Lipophilic Exudate Constituents of Some Rosaceae from the Southwestern USA

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The lipophilic epicuticular material of four shrubby Rosaceae from the Southwestern USA has been studied. They all exhibit triterpene acids as major products. *Adenostoma sparsifolium* and *Cowania mexicana var. glaber*, the two species in which glandular structures and a lipophilic excretion are obvious, produce free flavonoid aglycones as well. In *Adenostoma*, most of these are very rare compounds. *Cowania* exhibits some trivial and one rare flavone. In *Cercocarpus montanus* var. *glaber* and in *Fallugia paradoxa* the epicuticular material is devoid of flavonoids.

Introduction

In the course of our continuing research on lipophilic epicuticular materials in Angiosperms (Wollenweber, 1990) we have examined four Rosaceae from Arizona and California, all of which display a rich production of triterpene acids. Two of the species were also found to produce free flavonoids, whereas these are lacking in the other two.

Adenostoma sparsifolium Torrey, the red shank, is a treelike shrub, 2–6 m high, which is typical in the Californian chaparral. Its leaves and twigs are resinous-glandular (Munz, 1968); leaves are covered with a conspicuous layer of lipophilic resin.

Cercocarpus montanus var. *glaber* (S. Wats.) F.L. Martin forms shrubs or small trees that are also characteristic of the chaparral. Its wood is used for cabinet work and gave rise to the trivial name Mountain Mahagony (Benson and Darrow, 1981). Neither glandular structures nor exudate material are obvious on the leaf surface.

Cowania mexicana var. *Stansburiana* (Torrey) Jepson, the Cliffrose or Quinine Bush, is an intricately-branched shrub that occurs on hillsides and slopes in desert regions and grasslands throughout the southwestern USA and northern Mexico. The margins and the upper surfaces of the leaves show conspicuous, sticky, glandular dots. Twigs and flower calyces bear stalked glands (Benson and Darrow, 1981).

Fallugia paradoxa (D. Don) Endl., commonly known as Apache plume, is a shrub morphologically similar to *Cowania*, but differs in that the fruits have long, feathery beaks. It is widespread in the southwestern United States and in the mountains of adjacent, northern Mexico. (Benson and Darrow, 1981). As in *Cercocarpus*, neither secretory structures nor lipophilic exudates are obvious on leaves and/ or stems.

Materials and Methods

Aerial parts of *Adenostoma sparsifolium* were collected in July, 1984 in San Diego Co., CA (Campo exit off Insterstate 8). A voucher (G. Yatskievych 84–109, K. McCrary) is kept at The University of Arizona Herbarium (ARIZ). *Cercocarpus montanus* var. *glaber* was collected in May, 1990 in San Diego Co., CA (Cleveland National Forest, Indian Flats Campground). A voucher (G. Yatskievych 90–38, E. Wollenweber) has been deposited in the Missouri Botanical Garden Herbarium (MO). Twigs of flowering *Cowania mexicana* var. *Stansburiana* were collected in May, 1990 in Santa Cruz Co., AZ (near milepost #36 on State Route 83 N of Sonoita). A voucher (G. Yatskievych 90–74, E. Wollenweber) is accessioned in MO. *Fallugia paradoxa* was also collected in Santa Cruz Co., AZ (3.0 miles W of junction with State Highway 38 N of Sonoita); a voucher (G. Yatskievych 90–76, E. Wollenweber) is kept in MO.

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Air-dried aerial parts were rinsed with acetone to dissolve the epicuticular materials. From *Adenostoma sparsifolium* and *Cowania mexicana,* the material remaining after evaporation of the solvent was a brownish resin. These residues were dissolved in boiling methanol, cooled to room temperature, then to -10°C for 15 minutes and centrifuged, thereby eliminating waxy and fatty material. The supernatant solution was then subjected to column chromatography on Sephadex LH-20, eluted with methanol, to separate the phenolic fractions from the predominant terpenoids. Fractions containing flavonoid aglycones were further chromatographed over silica and/ or polyamide, eluted with toluene and increasing quantities of methylethyl ketone and methanol. Most of the flavonoid aglycones produced by *Adenostoma* were obtained in crystalline form, suitable for spectroscopic studies. Some others, as well as those present in the exudate of *Cowania*, were identified by direct TLC comparisons with markers. Fractions were monitored and chromatographic comparisons 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). – The acetone solutions washed from *Cercocarpus montanus* and *Fallugia paradoxa* both yielded solid residues: colourless cyrstalline material from *Cercocarpus*, a brown powder from *Fallugia*. Terpenoids were visualized by spraying silica plates with $MnCl_2$ reagent, followed by heating (Jork *et al.,* 1989). – Mass spectra were recorded at 70 eV. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 MHz and 50 MHz, respectively. Melting points are uncorrected.

