Flavonoids and Terpenoids from the Resinous Exudates of *Madia* Species (Asteraceae, Helenieae)

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Z. Naturforsch. **58c**, 153–160 (2003); received October 10/November 14, 2002

The resinous material accumulated on aerial parts of *Madia* species is shown to consist mainly of diterpenes, containing a series of flavonoid aglycones. A6- and/or 8-O-substitution is characteristic for many of these flavonoids. Three known rare diterpenes were found and the structure elucidation of a diterpene with a new carbon skeleton, named madiaol, is reported.

Key words: Madia, Flavonoid Aglycones, Diterpenes

Introduction

Madia is an Asteraceae genus (tribus Helenieae-Madiinae Benth.) that comprises 18 species of annual or perennial herbs, growing in the Western United States and in Chile (2 species). Within the subtribe, they are characterized by sophisticated features of their inflorescences (see Bremer, 1994, for further details). Depending on the species, glandular trichomes and resinous excretions are obvious on stems, leaves, and bracts, hence the trivial name tarweed. Little is known so far about the external accumulation of flavonoid aglycones and terpenoids, a phenomenon that is widespread in the family (Wollenweber and Valant-Vetschera, 1996). Bohm and co-workers previously reported the occurrence of flavonoid aglycones in the leaf exudate of *Madia sativa* (Bohm *et al.*, 1992). Wollenweber *et al.* (1997) studied the resinous leaf exudate of *Madia sativa* once more, and also that of *M. elegans*. They found a wide array of flavonoids for the first species, but very few for the latter. In the present study, we analyzed the exudate flavonoids and terpenoids of *M. anomala* Greene, *M. capitata* Nutt., *M. x citrigracilis* Keck, and *M. dissitiflora* Torr. & Gray as well as the terpenoids of *M. capitata* and *M. dissitiflora*.

Material and Methods

Madia anomala (seed: Botanischer Garten Bayreuth), *M. capitata* (seed: Botanischer Garten Halle), *M. citrigracilis* (seed: Botanischer Garten Bayreuth), *M. dissitiflora* (seed: Botanischer Garten Dijon) and *M. elegans* (seed: natural habitat in CA, coll. G. Yatskievych) were cultivated in the Botanischer Garten der TU Darmstadt. Voucher specimen are kept in the herbarium of the Institut fuer Botanik der TU Darmstadt. Aerial parts were collected during the flowering period (June–August) and briefly rinsed with acetone while fresh. The concentrated solutions were defatted (MeOH, – 10 °C; centrifugation) and passed over Sephadex LH-20, eluted with methanol, to separate the flavonoids from the prevailing terpenoids. Flavonoid portions were subjected to column chromatography on silica and/or on polyamide SC-6, eluted with toluene and increasing amounts of methylethyl ketone and methanol. The leaf and stem exudates of *Madia anomala* and *M. citrigracilis* exhibited the same flavonoid patterns and were, therefore, combined and subjected directly to SC on polyamide. Fractions were monitored and comparisons with markers were made by TLC on polyamide DC-11 with the solvents toluene-petrol

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ether 100–140 ° – MeCOEt-MeOH 12:6:2:1, toluene-dioxane-MeOH 8:1:1 v/v/v, and toluene-MeCOEt-MeOH 12:5:3 v/v/v, and on silica with the solvents toluene-MeCOEt 9:1 v/v and toluene-dioxane-HOAc 18:5:1 v/v/v. Chromatograms were viewed under UV (366 nm) before and after spraying with "Naturstoffreagenz A" (1% of diphenyl-boric acid -ethanolamine complex in MeOH).

Atmospheric pressure chemical ionization (APCI) and electrospray mass spectra were recorded by J. F. Stevens at OSU (Corvallis, OR) on a PE Sciex API *III*-plus triple quadrupole instrument (PE Sciex, Thornhill, Ontario, Canada) as described elsewhere (Stevens *et al.*, 1999).

