Chemodiversity of Surface Flavonoids in Solanaceae

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Several species of *Nicotiana* and *Solanum* and further members of the Solanaceae have been examined for their exudate flavonoids. Most of the aglycones are widespread flavonols, but rare and unusual flavonols were also found, *e.g.* in exudates of *Physalis* and *Solanum* species. Flavones occur throughout the family, but flavanones are rare. Our data are presented in comparison to previous results. The chemodiversity of the observed structures is discussed in relation to literature reports. Morphological and systematic aspects are briefly addressed.

Key words: Solanaceae, Exudates, Flavonoids

Introduction

Solanaceae have only rarely been studied for the occurrence of externally accumulated flavonoid aglycones, although in many species glandular trichomes and sometimes even their resinous exudates are obvious. Results on some Solanaceae genera have been published previously (Wollenweber, 1990; Wollenweber and Dörr, 1995), but comparative studies are still scant. Only recently, the occurrence of flavonoid trimethyl ethers and triterpenes was definitely proven in glandular trichomes of *Solanum paludosum* Moric. (Silva *et al.*, 2002), by isolating the trichomes from the leaves and subsequent extraction of the lipophilic material. Survey data on known flavonoid aglycones including those known of the Solanaceae will be available in the forthcoming book chapter on "Flavones and Flavonols" (Valant-Vetschera and Wollenweber, 2005). With the present publication we hope to contribute additional data to the still puzzling flavonoid chemistry of Solanaceae, with special reference to exudate flavonoids.

Materials and Methods

Plant material was cultivated in the Botanical Garden of the Technical University Darmstadt (except for *Fabiana imbricata*, which was collected by P. López in Chile, IV Región, Prov. De Nuble, Termas de Chillán, Dec. 2001). Voucher specimens are deposited in the Herbarium of the Institute of Botany, TU Darmstadt. Aerial plant material, either fresh or thoroughly air-dried, was briefly rinsed with acetone to avoid extraction of tissue constituents. The residues obtained after evaporation of the solvent were in most cases analyzed directly by TLC. Bulk material was routinely processed as reported previously. The flavonoids were identified by comparative TLC of Sephadex fractions with markers available in E. W.'s lab (cf. Wollenweber *et al.*, 2000), or else they were further characterized by spectroscopic methods.

From *Physalis alkekengi*, only dry red calyces (or husks) were used. Flavonoid containing fractions, as obtained from Sephadex LH 20, were further chromatographed over polyamide SC-6. Several flavonoids could then be identified in relevant fractions by direct comparison with markers. Some of the polyamide-fractions were rechromatographed on Sephadex LH 20 in chloroform/methanol 99:1. Individual compounds were then further purified by centrifugal thin layer chromatography (Chromatotron) on silica gel layers using benzene/2-propanol 19:1 as eluent. In this manner two pure crystalline compounds were isolated from one polyamide fraction; they were identified by NMR spectroscopy as the 3,7,3′,5′-tetramethyl ether of myricetin and the 3,7,3′-trimethyl ether of querce-

tin (pachypodol). The ^{1}H and ^{13}C NMR data of these products are given in Table I. For the complete list of compounds identified see Table IV.

From bulk material of *Solanum mammosum*, the flavonoid portion obtained from Sephadex CC was passed several times over acetylated polyamide, affording several flavonols in crystalline form: Herbacetin 3,8-diMe: M.p. 244 °C (Lit.: 242–244 °C, Roitman and James, 1985). – MS: *m/z* (rel. int.) = 330 $[M]^+$ (71), 315 $[M-Me]^+$ (100), 372 $[M-Me-COMe]^+$, (8), 287 $[M-COMe]^+$ (9).

Gossypetin 3,8-diMe: M.p. 303 °C (Lit.: 305–306 °C; Lit: 301–303 °C, Roitman and James, 1985). – MS: *m/z* (rel. int.) = 346 $[M]^+$ (53), 331 $[M-Me]^+$ (100), 303 $[M-COMe]^+$ (14), 288 $[M-Me-COMe]^+$ (13).