Results

Most of the leaf resin of *Adenostoma sparsifolium* consists of terpenoids, with ursolic acid being a major component. Its identity was cofirmed by GC/MS (Greenaway, unpubl.). Pinocembrin, galangin, 6-hydroxygalangin-5,6-dimethyl ether, 8-hydroxygalangin-8-methylether and 6-hydroxykaempferol-5,6-dimethyl ether, which have been reported from this plant previously (Proksch *et al.,* 1982 a, b), were also isolated from our material. The spectral data were in accord with those given by Proksch *et al.* (1982 a, b). The identities of 8-hydroxygalangin-8-methyl ether and of 6-hydroxygalangin-5,6-dimethyl ether were further confirmed by direct comparisons with authentic markers. The 5-methoxylated flavonols appear as prominent brilliant yellow spots on TLC (UV_{366}). Melting points have not been reported by Proksch *et al.* (1982 a, b). We measured 200–203° for 6-hydroxygalangin-5,6-dimethyl ether, 225–227° for 8-methoxy galangin (221–222°, Krishnamurti *et al.,* 1965), 242–244° for 6-hydroxykaempferol-5,6-dimethyl ether. In addition we identified kaempferol and detected six further flavonoid aglycones and an as yet unidentified phenolic acid ester.

^{13}C NMR data for 3,7-diOH-5,6-diOMe flavone were not reported by Proksch *et al.* (1982); they are, therefore, reported here: ^{13}C NMR δ ppm 141.9 (C-2), 139.0 (C-3), 171.2 (C-4), 153.0 (C-5), 138.2 (C-6), 156.4 (C-7), 99.3 (C-8), 151.6 (C-9), 109.2 (C-10), 131.2 (C-1'), 127.1 (C-2'), 128.5 (C-3'), 129.4 (C-4'), 128.5 (C-5'), 127.1 (C-6'), 61.8 and 61.0 (5-OMe and 6-OMe).

Spot colors given below are for polyamide plates viewed in UV_{366}.

6-Hydroxygalangin forms a dark spot that turns brown on spraying with NA. A very small amount of this flavonol was obtained as light yellow platelets, not completely pure, mp 234–242° (Wollenweber *et al.,* 1993: 250–252°). Its idientity was further confirmed by direct comparisons with a synthetic samples (Horie *et al.,* 1995). UV λ_{max} MeOH (nm): 335, 274; $AlCl_3$ 403, 285 (increase); + HCl 412, 370, 279; NaOH 380, 294 (slight decrease), NaOAc 381, 279, 257; + H_3BO_3 373, 255. MS m/z (rel. int.): 286 (100, M^+; $C_{15}H_{10}O_6$), 272 (18), 254 (22), 153 (24), 105 (10).

6-Hydroxygalangin-6-methyl ether (alnusin) forms a dark spot on polyamide that turns greenish-brown to brown, depending on concentration. A small amount of this product crystallized as fine yellow needles, mp 228–230° (Goudard and Chopin, 1976: 239–240°). Its UV and MS data agree with those previously reported from our lab (Wollenweber *et al.* 1986, 1993b).

Traces of 8-hydroxygalangin were identified by direct TLC comparison with a marker on polyamide and on silica. It forms a dark spot that remains dark in UV, but exhibits the typical bluish-violet colour of 5,7,8-trihydroxy compounds in daylight on spraying with NA (Wollenweber and Roitman, 1991).

6-Hydroxykaempferol-6-methyl ether appears as an orange-yellow spot that turns dullish green after spraying. It forms yellow needles, mp 260–271° (Lebreton *et al.*, 1971: 270°).

5,7-Dihydroxy-6-methoxy flavanone (dihydrooroxylin) and 5,7-dihydroxy-8-methoxy flavanone (dihydrowogonin) were isolated as a mixture from which the 6-methoxy flavanone crystallized with preference, forming yellow needles, mp 162–163°. It was identified by its spectral properties and by comparison with a synthetic sample, mp 171–172° (Iinuma, 1984, pers. comm.). UV λ_{max} MeOH (nm): 330, 292; $AlCl_3$ 380, 313; NaOAc 329, 251. MS m/z (rel.int.): 286 (53, M^+; $C_{16}H_{14}O_5$), 261 (6), 209 (13), 182 (51), 167 (100), 154 (17), 153 (16). The 8-Methoxy flavanone, which was enriched in the filtrate, was identified unambiguously by direct comparison with a marker (Wollenweber *et al.,* 1972). The two flavanones appear as clearly distinct spots on polyamide in the solvent toluene – $petrol_{100-140}$ – MeCOEt – MeOH 12:6:2:1. The 6-methoxy derivative occurs as an intense dark spot that turns dark reddish brown whereas the lower R_f spot of the 8-methoxy derivative is brownish and turns yellow-brown. Spots sprayed with NA also exhibit distinct colors on exposure to NH_3.