NMR spectra of compound **14** (acerosin) were run in Halle (A. Porzel and J. F.Stevens) on a Varian UNITY instrument at 500 MHz (1H) and 125 MHz (13C) in DMSO-d6 at room temperature. The solvent resonances (δ_H 2.50 and δ_C 39.51) were used as internal shift references. 2-Dimensional experiments (1H-1H COSY, 1H-13C HSQC and HMBC) were carried out using standard Varian pulse sequences.

The terpenoid portions of the five *Madia* species now studied showed the same TLC features in different solvents, thus indicating that the major components were identical. They were, therefore, combined to increase the starting amount. Separation of the crude materials by Sephadex LH-20 (*n*-hexane-CH_2CH_2, 7:2) gave compounds **4** and **5** as major components (*ca.* 3 g each), compounds **2** (7 mg) and **3** (12 mg) as minor constituents. Terpenoids were visualized by spraying silica plates with $MnCl_2$ reagent, followed by heating (Jork *et al.*, 1989).

EI mass spectra of terepenoids were recorded on a TSQ 70 quadruple mass spectrometer (Finnegan) at 70 eV and 200 °C ion source temperature. Exact mass measurements were performed using an AMD Intectra modified MAT 711A instrument with fragments from perfluorotributylamine as reference ions.

NMR spectra were recorded on a Bruker AMX 400 instrument in solvents given in the text. 2-Dimensional spectra were measured by means of standard Bruker puls sequences.

Results and Discussion

Structure elucidation

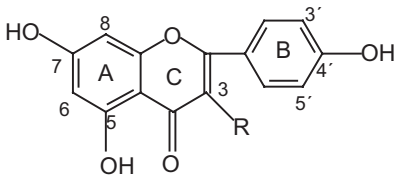
Flavonoids

From the lipophilic exudates accumulated on aereal parts of of four *Madia* species we identified a series of flavonoid aglycones (for structural formulae see Fig. 1). The following compounds were identified by a combination of APCI-MS and co-TLC with authentic markers: Apigenin-4′-O-methyl ether (MH^+ at *m/z* 285), isoscutellarein-8-O-methyl ether (MH^+ at *m/z* 301), isoscutellarein-8,4′-dimethyl ether (MH^+ at *m/z* 315), 8-methoxy-luteolin (MH^+ at *m/z* 317), 5,3′,4′-trihydroxy-6,7,8-trimethoxyflavone (MH^+ at *m/z* 361), 5,7,3′,4′-tetrahydroxy-3,6,8-trimethoxyflavone (MH^+ at *m/z* 377), 5,3′,4′-trihydroxy-3,6,7,8-tetramethoxyflavone (MH^+ at *m/z* 391). The remaining flavonoids (except No **14**) were identified by co-TLC with authentic markers available in E. W.'s lab.

Compound **14** was identified by mass spectrometry and NMR spectroscopy as 5,7,3′-trihydroxy-6,8,4′-trimethoxy flavone, trivially known as acerosin. ^{1}H NMR (500 MHz, DMSO-d6) δ_H 12.78 (s, OH-5), 10.43 and 9.58 (both br s, OH-7 and OH-3′), 7.56 (1H, dd, *J* = 8.4, 2.2 Hz, H-6′), 7.47 (1H, d, *J* = 2.2 Hz, H-2′), 7.11 (1H, d, *J* = 8.6 Hz, H-5′), 6.79 (1H, s, H-3), 3.88 (3H, s, 8-OMe), 3.87 (3H, s, 4′-OMe), 3.77 (3H, s, 6-OMe); ^{13}C (125 MHz, DMSO-d6) δ_C 182.0 (C-4), 163.1 (C-2), 151.0 (C-4′), 150.7 (C-9), 148.2 (C-5), 146.6 (C-3′), 145.2 (C-7), 131.4 (C-6), 127.8 (C-8), 122.9 (C-1′), 118.5 (C-6′), 112.7 (C-2′), 112.1 (C-5′), 102.89 and 102.85 (C-3 and C-10), 61.3, 60.1 and 55.7 (OMe-6, OMe-8 and OMe-4′). The position of the methoxy groups was determined by ^{1}H-^{13}C HMBC spectroscopy.