Gossypetin 3,8,3′-triMe: M.p. 215 °C (Lit.: 217–218 °C, Roitman and James, 1985). – MS: *m/z* (rel. int.) = 360 $[M]^+$ (60), 345 $[M-Me]^+$ (100), 317 $[M-COMe]^+$ (10), 302 $[M-Me-COMe]^+$ (14). For the complete list of compounds identified see Table III.

We also examined bulk material of *Petunia integrifolia* and of *P. parviflora*, respectively. *Petunia integrifolia* exhibited an unknown spot that moves slightly faster than Que-3,3′-diMe on polyamide (toluene/MeCOEt/MeOH 12:5:3 v/v/v), but slower on silica gel (toluene/MeCOEt 9:1 v/v). It appeared dark under UV_{366} and turned orange-yellow on spraying with NA. The flavonoid portion (from Sephadex CC) was passed over acetylated polyamide to yield, among others, fractions containing only Que-3,3′-diMe and an unknown product. The latter was then isolated by preparative TLC on silica gel (9/1) and crystallized from ethanol/acetic acid: M.p. 177 °C (not previously reported). – MS: *m/z* (rel. int.) = 360 $[M]^+$ (100), 345 $[M-Me]^+$ (70), 329 $[M-OMe]^+$ (10), 317 $[M-COMe]^+$ (49). The molecular ion peak at *m/z* 360 indicates a flavon/ol with 3 OH- and 3 OMe-groups. The ^{1}H NMR spectrum showed a downfield singlet for a strongly hydrogen bonded hydroxyl group (5-OH), two meta-coupled aromatic proton signals attributed to H-6 and H-8, a two proton singlet (H-2′ and H-6′) and two singlets corresponding to three methoxyl groups. The carbon spectrum had signals for A- and C-rings essentially identical to those of kaempferol 3-methyl ether confirming hydroxyl groups at C-5 and C-7 and a methoxyl group at C-3. The B-ring and methoxyl signals were identical to those of 5,7,4′-trihydroxy-3,6,8,3′,5′-pentamethoxyflavone (Roitman and James, 1985) and hence the *P. integrifolia* compound is the 3,3′,5′-trimethyl ether of myricetin. Myricetin 3,3′,5′-trimethyl ether has been found only once before as a natural product, from aerial parts of *Xanthocephalum gymnospermoides* (Yu *et al.*, 1987). The ^{1}H NMR data of our product agree with literature data; ^{13}C NMR data have not previously been reported.

In the case of *Petunia parviflora*, flavonoid fractions obtained from Sephadex were passed over polyamide SC-6. Several fractions exhibited a dark (UV_{366}) unknown spot just above luteolin 7,3′-diMe (polyamide, toluene/PE100–140/MeCOEt/MeOH 12:6:2:1 v/v/v/v). This substance (m.p. 218 °C) on spraying with NA, became somewhat ochre in color. After exposure to UV light for a while, it turned grayish, just as a series of apigenin-, luteolin- and tricetin-derivatives do. It was, therefore, assumed to be a structurally related flavone. Direct comparison with markers showed it to be tricetin 7,3′,5′-trimethyl ether. MS and NMR spectra were identical to those reported for the 7,3′,5′-trimethyl ether of tricetin, a very rare flavone first reported by Zahir *et al.* (1996) that we recently isolated from *Ceanothus velutinus* (Wollenweber *et al.*, 2004, erroneously listed as tricetin 7,3′,4′-triMe in Table I). MS and NMR data agree with previously reported data (Zahir *et al.*, 1996; Wollenweber *et al.*, 2004).

