

Flavonoids and Terpenoids from the Exudates of Some *Baccharis* Species

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Dedicated to Professor Hans Grisebach on the occasion of his 60th birthday

Baccharis (Compositae, Astereae), Aerial Parts, Exudates, Flavonoid Aglycones, Terpenoids

Seven species of the genus *Baccharis* have been analyzed for flavonoid aglycones. Many known methylated flavones, flavonols and flavanones were identified. From *B. sarothroides*, two novel flavonols were isolated and elucidated as 5,7,4'-trihydroxy-3,6,8-trimethoxyflavone and its methyl ether, 5,4'-dihydroxy-3,6,7,8-tetramethoxyflavone. Previous literature reports on flavonoids in *Baccharis* are summarized and their distribution and external occurrence is discussed. One novel diterpene and one rare triterpene were found in the terpenoid fractions that constitute most of the exudate material in these and other Compositae.

Introduction

Baccharis (Compositae, Astereae) is a large genus of more than 350 species that is widespread in the Americas. A comprehensive taxonomic treatment for this confusing assemblage is sadly lacking, although several workers have examined large regional species groups, primarily for floristic purposes [1–5]. The plants are mainly dioecious shrubs and small trees with numerous small discoid capitulae in cymes or panicles, and alternate leaves. Reports that many species are noticeably glutinous are common in the floristic literature and led us to investigate the exudate chemistry of some representative members of this interesting genus.

Since the early 1970's some 40 phytochemical publications on various species of *Baccharis* have appeared, about half of which reported aglycones and the remainder terpenoids (or both groups). However, in none of these publications did we find any hint to the localization of these more or less lipophilic natural products. Based on previous experience in this field (cf. [6, 7]) it was assumed that the flavonoid aglycones were deposited externally on leaves and twigs, as constituents of resinous material of terpenoid nature.

Samples of seven species of *Baccharis* were available for this study. Of these, the most widespread is

B. salicifolia (Ruiz and Pavon) Persoon (= *B. glutinosa* Persoon; see [2]), which ranges from the southwestern United States to Chile. It is an erect densely-branched shrub to 6 m tall, with linear-lanceolate leaves to 12 cm long, that is usually found near streams and rivers below 2800 m elevation. *B. heterophylla* H.B.K. appears much like *B. salicifolia*, but has leaves less than 5 cm long, with 1 to 4 teeth near the apices. It grows along streambeds from 1500 m to 2100 m, from Central Mexico to Guatemala. *B. sarothroides* A. Gray occurs at elevations below 2800 m in the southwestern United States and adjacent Mexico, and is commonly found on rocky slopes and in open areas. It is a densely fastigately-branched erect shrub with linear, quickly deciduous leaves on younger growth and leaves reduced to small scales on older branches. *Baccharis pteronioides* DC. is a common element of the grasslands in the southwestern United States (Arizona, New Mexico, and Texas), at elevations from 1500 to 3000 m, but is also found in arid mountains of Mexico as far south as Puebla. It is a low shrub with densely fascicled linear to spatulate leaves less than 10 mm long. *Baccharis bigelovii* A. Gray occurs in canyon habitats between 1500 and 3000 m elevation, and is distributed from southeastern Arizona to western Texas, and in adjacent Chihuahua and Coahuila, Mexico. The numerous slender branches of this low shrub often form a dense tangle and the thin obovate-cuneate leaves are often coarsely toothed. *B.*

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vaccinoides H.B.K. occurs in mountainous areas to 4000 m from southern Mexico to Honduras and El Salvador and forms dense rounded shrubs or small trees to 6 m tall with small elliptic entire or coarsely dentate leaves. *B. quitensis* H.B.K. is restricted to the coastal plains and lower foothills of the Andean Pacific slope in Ecuador and Peru, and is a densely branched shrub with oblong entire leaves to 5 cm in length.