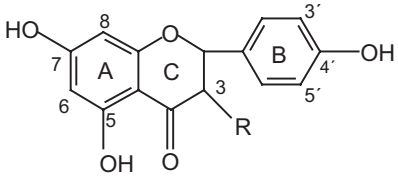
Terpenoids

Fractionation, by silica gel column chromatography, of the combined terpenoid portions yielded the new diterpene **2**, in addition to three known diterpenes, **3–5** (For structures see Fig. 2). Compound **2** was isolated as a yellow material, α[D] – 10.54 (*c* = 0.0023, CH_2Cl_2). IR cm^{-1}: 3400, 1610,895. HMBC correlations: H-18,19 correlated with C-2, C-4, C-5, H-20 correlated with C-1, C-5, C-10, exomethylene protons correlated with C-9, C-11, H-3 correlated with C-19, H-1 correlated



Flavones: R = H
5,7,5′-triOH: Apigenin
5,7,8,4′-tetraOH: Isoscutellarein
5,7,3′,4′-tetraOH: Luteolin
5,6,7,3′,4′-pentaOH: 6-Hydroxyluteolin
5,7,8,3′,4′-tetraOH: 8-hydroxyluteolin (Hypolaetin)

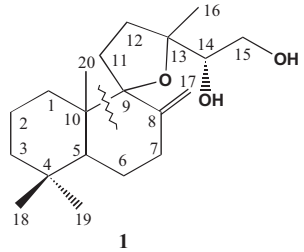
Flavonols: R = OH
3,5,7,4′-tetraOH: Kaemperol
3,5,7,3′,4′pentaOH: Quercetin
3,5,6,7,3′,4′-hexaOH: Quercetagetin
3,5,7,8,3′,4′-hexaOH: Gossypetin



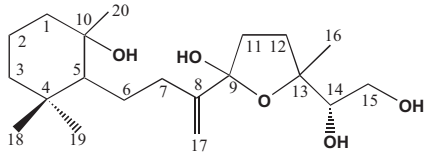
Flavonones: R = H
5,7,4′-triOH: Naringenin
5,7,3′,4′-etraOH: Eriodictyol

Flavanonols: R = OH
3,5,7,4′-tetraOH: Aromadendrin
3,5,7,3′,4′-pentaOH: Taxifolin

Fig. 1. Flavonoid stuctures.



1



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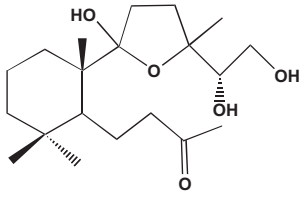

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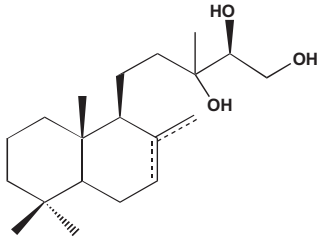

4: $\Delta^{8,17}$
5: Δ^{7}

Fig. 2. Diterpene structures **1**–**5**. **1** = proposed precursor of **2**, **2** = madiaol, **3** = blepharizone, **4** = 13,14,15-trihydroxylabd-8,17-ene, **5** = 13,14,15-trihydroxylabd-7-ene.