Results and Discussion

The genera studied belong to different groups of the large family Solanaceae. Taxonomic alignments are based upon a recent monographic publication on this family (Hunziker, 2001). Because of the morphological diversity present in this family, a considerable amount of chemodiversity was expected in their flavonoid profiles. However, in many cases only a limited number of flavonoid compounds was accumulated in the exudates. In the species studied, the number of flavonol derivatives was much higher than that of the corresponding flavones. Accumulation of 3-OMe-flavonols and their 7- and/or 4′-OMe-derivatives is observed in several genera of the Solanaceae. Frequently, the 3′,4′-hydroxylation pattern is predominant over 4′-hydroxylation. The most complex flavonoid profile was found in species of *Solanum* (Table III), with a tendency to produce 8-OH-derivatives both of flavones and flavonols, as well as tricetin- and myricetin-derivatives. Results are compared to literature data and presented as Ta-

Table I. NMR data of selected flavonoids from Solanaceae.

C	Myricetin 3,3′,5′-trimethyl ether	Myricetin 3,7,3′,5′-tetramethyl ether	Tricetin 7,3′,5′-trimethyl ether	Quercetin 3,7,3′-trimethyl ether
2	155.2	155.6	163.9	155.7
3	137.8	138.1	103.6	137.9
4	177.7	178.0	181.9	178.0
5	161.1	160.8	161.1	160.8
6	98.6	97.8	97.9	97.7
7	64.6	165.1	165.1	165.1
8	93.9	92.5	92.7	92.4
9	156.3	156.2	157.2	156.2
10	103.9	105.1	104.64	105.1
1′	119.5	119.4	119.9	120.6
2′	106.2	106.3	104.58	112.1
3′	147.7	147.8	148.2	147.4
4′	139.0	139.2	140.4	149.9
5′	147.7	147.8	148.2	115.6
6′	106.2	106.3	104.58	122.3
3-OMe	59.6	59.7		59.6
7-OMe		56.1	56.0	56.0
3′-OMe	56.1	56.2	56.4	55.7
5′-OMe	56.1	56.2	56.4	
H				
5-OH	12.64, s	12.65, s	12.97, s	12.66, s
4′-OH		9.30, s		9.90, s
3			7.03, s	
6	6.20, d, J = 2 Hz	6.38, d, J = 2.0 Hz	6.37, d, J = 2.4 Hz	6.38, d, J = 2.2 Hz
8	6.50, d, J = 2 Hz	6.82, d, J = 2.0 Hz	6.85, d, J = 2.4 Hz	6.78, d, J = 2.2 Hz
2′	7.38, s	7.44, s	7.36, s	7.67, d, J = 2.1 Hz
5′				6.97, d, J = 8.4 Hz
6′	7.38, s	.44, s	7.36, s	7.63, dd, J = 8.4, 2.1 Hz
3-OMe	3.82, s	3.84, s		3.82, s
7-OMe		3.88, s	3.886, s	3.87, s
3′-OMe	3.86, s	3.87, s	3.892, s	3.87, s
5′-OMe	3.86, s	3.87, s	3.892, s	

bles II–IV. Species lacking detectable amounts of exudate flavonoids are listed at the end of the respective tables. Finally, the rather rare occurrence of flavonoid glycosides in exudates of some Solanaceae genera is separately discussed in relation to glandular trichome morphology.

Flavonoid aglycones from Cestroideae-Nicotianeae

The genus *Nicotiana* comprises about 79 species grouped in various subgenera and sections (Hunziker, 2001; Goodspeed, 1954). The species with known flavonoid aglycone composition including the newly studied taxa belong to subgen. *Rustica*, subgen. *Tabacum* and subgen. *Petunioides*, respectively. According to Hunziker (2001), the genera *Petunia* and *Fabiana* are associated with *Nicotiana.* In *Nicotiana*, general trends observed are the formation of flavonols and their methyl ethers, predominantly derivates of quercetin. In species from subgenera *Tabacum* and *Petunioides*, kaempferol- and quercetin-derivatives with corresponding substitution patterns were found. Only *N. debneyi* of subgen. *Petunioides* is known thus far for producing flavones in its exudates. Species of *Petunia* share the flavonol patterns in part, but trend towards flavone formation (Table II).