Material and Methods

Plant material

Bulk samples (aerial parts) of each species (except *B. quitensis*) were collected in the field and air-dried at room temperature in paper bags. Pressed vouchers are at the herbarium of the University of Arizona (ARIZ) or in the personal herbarium of the senior author at Darmstadt. For *B. quitensis*, only a small twig of a specimen at the herbarium of the University of Heidelberg (HEID) was available for study. General data for each collection follow (more detailed locality information is present on the voucher specimens): *B. bigelovii* – USA, Arizona, Cochise Co., Yatskievych 84–193; *B. heterophylla* – Mexico, Oaxaca, Yatskievych and Wollenweber 83–152; *B. pteronoides* – USA, Arizona, Santa Cruz Co., Yatskievych 84–191; *B. quitensis* – Peru, Hutchison and Wright 4463; *B. salicifolia* – USA, Arizona, Cochise Co., Yatskievych and McCrary 84–101; *B. sarothroides* – USA, Arizona, 1. coll. = Pima Co., Yatskievych on May 25, 1982, 2. coll. = Cochise Co., Yatskievych on August 6, 1982; *B. vaccinoides* – Mexico, Hidalgo, Yatskievych and Wollenweber 83–129A.

The exudate material was obtained by rinsing the air-dried plant material with acetone or by dipping it in acetone for a short time. The following exudate yields were obtained: *B. bigelovii* 2.3% of plant dry weight, *B. heterophylla* 8% d.w., *B. pteronoides* 8.9% d.w., *B. salicifolia* 6.1% d.w., *B. sarothroides*: 1. coll. 6% d.w., 2. coll. 7.8% d.w., *B. vaccinoides* 14% d.w. The average production of leaf and stem resin in these species was thus ca. 7.6% of plant dry weight. – The concentrated solutions were normally subjected to CC or used directly for TLC comparisons (*B. quitensis*).

Chromatography

CC was done with silica (Kieselgel N) or with polyamide (Polyamid SC-6). Elution was with toluene

and increasing quantities of MeCOEt and MeOH. Isolated flavonoids were purified by recrystallization, in some cases also by preparative TLC on silica (SILGUR-25). TLC was on polyamide (Polyamid DC-11) with the following solvents: A) toluene – petrol (100–140 °C) – MeCOEt – MeOH 30:90:2:1.5; B) toluene – petrol (100–140 °C) – MeCOEt – MeOH 60:30:10:5; C) toluene – dioxane – MeOH 80:10:10; D) toluene – MeCOEt – MeOH 60:25:15. For silica plates we used solvents E) toluene – MeCOEt 90:10 and F) toluene – dioxane – HOAc 90:25:4. Plates were viewed under UV-light (366 nm) before and after spraying with Naturstoff-reagenz A (NA; 0.5% in MeOH), for evaluation of flavonoids. Terpenoids on silica were visualized by spraying with MnCl₂ reagent (3 g MnCl₂ diss. in 150 ml H₂O. 750 ml MeOH and 30 ml conc. H₂SO₄ added), followed by heating to 120 °C. – Adsorbents for CC and TLC were from Macherey-Nagel, Düren.

Most flavonoid aglycones were identified unambiguously by direct comparisons with markers available in the senior author's laboratory. From *Baccharis bigelovii* we isolated comp. **3** (m.p. 170–172 °C; M⁺ 302), comp. **4** (m.p. 287–290 °C; M⁺ 272) and comp. **5** (m.p. 191–192 °C; M⁺ 358). From *B. salicifolia* comp. **6** (m.p. 170–172 °C; M⁺ 286) was obtained. *Baccharis sarothroides* yielded the new flavonols, comp. **1** and comp. **2**.

Compound **1**: Yellow needles, m.p. 241–243 °C (benzene/acetone). UV $\lambda_{\text{max}}^{\text{MeOH}}$ 340, 280; AlCl₃ 372 (319), 292; NaOH 408 (336), 295; NaOAc 398, 287. MS *m/z* (rel. int.) 360 (72%, M⁺), 345 (100%), 330 (16), 327 (8), 315 (9), 197 (8), 180 (6), 169 (8), 134 (19), 121 (30), 105 (18). ¹H-NMR (ppm) δ 11.69 (1 H, s; OH-5), 7.98 (2 H, d; H-2'/H-6'), 7.00 (2 H, d; H-3'/H-5'), 3.89, 3.82, 3.80 (3 H each, s; 3 × OCH₃).

Compound **2**: Yellow crystals, m.p. not determined. UV $\lambda_{\text{max}}^{\text{MeOH}}$ 338, 282; AlCl₃ 363, 288; NaOH 402, 279 (258); NaOAc 401, 278. MS *m/z* (rel. int.) 374 (71%, M⁺), 359 (100), 341 (6), 248 (17), 247 (12), 211 (7), 164 (100). ¹H-NMR δ (ppm) 7.98 (2 H, d; H-2'/H-6'), 7.01 (2 H, d; H-3'/H-5'), 4.08, 3.85, 3.86, 3.85 (3 H each, s; 4 × OCH₃) (OH-5 exchanged).