with C-2, H-6 correlated with C-7, H-12 correlated with C-11. EIMS *m/z* (%): 338 $(M-H_2O)^{+\cdot}$. HR-EIMS *m/z*: Calcd for $C_{20}H_{34}O_4$ ($M-H_2O)^{+\cdot}$: 338.2457. Found: 338.247. The ^1H and ^{13}C chemical shifts of compound **2** (see Tables I and II), were determined by a series of 1D and 2D NMR experiments. The ^1H and ^{13}C NMR of **2**, in $CDCl_3$, was in part identical to compound **3** in the presence of H-14 at δ 3.75 (*J* = 4, 10.5 Hz), H-15 at δ 3.99 (*J* = 4, 10.5 Hz) and 3.46 (*J* = 10.5, 10.5 Hz) and their carbons at δ 68.7 (d, C-14) and 64.9 (t, C-15). Therefore, the furan ring and its substitution at C-13 were the same in both compounds. The difference in the chemical shift of C-9, at δ 107.5 in compound **2**, compared to 112.3 in compound **3**, suggested a different substitution at C-10. The overlapping of the seven methylene protons in $CDCl_3$ was solved by the measurements of ^1H NMR in pyridine-d_5. The sequence and connectivities from C-1 to C-8 were established by HMQC and HMBC experiments.

Table I. ^{1}H-NMR spectral data of compounds **2**–**5** [$CDCl_3$, 400 MHz, TMS as internal standard].

protons	2		3	4	5
	in $CDCl_3$	In C_5D_5N			
H-1	m, 1.7	m, 1.67 m, 1.92	m, 1.28		
H-2	m, 1.2–1.6	m, 1.25	m, 1.28		
H-3	m, 1.2–1.6	m, 1.50	m, 1.04 m, 1.28		
H-5	m, 1.2–1.6	m, 1.50	t, 1.52, *J* = 3.4	dd, 1.11, *J* = 2.5, 12.5	
H-6	m, 1.2–1.6	m, 2.26	m, 2.04		
H-7	m, 1.2–1.6 m, 2.11	m, 1.57 m, 2.46	ddd, 2.30, *J* = 5, 12.5, 16.1 ddd, 2.83, *J* = 3.8, 12.5, 16.1	ddd, 1.95, *J* = 2.5, 12.5, 12.5 ddd, 2.45, *J* = 4.5, 12.5, 12.5	
H-11	m, 2.10 m, 2.21	ddd, 2.57, *J* = 4, 11.3 ddd, 2.91, *J* = 4, 11.3	m, 1.70 m, 2.04		
H-12	m, 1.2–1.6	m, 1.72 m, 2.10	m, 1.95 m, 1.28		
H-14	dd, 3.75, *J* = 4, 10.5	dd, 4.0, *J* = 4, 10.5	dd, 3.62, *J* = 6.1, 9.4	br. t, 3.50	br. t, 3.53
H-15	t, 3.46, *J* = 10.38 dd, 3.99, *J* = 5.8, 11	dd, 3.81, *J* = 10.5, 10.5 dd, 4.24, *J* = 4, 10.5	t, 3.34, *J* = 10.7 dd, 3.93, *J* = 6.1, 10.7	br. d, 3.76	br. d, 3.77
H-16	s, 1.41	s, 1.59	s, 1.28	s, 1.17	s, 1.18
H-17	d, 4.97, *J* = 1.2 d, 5.29, *J* = 1.2	br. s, 5.20 br. s, 5.67	s, 2.12	br. s, 4.83 br. s, 4.52	br. s, 1.68
H-18	s, 0.78	s, 0.85	s, 0.87	s, 0.85	s, 0.86
H-19	s, 0.93	s, 0.98	s, 0.85	s, 0.79	s, 0.84
H-20	s, 1.17	s, 1.36	s, 0.93	s, 0.67	s, 0.75

Table II. ^{13}C-NMR spectral data of compounds **2**–**4** [$CDCl_3$, 400 MHz, TMS as internal standard].

carbons	2	3	4
C-1	42.4	35.0	39.1
C-2	41.5	18.4	19.4
C-3	20.4	41.6	42.1
C-4	35.4	35.4	33.6
C-5	56.9	47.1	55.5
C-6	34.9	22.1	24.2
C-7	30.0	47.4	38.3
C-8	148.3	210.8	148.6
C-9	107.5	112.3	57.3
C-10	74.3	43.4	39.8
C-11	35.0	31.2	17.2
C-12	26.1	28.1	38.4
C-13	84.0	83.1	74.7
C-14	68.7	69.0	75.4
C-15	64.9	64.7	63.3
C-16	21.2	22.0	22.1
C-17	111.9	29.4	106.4
C-18	22.4	33.1	33.6
C-19	32.7	22.5	21.7
C-20	23.6	15.7	14.5