The generic concept of *Petunia* is somewhat controversial. Thus, *P. parviflora* is sometimes considered to be part of the genus *Calibrachoa*, whereas the other two species analyzed are sometimes separated as genus *Stimoryne* (Wijsman and De Jong, 1985; Wijsman, 1990), a concept not accepted by Hunziker (2001). Seed morphology differences

Table II. Flavonoid aglycones from *Nicotiana* spp. and *Petunia* spp. (Cestroideae-Nicotianeae) (Me, methyl ether).

	Nicotiana subgen. *Rustica*				*Nicotiana* subgen. *Tabacum*		*Nicotiana* subgen. *Petunioides*					*Petunia*			
	paniculata L.	*knightiana* Goodsp.	*solanifolia* Walp.	*Nicotiana rustica* L.	*glutinosa* L.	*tabacum* L.	*undulata* Vent.	*trigonophylla* Dun.	*acuminata* Hook.	*benthamiana* Domin	*debneyi* Domin	*plumbaginifolia* Viv.	*hybrida "surfina"*	*integrifolia* (Hook.) Schintz & Thell.	*parviflora* Juss.
References				1		2							1		
Flavones															
Apigenin															x
Ap-7-Me											x				x
Luteolin															x
Lut-7-Me															x
Lut-3′-Me															x
Lut–7,3′-diMe											x				x
Tricetin 7,3′,5′-triMe															x
Flavonols															
Kaempferol					x										
Kae-3-Me						x			x		x		x	x	
Kae-7-Me					x			x							
Kae-3,7-diMe					x			x		x	x				
Kae-3,4′-diMe										x			x		
Kae-7,4′-diMe					x					x					
Kae-3,7,4′-triMe					x					x					
Quercetin	x		x		x		x	x							
Que-3-Me	x		x	x	x	x	x	x	x			x	x	x	
Que-7-Me								x							
Que-3′-Me	x	x	x			x	x					x			
Que-3,7-diMe					x	x		x			x		x		
Que-3,3′-diMe	x			x		x		x	x		x	x		x	
Que-3,4′-diMe													x		
Que-7,3′-diMe	x	x			x			x				x			
Que-3,7,3′-triMe	x							x			x				
Que-3,7,4′-triMe					x							x	x		
Que-3,3′,4′-triMe													x		
Que-3,7,3′,4′-tetraMe	x											x			
Quercetagetin 3,6-diMe														x	
Queg-3,6,3′-triMe										x					
Myricetin 3,3′,5′-triMe														x	

No exudate flavonoids were detected in the following Cestroideae: *Cestrum parqui* Benth.; *Cestrum* elegans Schlecht.; *Nicotiana langsdorfii* Schrank.; *N. megalosiphon* Heurck & Muell. Arg.; *Vestia foetida* (Ruiz & Pav.) Hoffm.

References: 1, Wollenweber and Dörr (1995); 2, Wollenweber (1990).

support this division (Watanabe *et al.*, 1999). Hunziker (2001) further noted that *Petunia* spp. do not accumulate alkaloids as *Nicotiana* species do. Additionally, chloroplast DNA sequencing data revealed a greater phylogenetic distance between *Petunia* and *Nicotiana* (Olmstead *et al.*, 1999). Judging by the known flavonoid composition, the studied Petunias appear to fall into two groups coinciding with the proposed concept of Wijsman (1990), but infraspecific and intrageneric variation is not well enough documented. The apparent phylogenetic distance between those two genera is not yet obvious from their exudate flavonoid profiles, but the occurrence of the rare myricetin 3,3′,5′-trimethyl ether, not found in the other studied taxa of this group, may be significant (Table II).