¹H-NMR spectra of flavonoids were recorded on a Bruker HFX 90 (DMSO/TMS); ¹H-NMR and ¹³C-NMR spectra of terpenoids were obtained on a Bruker WP-200-SY at 200 and 50.13 MHz, respec-

tively (CDCl_3/TMS). Mass spectra were recorded on a Varian MAT 311. Mps are uncorrected.

Results

Structure elucidation of compounds **1** and **2**

Compound **1** appears on polyamide thin layer as a dark spot that shows no reaction with NA. The MS exhibits M^+ at m/z 360, thus indicating a flavone or a flavonol with 3 OH and 3 OMe groups. The ^1H -NMR shows no A-ring protons and exhibits signals for a AA'BB' system. Hence the A-ring is completely substituted while the B-ring is substituted at C-4'. UV spectral shifts with AlCl_3 , with NaOAc and with NaOH indicate free OH groups at positions C-5, C-7 and C-4', respectively. The three methoxy groups must therefore be located at C-3, C-6 and C-8. Compound **1** is therefore 5,7,4' trihydroxy-3,6,8-trimethoxy flavone.

Compound **2** exhibits the same colour behaviour on TLC as compound **1**, but it is less polar. The R_f difference indicates that it might be a methyl derivative of comp. **1**. The MS exhibits M^+ indeed at m/z 374 m as for a flavone or flavonol with 2 OH- and 4 OMe-groups. The PMR also shows the signals of an AA'BB' system and an additional signal for OCH_3 protons. In the UV shifts are observed with AlCl_3 and with NaOH only. The structure of compound **2** is thus deduced to be 5,4'-dihydroxy-3,6,7,8-tetramethoxy flavone.

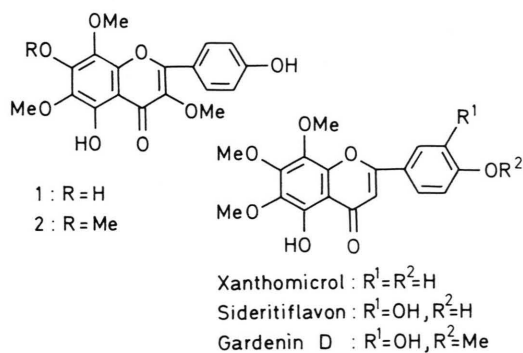
Compounds **3**–**6** are still under investigation. Their elucidation will be reported elsewhere. All other flavonoids reported were readily identified by direct comparisons with markers, by their UV spectra and occasionally by MS spectra.

Distribution of flavonoid aglycones

Of the seven *Baccharis* species studied here, three had been reported previously to "contain" flavonoid aglycones, namely *B. quitensis* (5,4'-dihydroxy 6,7,8-trimethoxy flavone and 5,4'-dihydroxy 6,7,8,3'-tetramethoxy flavone [8]), *B. salicifolia* (pinocembrin [9], as *B. glutinosa*; naringenin 7-Me and luteolin 7,3'-diMe [10]), and *B. sarothroides* (quercetin 3,4'-diMe and quercetagenin 3,6,4'-triMe [11]).

The sample of *Baccharis quitensis* available to us was extremely small but nevertheless allowed several chromatographic comparisons. We found that the leaf resin of this voucher indeed contained xanthomicrol (5,4'-dihydroxy 6,7,8-trimethoxy flavone) as reported earlier [8] for this species. The reported 5,4'-dihydroxy 6,7,8,3'-tetramethoxy flavone, however, was not detected in this sample. Instead we found its isomer, 5,3'-dihydroxy 6,7,8,4'-tetramethoxy flavone (gardenin D). In addition to these two flavones we observed a third compound that appeared on polyamide TLC as a prominent orange spot after spraying with NA (dark before spraying). By direct comparisons with a marker in different systems it was identified unambiguously as 5,3',4'-trihydroxy 6,7,8-trimethoxy flavone (4'-desmethyl-gardenin D = sideritiflavone). Sideritiflavone was first described from Labiatae, namely from *Sideritis leucantha* [12] and *S. flavovirens* [13, 14]; and recently from *Mentha piperita* [15]. This is the first report of its encounter in Compositae. 5,4'-Dihydroxy 6,7,8,3'-tetramethoxy flavone (3'-methyl sudachitin) is not so rare; it was previously found in three *Sideritis* species (see [16], in *Citrus sudachii* [17], in *Thymus vulgaris* [18], and in *Baccharis incarum* [19]). 5,4'-dihydroxy 6,7,8-trimethoxy flavone (xanthomicrol) has been found associated with the latter flavone in *Citrus sudachii* [17] and with sideritiflavone in *Mentha piperita* [15]. It is also found in *Sideritis* species [20], *Thymus* [21, 22] and *Baccharis tucumanensis* [23]. It may be mentioned that we recently detected xanthomicrol in a propolis sample from Arizona (Wollenweber and Weigel, unpubl.).