From ^{1}H-^{1}H COSY and HMBC, pyridine-d_5, H-15$_a$ at δ 4.24 showed a correlation with C-13 at δ 84.0, H-16 at δ 1.59 correlated with C-14 at δ 68.7. The exomethylene protons at δ 5.67 and 5.20 showed a correlation with C-9 at δ 107.5. Additionally, the two exomethylene protons correlated with a carbon signal at δ 30.0 (t), assigned for C-7. These data, together with the HMBC correlation between H-20 and C-1, H-18, H-19 and C-4, unambiguously established the molecular framework of compound **2**. The proposed structure of compound **2** was supported by HREI of the $[M\text{-}H_2O]^{+\cdot}$ at *m/z* 338.2474, $C_{20}H_{34}O_4$ (Calcd. 338.2457), and the interesting fragmentation pattern. In Fig. 3, the electron impact induced formation of the main fragments is summarized.. Most likely, compound **2** was formed by biooxidation of the C9-C10 bond of compound **1**. To our knowledge, compound **2** is a diterpene with a new carbon skeleton, to which we assign the trivial name madiaol.

Compound **3** was identical with blepharizone (Jolad *et al.*, 1990) The structure was established by NMR measurements. The complete ^{1}H and ^{13}C NMR assignments were achieved with the