Fabiana imbricata Ruiz and Pav. yielded only coumarin-derivatives, such as scopoletin and its 7-prenyl-derivative in its exudates, thus differing from the other studied taxa. This is not so exceptional, since *e.g.* aerial parts of some *Artemisia* species (Valant-Vetschera *et al.*, 2003a and references therein) or bud exudates of *Aesculus* spp. and *Fraxinus* spp. (Wollenweber, unpublished) were also found to accumulate free coumarins externally. Unfortunately, no systematic comparison on exudate coumarin formation in plants has been carried out thus far. Only caffeic and chlorogenic acid were identified from the exudates of *Cestrum elegans* Schlecht. A relatively simple profile consisting of quercetin- and kaempferol 3-methyl ethers was earlier found to be characteristic of *Browallia grandiflora*, also belonging to subfamily Cestroideae (Wollenweber and Dörr, 1995). Summarizing the flavonoid aglycone profiles of this subfamily thus far known, the degree of chemodiversity is not very high, with flavonols and their methyl ethers predominating.

Flavonoid aglycones from Solanoideae

The other genera studied here belong to the subfamily Solanoideae, which is larger by far than the previous one. In particular, the genus *Solanum* comprises some 1,200 species. Species delimitation is often problematic, and the infrageneric taxonomy is still controversial, being resolved only for parts of the genus (Hunziker, 2001; Agra, 1999; Nee, 1999). Despite the size of the genus, only some smaller groups or single species have been analyzed for flavonoids thus far, and even less is known about the occurrence of exudate flavonoids. Flavonoid aglycones from *Solanum* spp. are presented in Table III. Most of the literature concerns reports on extracts (for references see Table III). However, the aglycones reported as extract components are also most probably exudate constituents, which is evident from their occurrence on the leaf surfaces of the species now studied. A series of 8-substituted flavones and flavonols was isolated from the exudates of *S. mammosum* L. and their structures were confirmed by MS-data. Tricetin-derivatives were also found. The profile of this species is in good agreement with the trends observed in other taxa of subgen. *Leptostemonum.* By contrast, relatively simple flavonol methyl ethers were found in *S. lyratum* Thunb. of subgen. *Solanum.* Only two further species have been studied thus far, with *S. oblongifolium* being quite divergent (Cueva and Usubillaga, 1988). Earlier, accumulation trends of flavonoid glycosides were found to be useful characters at least for some sections of *Solanum*, excluding section *Leptostemonum* (Steinharter *et al.*, 1986).

Several further genera of subfamily Solanoideae were tested for their exudate flavonoid composition and compared to literature data (see Table IV). Taxa are listed according to their position within the Solanoideae (Hunziker, 2001). For most of the genera, data appear to be rather randomly scattered, making interpretation difficult.

Within the genus *Datura*, exudate aglycone production was confirmed herein for *Datura inoxia* Mill. only. (Table IV). Other aglycones were isolated from hydrolyzed extracts of *D. stramonium* L. (Lakshmi and Krishnamoorthy, 1991), but no free aglycones could be detected in the leaf wash of this species, indicating that these aglycones most probably occur in glycosidic form as tissue constituents. Earlier, glycoside patterns have been reported for five *Datura* spp. (Pate and Averett, 1986), but no chemosystematic conclusions were drawn because large variation was noted.

Data on *Physalis* are also not fully comparable, since exudate flavonoids of *P. alkekengi* L. (leaves and calyces) were analyzed here, whereas whole plants of *P. minima* L. were used for extraction earlier (Ser, 1988). The accumulation of a series of rare myricetin-derivatives both on leaves and the calyces of *P. alkekengi* is remarkable (Table IV). Several other reports concern the accumulation of quercetin- and kaempferol 3-*O*-glycosides in leaves of *P. peruviana* L. (Elliger *et al.*, 1992) and

Table III. Flavonoid aglycones from *Solanum* spp. (Solanoideae-Solaneae).

