K., Hochwart S. and Yatskievych G. (1989), Exudate flavonoids in miscellaneous Asteraceae. Phytochem. Bull. **21**, 19–23.

Wollenweber E., Mann K., Dörr M., Fritz H., Roitman J. N. and Yatskievych G. (1995), Exudate flavonoids in three *Ambrosia* species. Natural Product Letters **7**, 109–116.

Wollenweber E., Henrich B., Mann K., and Roitman J. N. (1996), Lipophilic exudate constituents of some Rosaceae from the Southwestern USA. Z. Naturforsch. **51c**, 296–300

Wollenweber E., Dörr M., Fritz H. and Valant-Vetschera K. M. (1997), Exudate flavonoids in several Asteroideae and Cichorioideae (Asteraceae). Z. Naturforsch. **52c**, 137–143.

Yu S., Fang N. and Mabry T. J. (1986), Flavonoids from *Ageratina saltillensis*. J. Nat. Prod. **49**, 1178–1179.

Yu S., Fang N and Mabry T. J. (1988), Flavonoids from *Gymnosperma glutinosum*. Phytochemistry **27**, 171–177.