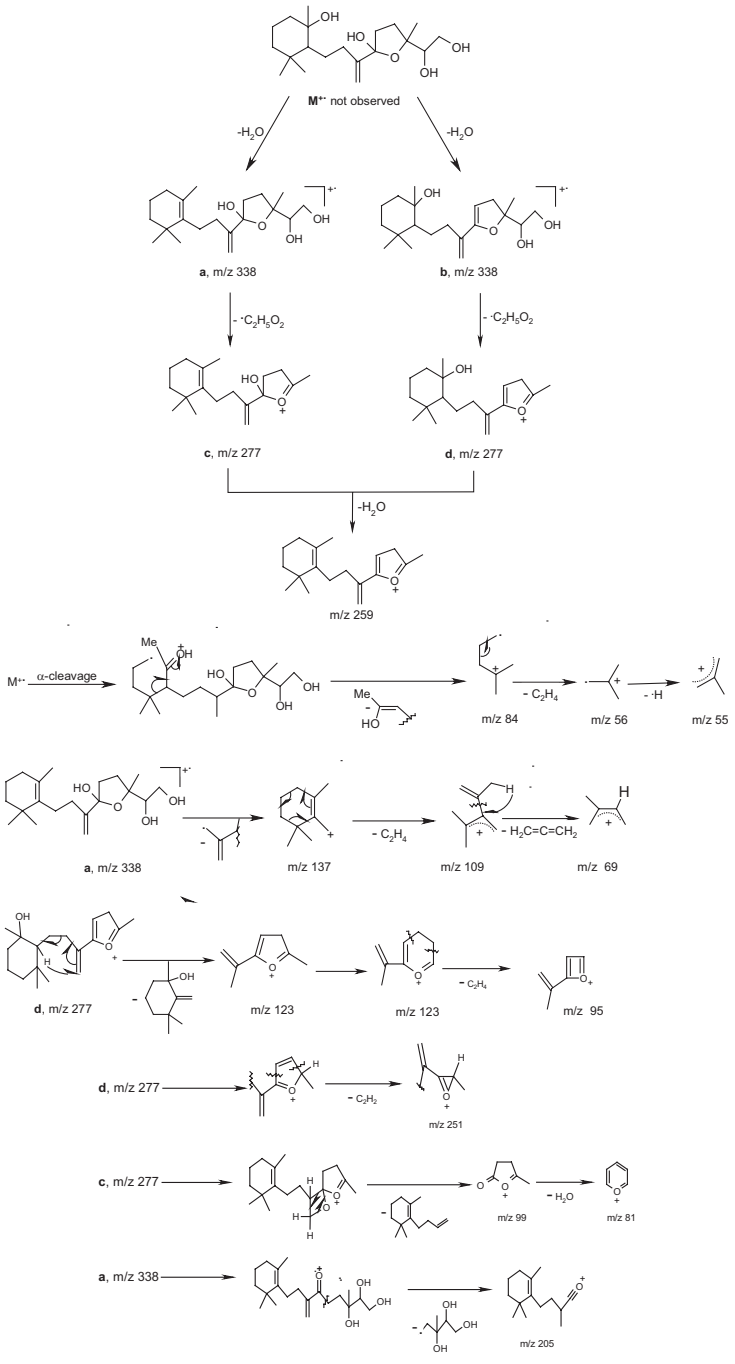

Fig. 3. Fragmentation pattern of compound **2** (madiaol); for the fragment structures **a**, **c** and **d** see upper part of the fragmentation scheme.

help of 1H-1H COSY, HMQC and HMBC. Compounds **4** (13,14,15-trihydroxylabd-8,17-ene) and **5** (13,14,15-trihydroxylabd-7-ene) were previously reported from *Madia sativa* (Bohlmann *et al.*, 1982). The unreported ^{13}C NMR of compound **4** is given in Table II.

Flavonoid distribution

Table III, in which literature data for two further species are included, lists 36 flavonoids in total. They comprise 15 flavones, 14 flavonols, and 7 flavanones and flavanonols, respectively. Isoscutellarein-8,4′-dimethyl ether (bucegin, (**4**)), 8-methoxy luteolin (onopordin, (**12**)) and 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone are rare flavones. The two latter were so far only found in Asteraceae, whereas the rare 5,7,3′-trihydroxy-6,8,4′-tetramethoxyflavone (acerosin, compd. **14**) was reported from three Asteraceae and three members of other families. Only one out of 43 reports on the occurrence of quercetagetin-3,6-dimethyl ether (axillarin) does NOT concern Asteraceae. Gossypetin-3,8-dimethyl ether, gossypetin-3,7,8-trimethyl ether, and the 3,6,8-trimethyl, 3,6,7,8-tetramethyl and 3,6,7,8,3′-pentamethyl ethers of "6,8-dihyroxyquercetin" also are relatively rare flavonols. Among 47 reports in total, there are only seven (in 4 families) outside the Asteraceae.

As has been mentioned in the Introduction, only two species of *Madia* have been studied for their flavonoid aglycones previously. Bohm *et al.* (1992) reported two flavonols (kaempferol-7-Me and quercetagetin-3,6,7-triMe), four flavanones (naringenin and the 7-, 7,3′- and 7,3′,4′-methyl ether of eriodictyol) and a dihydroflavonol (aromadendrin-7-Me) from *M. sativa.* A rather different and more complex flavonoid pattern was found for this species by Wollenweber *et al.* (1997), see Table III. The latter authors suggested the existence of chemical races, therefore – not surprising for a cultivated species (seeds of *M. sativa* yield a sweet, edible oil). Literature data for *M. sativa* as well as those for *M. elegans* (Wollenweber *et al.*, 1997) have been included in Table III. This table thus surveys the flavonoid profiles of six out of 18 recognized species in the genus *Madia.* There seems to be a tendency that *M. anomala*, *M. capitata*, *M. citrigracilis* and *M. dissitiflora* on the one hand and *M. elegans* and *M. sativa* on the other hand group together. *M. anomala and M. citrigracilis* even show an identical flavonoid profile, whereas *M. capitata* exhibits some specific compounds. As Bohm and Stuessy (2001) pointed out, only few unique features are evident in the flavonoid profiles among members of the subtribe Madiinae (tarweeds). When they prepared their table on distribution of flavonoid classes and structural features in Helenieae, flavonoid data of only one species were availabale, so they noted a maximum of 3 methoxy groups for the genus *Madia.* Our present results show that the "highest level of methylation" in the genus must now be corrected to 5, a number that has been observed within the Helenieae only in the genus *Bahia* so far (Zdero *et al.*, 1990).