Solanum	Subgen. *Solanum*			Subgen. *Leptostemonum*																
	lyratum Thunb.	*oblongifolium* Bitter	*sarrachoides* Sendt.	*angustifolium* Mill.	*citrullifolium var. Setigerum Bartlett*	*citrullifolium* A. Braun *var. citrullifolium*	*davisense* Whalen	*heterodoxum* Dunal *var. heterodoxum*	*heterodoxum var. setigeroides* M. D.Whalen	*tenuipes* Bartlett	*grayi* Rose	*pubescens* Willd.	*sisymbriifolium* Lam.	*stramonifolium* Jacq.	*mammosum* L.	*agrarium* Sendt.	*paludosum* Moric.	*jabrense* Agra & M.Nee	*paraibanum* Agra	*rhytidoandrum* Sendt
References		1	2	3	3, 4	3	3	3, 4	3	7, 3		6		7		7	8	7	7	7
Isosakuranetin		x																		
Flavones																				
Apigenin								x		x					x					
Ap-7-Me																	x	x		x
Luteolin										x	x				x					
Lut-3′-Me															x					
Lut-4′-Me										x										
Lut-7,3′-diMe											x									
8-OH-Lut-7,3′-diMe											x									
8-OH-Lut-8-Me															x					
8-OH-Lut- 8,3′-diMe											x									
Tricetin 3′,5′-diMe															x					
Tric-3′,4′,5′-triMe										x										
Flavonols																				
Kaempferol												x				x		x		
Kae-3-Me	x		x										x		x					
Kae-7-Me																	x	x	x	x
Kae-3,7-diMe	x											x					x	x	x	x
Kae-3,4′-diMe	x			x			x			x		x								
Kae-3,7,4′-triMe	x											x								
Herbacetin 3,8-diMe															x					
Quercetin												x								
Que-3-Me	x		x										x				x			
Que-3,7-diMe	x												x							
Que-3,3′-diMe	x											x								
Que-3,4′-diMe				x						x										
Que-3,7,3′-triMe	x											x								
Que-3,7,4′-triMe												x								
Que-3,7,3′,4′-tetraMe	x											x					x	x	x	x
Gossypetin 3,8-diMe															x					
Goss-3,8,3′-triMe															x					
Goss-3,7,3′,4′-tetraMe														x				x	x	x
Goss-3,7,8,4′-tetraMe																	x			
Goss-3,7,8,3′4′tetraMe																	x	x	x	x
Myricetin 3-Me							x													
Myr-3,7,3′-triMe												x	x							
Myr–3,7,3′,5′-tetraMe												x								
8-OH-Myr-3,7,4′-triMe					x	x		x		x										
8-OH-Myr-3,7,8,4′-tetraMe					x			x		x										

No exudate flavonoids detected in the following *Solanum* spp.: *S. aethiopicum* L.; *S. luteum* Mill.; *S. muricatum* Ait.; *S. sodmeum* L.

References: 1, Cueva and Usubillaga (1988) (extract); 2, Schilling (1984) (extract); 3, Whalen (1978) (extract); 4, Whalen and Mabry (1979) (extract); 5, Horie *et al.* (1983); Kumari *et al.* (1984) (extract); 6, Kumari *et al.* (1985) (extract); 7, Silva *et al.* (2004); 8, Silva *et al.* (2002).

Table IV. Flavonoid aglycones from genera of tribes from subfamily Solanoideae (OH, hydroxy; Me, methyl ether; OMe, methoxy).