In *Baccharis salicifolia* the earlier reported flavanone pinocembrin was found to be a major flavonoid also in the leaf and stem resin of the material that we studied, while naringenin 7-Me, naringenin 7,4'-diMe and luteolin 7,3'-diMe, also reported previously for this species, were not detected here. We found instead luteolin-3'-Me and luteolin 3',4'-



diMe as minor constituents. The major flavonoid in our material is penduletin (6-hydroxykaempferol 3,6,7-triMe). Further we isolated compound **6**. In addition the flavonoids chrysin, apigenin and ap-4'-Me, kaempferol, kae-3-Me, kae-4'-Me, quercetin, qu-3'-Me, qu-3',4'-Me and qu-3,3',4'-Me were encountered. One of the terpenoids which constitute the resin was obtained in crystalline form and identified to be the rare triterpene maniladiol [45].

The two flavonols reported earlier from *Baccharis sarothroides* were not encountered in the material that we studied. We found (1 coll.), besides kaempferol and its 3-Me and 3,7-diMe the 3,6-diMe and 3,6,7-triMe of 6-hydroxykaempferol, the rare 3,8-diMe of 8-hydroxykaempferol (herbacetin 3,8-diMe) and the new flavonols 3,6,8-trimethylether and 3,6,7,8-tetramethylether of "6,8-dihydroxykaempferol" (compounds **1** and **2**, resp.). Compound **1** is the major resin flavonoid of the 1st coll., followed by penduletin. Compound **2** and penduletin were not detected in the leaf resin of the 2nd coll. Herbacetin 3,8-dimethylether has been previously found only twice as a natural product, namely in *Cyanostegia angustifolia* [24] and in the frond exudate of the fern *Pityrogramma triangularis* var. *viscosa* [25]. It was identified by direct comparison with a synthetic marker. The two methyl derivatives of "6,8-dihydroxykaempferol" are to our knowledge novel natural products. Their properties and structural elucidation are therefore reported in some detail (see Materials and Methods). — As major terpenoids in the resin of both collections we isolated the trivial triterpene oleanolic acid, the rare diterpene hautriwaic acid, and its new 2- β -hydroxy derivative. Oleanolic acid was readily identified by its physical data and by direct comparison with an authentic sample. Identification of hautriwaic and structure elucidation of 2- β -hydroxy hautriwaic acid are described elsewhere [45].

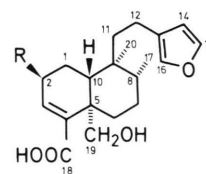
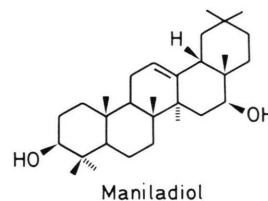
In *Baccharis bigelovii* chrysin is the major resin flavonoid, followed by compounds **3**, **4** and **5**. Minor flavonoids are apigenin, galangin, kaempferol, kae-7,4'-diMe, quercetin, qu-3'-Me, pinocembrin, and pinobanksin. Luteolin and its 3'- and 4'-methylethers are trace constituents. Traces of three more flavonoids could not be identified. The bulk of the resinous material consists of rather polar terpenoids that have not been studied yet.

Baccharis heterophylla exhibits only three flavonoids, namely apigenin, apigenin-7-Me and

naringenin. The triterpenes oleanolic acid and maniladiol were isolated in crystalline form.

The resin of *Baccharis pteronioides* also consists of a mixture of more or less polar terpenoids of unknown nature. The flavonoid aglycones present in very low quantity are trivial polar flavonoids which after concentration by CC, were readily identified by co-TLC with markers. They are apigenin, ap-7-Me, luteolin, lut-3'-Me, kaempferol, quercetin, qu-3'-Me and naringenin 7-Me.