Acknowledgements

This work was supported by the Egyptian-European Cooperation project (scholarship to Abou El-Hamd H.) and Deutsche Forschungsgemeinschaft (visiting Professorship to Prof. Ahmed A. A. at University of Tübingen; financial support to E. W.). We would like to thank the members of the NMR and mass spectrometry laboratories at the University of Tübingen (P. I. Nguyen, B. Maier, H. Bartholomä, Dr. R. Müller) and the Leibniz Institute for Plant Biochemistry, Halle/Saale (Dr. J. F. Stevens and Dr. A. Porzel) for their expert help in obtaining the spectral data. Thanks are also due to Mr Helmut Groh and his colleagues at the Botanischer Garten der TU Darmstadt who cultivated the plant material and to Mrs Christa Zdero, Berlin, for help with some literature search.

Table III. Distribution of flavonoid aglycones in 6 species of *Madia*.

No.	Flavonoid	M. anomala	M. capitata	M. citrigrac.	M. dissitifl.	M. elegans[a]	M. sativa[b]	M. sativa[a]
	Flavones							
1	Apigenin		X					
2	4′-methyl ether (acacetin)	X		X				
	Isoscutellarein							
3	8-methyl ether	X	X	X				
4	8,4′-dimethylether (bucegin)	X	X	X				X
5	Luteolin	X	X	X	X	X		X
6	3′-methyl ether (chrysoeriol)							X
7	7,3′-dimethyl ether (velutin)							X
8	5,7,4′-Trihydroxy-6,8-dimethoxy flavone (dimethoxysudachitin)		X					
9	5,7-dihydroxy-6,8,4′-trimethoxy flavone (nevadensin)		X					
	6-Hydroxyluteolin							
10	6-methyl ether (nepetin)							X
11	6,7-dimethyl ether (cirsiliol)							X
	8-Hydroxyluteolin (hypolaetin)							
12	8-methyl ether (onopordin)	X	X	X	X			
13	5,3′,4′-Trihydroxy-6,7,8-trimethoxy flavone (sideritiflavone)	X		X	X			
14	5,7,3′-Trihydroxy-6,8,4′-trimethoxy flavone (acerosin)		X					
15	5,4′-dihydroxy-6,7,8,3′-tetramethoxy flavone				X			
	Flavonols							
	Kaempferol							
16	7-methyl ether (rhamnocitrin)					X	X	
17	7,4′-dimethyl ether					X		
18	Quercetin		X		X			X
19	3-methyl ether	X	X	X	X			X
20	7-methyl ether (rhamnetin)					X		
21	7,3′-dimethyl ether (rhamnazin)					X		
	Quercetagetin							
22	3,6-dimethyl ether (axillarin)	X		X	X		X	
23	3,7-diMe (tomentin)							X
24	3,6,7-triMe (chrysosplenol-D)						X	X
	Gossypetin							
25	3,8-dimethyl ether	X		X	X			X
26	3,7,8-trimethyl ether	X			(X)			
27	5,7,3′,4′-tetrahydroxy-3,6,8-trimethoxy flavone	X		X	X			
28	5,3′,4′-trihydroxy-3,6,7,8-tetramethoxy flavone	X		X	X			
29	5,4′-dihydroxy-3,6,7,8,3′-pentamethoxy flavone				X			
	Flavanones							
30	Naringenin						X	
31	Eriodictyol					X		X
32	7-methyl ether						X	X
33	7,3′-dimethyl ether						X	
34	7,3′,4′-trimethyl ether						X	
	Dihydroflavonols							
	Aromadendrin							
35	7-methyl ether						X	
	Taxifolin							
36	7-methyl ether (padmatin)					X		

[a] Wollenweber *et al.*, 1997; [b] Bohm *et al.*, 1992.

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