	Datura inoxia Mill.	*Datura stramonium* L.	*Physalis alkekengi* L.	*Physalis minima* L.	*Chamaesaracha viscosa* (Schrad.) Huntz.	*Chamaesaracha sordida* (Dunal) Gray	*Iochroma australe* Griseb.	*Iochroma warscewiczii* Regel	*Atropa belladonna* L.	*Hyoscyamus albus* L.	*Salpiglossis sinuata* Ruiz & Pav.
References		1		2		3		4			3
Flavanones/Flavanonols											
Liquiritigenin		x									
Naringenin		x									
Pinocembrin					x						
Pinocembrin–7-Me					x						
Flavones											
Chrysin		x			x		x				
5-OH-6,7-diOMe-flavone					x						
5,6,7-triOMe-flavone				x							
5-OMe-6,7-methylene dioxyflavone				x							
Apigenin 7-Me											x
Apigenin 4′-Me					x		x				
Luteolin											x
Lut–3′-Me	x						x				x
Lut-7-Me							x				x
Lut–7,3′-diMe											x
Lut-3′,4′-diMe	x										
Lut-7,3′,4′-triMe	x										
Flavonols											
Galangin					x						
Galangin 7-Me					x						
Kaempferol		x									
Kae-3-Me					x	x	x			x	
Kae-7-Me					x						
Kae-3,7-diMe						x					
Kae-3,4′-diMe					x						
Kae-7,4′-diMe					x						
Quercetin		x	x								
Que-3-Me			x				x		x		x
Que-3′-Me											x
Que-3,3′-diMe			x		x		x	x	x		x
Que-3,7-diMe			x				x				x
Que-7,3′-diMe											x
Que-3,7,3′-triMe			x			x	x	x			x
Que-3,3′,4′-triMe								x			
Que-3,7,3′,4′-tetraMe							x	x			
Myricetin 3,7,3′-triMe			x				x	x			
Myr-3,7,3′,5′-tetraMe											
Myr-7,3′,4′,5′-tetraMe			x				x				
Myr-3,7,3′,4′,5′-pentaMe							x	x			

No exudate flavonoids detected in the following Solanoideae: *Datura meteloides* DC. ex. Dun.; *Datura stramonium* L.; *Hyoscyamus niger* L.; *Iochroma gesnerioides* Miers.; *Nicandra physalodes* (L.) Gaertn.; *Physalis peruviana* L.

References: 1, Lakshmi and Krishnamoorthy (1991) (extract); 2, Ser (1988) (extract); 3, Wollenweber and Dörr (1995); 4, Wollenweber (1990).

of myricetin 3-*O*-neohesperidoside in leaves of *P. angulata* L. (Ismail and Alam, 2001).

Exudate aglycone profiles are different in the two analyzed species of *Chamaesaracha*, with *C. viscosa* (Schrad.) Huntz. affording the larger number of derivatives with somewhat complex structures. A similar diversity is obvious in the *Iochroma* species studied thus far. *Iochroma gesnerioides* (Kunth.) Miers yielded quercetin and kaempferol and a series of sophorosides based upon these aglycones (Alfonso and Kapetanides, 1994), but no free aglycones were detected in the leaf wash. *Atropa belladonna* L. and *Hyoscyamus albus* L. exhibited a rather poor exudate profile, and *H. niger* L. yielded no detectable amounts of exudate flavonoids. Although these plants are of pharmaceutical interest, little is known about the overall flavonoid composition of these taxa, except for an early publication on glycosides of *A. belladonna* (Clair *et al.*, 1976). *Salpiglossis sinuata* Ruiz and Pav., being rather isolated within this subfamily, showed the most commonly observed aglycone profile, consisting of derivatives of luteolin and quercetin (Wollenweber and Dörr, 1995).

Production of the rather rare 5,6,7-trihydoxy flavone-derivatives in *Physalis* and *Chamaesaracha* underlines their relationship as proposed by Hunziker (2001). Different views exist on *Salpiglossis* which is now nested within the Cestroideae (Olmstead, 1999), contrary to its position within Solanoideae (Hunziker, 2001). In this case the flavonoid aglycone composition known thus far is not very suggestive of the taxonomic position.