Baccharis vaccinioides exhibits the highest number of flavonoid aglycones yet found in any *Baccharis* species. Major flavonoids are scutellarein 6,7-diMe and scut 6,4'-diMe; scut 6-Me is also present. Further we found apigenin and its 7-Me, 4'-Me and 7,4'-diMe, kaempferol and its 3-, 7-, 4'-, 3,7-, 3,4'-, 7,4'- and 3,7,4'-methylethers, the 6-, 3,6-, 6,7-, 6,4'-, 3,6,7-, 3,7,4'- and 3,6,7,4'-methyl ethers of 6-hydroxykaempferol, and the flavanones pinocembrin and naringenin 4'-Me. The triterpenes we identified are oleanolic acid and maniladiol. The diterpene hautriwaic acid was also found in this species.



R=H : Hautriwaic acid

R=OH : 2- β -Hydroxyhautriwaic acid

Discussion

The flavonoid patterns observed in the species studied here are similar for *B. bigelovii*, *B. pteronioides*, and *B. salicifolia*. They all exhibit apigenin, luteolin, kaempferol, quercetin and methyl ethers of these flavonoids and either pinocembrin (in *B. bigelovii* and *B. salicifolia*) or naringenin 7-Me (*B. pteronioides*). *B. heterophylla* and *B. quitensis*

are remarkable for their paucity of resin flavonoids (three each); *B. vaccinoides* is outstanding for the rather high number of aglycones (twenty). The highest number of flavonoids reported for any *Baccharis* species previously is five (in *B. trinervis* [26]). Also, those species dealt with to date in the literature show a tendency for accumulation of derivatives of apigenin (9 species) and naringenin (9 species); luteolin methyl ethers, pinocembrin and eriodictyol or methyl ethers of this flavanone are found in 3 species each. Attention is drawn to the presence of natural 3-acetates of naringenin and eriodictyol, respectively, in *B. varians* ([27; cf. [28]).

Comparisons of flavonoid patterns, for this study as well as for literature data, are most clearly presented in tables. Such tables often occupy incongruous space, however, because of a paucity of entries in individual columns. Since it seems desirable to here summarize data available from the literature to date, the following summary of flavonoids found in *Baccharis* (our enumeration includes references back to 1971) is presented in text format and is alphabetized by species (with the exception of *B. quitensis*, *B. salicifolia*, and *B. sarothroides*, which have already been described). Only such reports which deal aerial plant parts are considered here.

B. alaternoides: kaempferol 3-Me [54]; naringenin, nar 4'-Me and nar 7,4'-diMe [29]. *B. articulata*: apigenin 7-Me, ap-4'-Me, ap 7,4'-diMe, scutellarein 6,7-diMe, scut 6,7,4'-triMe [30]. *B. concinna*: pinocembrin [8]. *B. crispa*: apigenin, ap 7-Me [31], apigenin 7,4'-diMe and luteolin 7,4'-diMe [32]. *B. decussata*: scutellarein 6,4'-diMe, 5,7-dihydroxy-6,8,4'-trimethoxy flavone (nevadensin) [33]. *B. flabellata*: 6-hydroxyluteolin-6,7-diMe and -6,3'-diMe [34]. *B. genistelloides*: scutellarein-6-Me, kaempferol and quercetin [35]. *B. gilliesii*: quercetagen 3,6,3'-triMe [30]. *B. grandicapitulata*: apigenin-4'-Me and kaempferol-4'-Me [36]. *B. incarum*: 5,4'-dihydroxy-6,7,8,3'-tetramethoxy- and 5,4'-dihydroxy-3,6,7,8,3'-pentamethoxyflavone [37]. *B. kingii*: quercetin-3,3'-diMe [38]. *B. letocephala* (roots): naringenin 7-Me, nar 4'-Me [8]. *B. magellanica*: scutellarein 6-Me [39]. *B. maritima*: kaempferol and quercetin [40]. *B. medulosa*: apigenin-7-Me [34]. *B. microcephala*: luteolin, lut-7-Me [36]. *B. notoserigila*: apigenin, ap 7-Me [31]. *B. oxydonta*: pinocembrin and pinobanksin [8]. *B. pylicoides*: naringenin-4'-Me and nar-7,4'-Me (if this meant by "sakuranetin-7-Me") [36]. *B. ramosissimum*: apige-