Finally, we isolated a colourless product (AS-8), mp 111–113° (from benzene), which is not a flavonoid. Its spot on polyamide (R_f 0.66 in the above solvent) exhibits dark blue fluorescence which is unchanged on spraying with NA. Evaluation of its mass spectrum and NMR spectra indicates that it is hydroconiferyl ferulate. This structure, however, still needs to be confirmed and will be reported separately.

In *Cowania mexicana* var. *stansburiana* most of the resinous exudate also consists of terpenoids, among which oleanolic acid and ursolic acid are predominant. We identified the following aglycones in the flavonoid fraction: scutellarein-6-methyl ether, scutellarein-6,7-dimethyl ether and scutellarein-6,4'-dimethyl ether and traces of quercetin and apigenin. A nonpolar flavonoid (**1**) that appears as a dark spot before and after spraying with NA was identified as a tetramethyl ether of 8-hydroxylutolin (hypolaetin). An additional product (**2**), that appears as a dark spot between those of the two scutellarein-dimethyl ethers, was identified as trimethyl ether of hypolaetin. A minor constituent with the R_f of kaempferol that appears dark and turns orange on spraying with NA remains unidentified.

Hypolaetin-7,8,3',4'-tetramethyl ether (**1**) was isolated as fine yellow crystals, mp 205–209° (Farid, 1967: 210–212°). We prepared a marker by partial methylation of synthetic 5,3'-dihydroxy-7,8,4'-trimethoxy flavone (see acknowledgement). We here report the complete spectral data of **1**, since Farid (1967) gave only ^1H NMR data and Tatum and Berry (1972) gave mp, UV and IR data. UV λ_{max} (MeOH) nm: 340, (290), 275, 255; + $AlCl_3$ (400), 352, (195), 280, unchanged wih HCl. MS m/z (rel.int.): 358 (25%, M^+; $C_{19}H_{18}O_7$), 343 (100, M-15), 181 (11), 153 (28). ^1H NMR δ ppm (d_6-DMSO): 12.73 (s, 5-OH), 7.70 (dd, *J* 2 and 9 Hz; H-6'), 7.59 (d, *J* 2 Hz; H-2'),7.19 (d, *J* 9 Hz; H-5'), 7.04 (s, H-3), 6.59 (s; H-6), 3.92, 3.89, 3.87, 3.86 (s, 4 x OMe). [Chemical shifts of Farid's data (Farid, 1967) differ from ours because his data were obtained in $CDCl_3$.] ^{13}C NMR δ ppm: 163.4 (C-2), 103.6 (C-3), 182.2 (C-4), 156.6 (C-5), 96.0 (C-6), 158.4 (C-7), 128.4 (C-8), 149.0 (C-9), 103.9 (C-10), 122.9 (C-1'), 109.3 (C-2'), 149.0 (C-3'), 152.3 (C-4'), 111.9 (C-5'), 120.0 (C-6'), 61.1 (8-OMe), 55.7, 55.7, 56.5 (OMe-3',4',7). These data are in very good agreement with those of a synthetic sample of 5,3'-dihydroxy-7,8,4'-trimethoxy flavone and thus confirm the structure of trimethoxy-wogonin.

A very small amount of hypolaetin-8,3',4'-trimethyl ether (**2**) was obtained by preparative TLC on silica. It forms fine yellow needles, mp 225–228° (Krishnamurti *et al.,* 1972: 230–231°). UV λ_{max} (MeOH) nm: 333, 277; + NaOH (376), 283; + $AlCl_3$ (390), 350, 280, unchanged with HCl; NaOAc (310), 286. MS *m/z* (rel.int.): 344 (40%, M^+), 329 (100), 301 (24). ^1H NMR δ ppm (d_6-DMSO): 12.58 (br s, 5-OH), 7.68 (dd, *J* 1.5 and 8 Hz; H-6'), 7.57 (d, *J* 1.5 Hz; H-2'), 7.17 (d, *J* 8 Hz; H-5'), 6.94 (s, H-3), 6.29 (s, H-6), 3.88, 3.86, 3.85 (s, 3 x OMe). ^{13}C NMR δ ppm: 162.8 (C-2), 103.6 (C-3), 181.8 (C-4), 152.6 (C-5), 99.4 (C-6), 156.2