Flavonol glycosides and trichome differentiation in Solanaceae

A few genera of different subfamilies were found to accumulate flavonol glycosides based upon quercetin and kaempferol as exudate compounds, either in combination with free aglycones or as the sole exudate flavonoids. Species accumulating flavonol glycosides only were *S. lidii* Sunding (kaempferol 3-*O*-glucoside), *Jaltomata edulis* Schltdl. (quercetin 3-*O*-rhamnoglucoside), *P. axillaris* (Lam.) Britton (quercetin 3-*O*-glucoside) and *Nicandra physalodes* (L.) Gaertn. (kaempferol 3-*O*-glucoside; quercetin 3-*O*-glucoside; plus chlorogenic acid). A few other species accumulate glycosides in addition to exudate aglycones: *S. lyratum* (quercetin 3-*O*-glucoside; quercetin 3-*O*-rhamnoglucoside); *S. sisymbrifolium* (kaempferol 3-*O*-glucoside) and *N. plumbaginifolia* (quercetin 3-*O*-rhamnoglucoside).

Several reports exist on the accumulation of flavonol glycosides in the whole plant extract of *Solanum* spp. (Walkowiak et *al.*, 1990; Wietschel and Reznik, 1980a, b; Reznik and Wietschel, 1979), which agree with a general report on the flavonoids of the Solanaceae (Harborne and Swain, 1979). In most cases, flavonol glycosides appear to be predominant, but flavone glycosides and *C*-glycosylflavones have also been reported to occur in species of *Solanum* section *Androceras* (Whalen, 1978). In none of these studies is reference made as to the site of flavonoid accumulation.

Only recently, more attention is focused on flavonoid glycosides being externally deposited on plant surfaces, *e.g.* in species of *Lycopersicon* (Wollenweber, 1990) or *Nothofagus antarctica* and a few other sources (Wollenweber *et al.*, 1997). Correlation between secondary product formation and glandular trichome morphology was established especially for *Nicotiana*, where two different types of glandular trichomes are present. The long type trichomes were found to yield resinous material, whereas the short type trichomes were shown to produce aqueous droplets containing the alkaloid nicotine for example, which is accumulated around the short trichomes on the plant surface. Ultrastructurally, these trichome types are also different. Thus, the head cells of the short type do not have the subcellular structures to synthesize the secreted compounds. Therefore, compounds present in the aqueous exudates are most probably synthesized elsewhere and then translocated to the leaf surface (Meyberg *et al.*, 1991). This has been proven for the alkaloid nicotine, which is transported from roots to leaves (Wagner *et al.*, 2004). It may be speculated that the flavonoid glycosides are rather transported to the plant surface via the short type trichomes, whereas the flavonoid aglycones are most probably produced in the head cells of the long type trichomes.

In *Solanum*, different types of hairs including glandular trichomes are present and may be used for subgeneric classification (Seithe, 1979). In *S. berthaultii* Hawkes, two different types of glandular trichomes were observed: type A secreted a viscious exudate through a tetralobate gland, while type B produced droplets, consisting of sucrose esters and fatty acids being continuously secreted (Sonnino *et al.*, 1999). In *S. paludosum*, glandular trichomes were proven to be the accu-

mulation site of exudate flavonoids, yet without specification of the trichome type (Silva *et al.*, 2002). Recently, histochemical studies indicated different types of products accumulated in three types of glandular trichomes of *Salvia* (see Valant-Vetschera *et al.*, 2003b). These data are suggestive of a differentiated mechanism of secondary compound secretion.

As far as the complexity of exuded flavonoid aglycones is concerned, correlations between the presence of more complex hair structures ("stellate-glandular trichomes") and production of complex flavones in *Solanum* spp. have recently been postulated (Silva *et al.*, 2004). For a better understanding of exudate production of both aglycones and glycosides, the type of glandular trichome morphology should be more thoroughly investigated. This would certainly help in comparing flavonoid profiles that originate from corresponding accumulation sites, and are a strong prerequisite for any chemosystematic study.

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