nin and naringenin [8]. *B. reticulata*: eriodictyol [27]. *B. retusa*: naringenin 7-Me [41]. *B. rhomboidalis*: apigenin 7,4'-diMe [42]. *B. salzmännii*: naringenin [27]. *B. serratula*: naringenin 7-Me [27]. *B. tola*: apigenin, ap 7,4'-diMe [43]. *B. trimera*: 6-hydroxyluteolin-6,7,4'-triMe [41]. *B. trinervis*: apigenin, ap 7-Me, ap 4'-Me, ap 7,4'-diMe and luteolin 7,4'-diMe [26]. *B. trinervis* var. *rhexoides*: naringenin 7-Me [29]. *B. truncata*: eriodictyol 3'-Me [8]. *B. tucumanensis*: scutellarein 7,4'-diMe and 5,4'-dihydroxy-6,7,8-methoxy flavone (xanthomicrol) [23]. *B. varians*: naringenin and eriodictyol and their 3-O-acetates [44].

Considering our present results with *B. salicifolia*, *B. sarothroides*, and to a certain extent *B. quitensis*, it is assumed that reinvestigations of the species studied earlier would yield numerous additional flavonoids. In part this is probably due to the fact that the major purpose of most previous studies was analysis of terpenoids, with flavonoids found incidentally. A further reason might be that the flavonoids are much more difficult to isolate and/or identify when whole plant material is worked up as was the case in all previous studies.

While Compositae in general are well known to produce 6-O-substituted flavonoids, such compounds are rather sporadically known from *Baccharis* to date: scutellarein methyl ethers in six species, derivatives of 6-hydroxyluteolin in two species, methyl ethers of 6-hydroxykaempferol in three species and of quercetagenin in two species. A derivative of a 8-hydroxyflavonol has been found only once (herbacetin 3,8-diMe in *B. sarothroides*). The outstanding compounds are the methyl ethers of "6,8-dihydroxy-apigenin" and of "6,8-dihydroxyluteolin" as found in *B. decussata*, *B. incarum*, *B. quitensis* and *B. tucumanensis* and of "6,8-dihydroxykaempferol" in *B. sarothroides* (compounds **1** and **2**). For all such considerations it must be kept in mind, however, that the 37 species as yet studied still represent less than 10% of the known species of this large genus.

With respect to terpenoids, only those compounds that were obtained in crystalline form as major products have as yet been studied. In the present study three species (*B. heterophylla* and *B. sarothroides* and *B. vaccinoides*) afforded the trivial triterpene oleanolic acid which has been previously found in other species of this genus as well (*B. chilco*, *B. flabellata*, *B. pylicoides*, *B. rhomboidalis*, *B.*

scoparia, *B. tola*, *B. tricuneata*). However, the unusual triterpene maniladiol which we have found in *B. heterophylla* and *B. vaccinioides* is reported here for the first time in this genus. The diterpene hautriwaic acid, isolated from *B. sarothroides* and *B. vaccinioides*, was also reported previously in *B. crispa* and *B. tricuneata*, while its derivative 2- β -hydroxyhautriwaic acid isolated from *B. sarothroides* is reported here as a novel product. Its structural elucidation is described elsewhere [45]. Further clerodane-type diterpenes have been reported in nine species of this genus.

The present study confirms our assumption that a considerable number of free flavonoid aglycones occur externally in *Baccharis* as components of leaf and stem resins that mostly consist of terpenoid material. This agrees with our previous findings in other Compositae originating from xeric habitats (*Achillea* [46], *Ericameria* [47], *Fluorensia* [48], *Hazarida* [49], *Heterotheca* [50], *Hymenoclea* [51], *Pluchea* [52]). It is assumed that closer investigation of the *Baccharis* species already studied would reveal further flavonoid aglycones from the species cited here from

literature and would also very probably show them to be exudate constituents. Further, many of the terpenoids as yet described from *Baccharis* species are in all probability components of leaf and stem resins. We feel prompted once more (*cf.* [53]) to claim that future phytochemical studies, in particular on lipophilic products such as flavonoid aglycones and terpenoids, should take into account the localization of these natural products.

Acknowledgements

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Note added in proof: After submission of our manuscript we realized that compound **1** was reported as constituent of *Gutierrezia microcephala* [55].

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