(C-7), 127.9 (C-8), 149.4* (C-9), 102.5 (C-10), 123.1 (C-1'), 109.2 (C-2'), 149.0* (C-3'), 152.1 (C-4'), 111.9 (C-5'), 119.7 (C-6'), 60.8 (8-OMe), 55.74, 55.70 (3'-OMe, 4'-OMe) (* signals may be interchanged). These data confirm the structure of dimethoxy-wogonin. They are in accordance with those of a sample of hypolaetin-8,3',4'-trimethyl ether isolated in our lab from Dikamali gum (cf. Krishnamurti *et al.,* 1972).

The exudate material obtained from *Cercocarpus montanus* var. *glaber* was found to be a mixture of oleanolic acid with ursolic acid and some minor terpenoids. The same was found to be true for *Fallugia paradoxa*. In both species the epicuticular material lacks flavonoid aglycones.

Discussion

Of the four Rosaceae examined in this phytochemical study, there are two which exhibit a conspicuous resinous exudate consisting mainly of terpenoids. They both accumulate flavonoid aglycones in addition to the predominant terpenoids. Among the terpenoids, ursolic acid is the most abundant component in the four investigated species.

Adenostoma sparsifoliaum has been the subject of an extensive study by Proksch *et al.* (1982 a, b) and by Proksch (1983) who reported pinocembrin, galangin, 6-hydroxygalangin-5,6-dimethyl ether, 8-hydroxygalangin-8-methylether and 6-hydroxykaempferol-5,6-dimethyl ether. From the same species we have identified seven additional flavonoid aglycones, most of which were isolated: 6-hydroxygalangin and its 6-methyl ether, traces of 8-hydroxygalangin, kaempferol, 6-hydroxykaempferol-6-methyl ether, 5,7-dihydroxy-6-methoxy flavanone (dihydrooroxylin) and 5,7-dihydroxy-8-methoxy flavanone (dihydrowogonin).

6-Hydroxygalangin is reported here only for the second time as a natural product; it has been found previously in *Cassinia quinquefaria* exudate (Wollenweber *et al.,* 1993a). Its 6-methyl ether (alnusin) is known from *Alnus sieboldiana* bud exudate, from aerial parts of *Chromolaena chaslaea*, and from the leaf exudates of *Anaphalis margaritacea* (Wollenweber *et al.,*1993b and refs. therein) and *Baccharis bigelovii* (Wollenweber *et al.,* 1986). Dihydrooroxylin has been found once before as a natural product in a *Piper* species (Sauer and Hänsel, 1967). Dihydrowogonin was thus far known only from the heartwood and from bud exudate of *Prunus* species (cf. Wollenweber *et al.,* 1972).

It should be mentioned that according to Proksch (1983), the epicuticular material of *Adenostema fasciculata* does not contain any flavonoid aglycones.

The occurrence of exudate flavonoids from *Cowania mexicana* has been mentioned earlier (Wollenweber, 1990), but at that time none of them had been identified. We have now identified scutellarein-6-methyl ether, scutellarein-6,7-dimethyl ether and scutellarein-6,4'-dimethyl ether along with traces of apigenin and quercetin, and we have isolated the very rare flavones, 5-hydroxy-7,8,3',4'-tetramethoxy flavone (**1**) and 5,7-dihydroxy-8,3',4'-trimethoxyflavone (**2**). Hypolaetin-7,8,3',4'-tetramethyl ether (trimethoxy-wogonin) has been previously reported only from bergamot oil (Farid, 1967), from "dikamali gum" (Krishnamurti *et al.,* 1972), and from aerial parts of *Lychnophora affinis* (Le Quesne *et al.,* 1976). Hypolaetin-8,3',4'-trimethyl ether (dimethoxy-wogonin) was reported from "dikamali gum" (Krishnamurti *et al.,* 1972) and later from leaves of *Gardenia lucida* (Kumari, 1989).

Few Rosaceae were previously known to accumulate flavonoid aglycones externally on the surfaces of aerial parts. They were found on leaves of several *Cotoneaster* species (Wollenweber, 1990), on *Rosa centifolia* cv. *muscosa* and on *Rubus phoenicolasius* (Wollenweber *et al.,* 1993c).

Rich production of triterpene acids is typical for the epicuticular material in Rosaceae in general (Hegnauer, 1990). Our results with the four Rosaceae studied here are in agreement with this generalization.

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