Phytochemistry, Vol. 26, No. 11, pp. 3059–3064, 1987.
Printed in Great Britain.

0031–9422/87 \$3.00 + 0.00

FLAVONOIDS OF *ARTEMISIA JUDAICA*, *A. MONOSPERMA* AND *A. HERBA-ALBA*

NABIEL A. M. SALEH, SABRY I. EL-NEGOUMY and MAMDOUH M. ABOU-ZAID

National Research Centre, El-Dokki, Cairo, Egypt

(*Received* 21 *January* 1987)

Key Word Index—*Artemisia judaica*; *A. monosperma*; *A. herba-alba*; Compositae; flavone and flavonol glycosides; flavone *C*-glycosides; 6-methoxyflavones.

Abstract—Seventeen flavonoid glycosides were isolated and identified from *Artemisia judaica*: the 7-glucoside, 7-glucuronide, 4′-glucoside, 7-gentiobioside, 7-diglucuronide, 7-rutinoside of apigenin and chrysoeriol; the 7,3′-diglucoside of chrysoeriol; the 3′-glucoside, 4′-glucoside, 7-gentiobioside, 7,3′-diglucoside of luteolin; as well as the *C*-glycosides vicenin-2, schaftoside, isoschaftoside, neoschaftoside and neoisoschaftoside. From *A. judaica*, *A. monosperma* and *A. herba-alba* 12 aglycones were isolated and identified as casticin, apigenin, acacetin, hispidulin, pectolinarigenin, cirsimaritin, luteolin, chrysoeriol, jaceosidin, eupatilin, cirsilineol and 5,7,3′-trihydroxy-4′,5′-trimethoxyflavone.

INTRODUCTION

Artemisia L. belongs to the tribe Anthemideae of the Compositae, In continuation of the investigation of the genus *Artemisia* [1], we report the characterisation of the flavonoids of three local species. In a previous study [1] a number of flavonoid glycosides of *Artemisia monosperma* Del. and *A. herba-alba* Asso. were identified, but the methylated flavonoids of both plants were not identified. The present study is a complete investigation of the flavonoids of *A. judaica* L., along with the methylated flavonoids of *A. monosperma* and *A. herba-alba*.

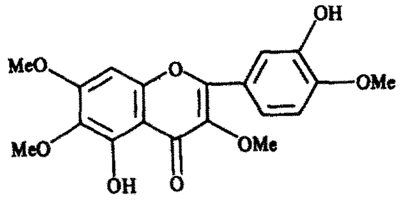
RESULTS AND DISCUSSION

The leaves and stems of *Artemisia judaica*, *A. monosperma* and *A. herba-alba* were extracted with 70% ethanol and their flavonoids isolated and identified. In the present study, a total of 22 flavonoid *O*- and *C*-glycosides were identified in *A. judaica* (Table 1), while 13 glycosides had previously been identified in both *A. monosperma* and *A. herba-alba* [1]. In addition, 10 aglycones were identified in *A. judaica*, seven in *A. monosperma* and eight in *A. herba-alba*. The distribution of the flavonoids in the three species is outlined in Table 1.

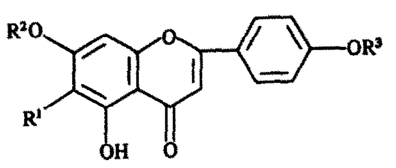
In the present study, a total of 12 aglycones were isolated and identified in the three *Artemisia* species. The four simple flavones apigenin, acacetin, luteolin and chrysoeriol were identified through demethylation (acacetin → apigenin; chrysoeriol → luteolin); co-chromatography with authentic samples and UV spectral data. The identity of acacetin was further confirmed by mass spectroscopy [1]. Simple flavones have been identified in other *Artemisia* species. Thus apigenin and chrysoeriol were detected in *A. frigida* [2], as was luteolin [2], which was also isolated from *A. tridentata* [3]. Acacetin was isolated from *A. pygmaea* [4].

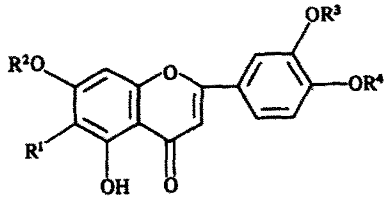
Only one 6-methoxyflavonol, casticin (5,3′-dihydroxy-3,6,7,4′-tetramethoxyflavone) **1** was isolated and identified in *A. judaica* (Table 1). Demethylation gave rise to quercetagetin. The mass spectrum exhibited a molecular ion peak at m/z 374. The fragments corresponding to [M − Me] and [M − Me − CO] were characteristic for 6-methoxyl groups [5, 6]. Other fragments indicated the presence of two methoxyl groups in ring A and one in ring B (Table 2). The UV indicated a free 5 hydroxyl and a substituted 3 hydroxyl group ($AlCl_3$–HCl complex), position 7 was substituted (no shift of band II with NaOAc, absence of a 320–330 band with NaOMe), and position 4′ was also substituted as the intensity of peak I with NaOMe was far less than that of the methanol spectrum (Table 3). Casticin (**1**) co-chromatographed with an authentic sample (see Table 1 for R_f values). The presence of patuletin (3,5,7,3′,4′-pentahydroxy-6-methoxyflavone) and its methylated derivatives in *Artemisia* species is not uncommon. Thus it has been detected in *A. absinthium* and *A. dracunculus* [7], and in our previous studies on *A. monosperma* and *A. herba-alba* [1]. The methylated derivatives of patuletin are also common. Axillarin (5,7,3′,4′-tetrahydroxy-3,6-dimethoxyflavone) has been isolated from *A. taurica* [8], *A. incanescens* [9] and *A. ludoviciana* [10]. 3,5,3′,4′-Tetrahydroxy-6,7-dimethoxyflavone was identified in *A. scoparia* (11), while the highly methylated derivatives 3,5-dihydroxy-6,7,3′,4′-tetramethoxyflavone and 5,7-dihydroxy-3,6,3′,4′-tetramethoxyflavone were isolated from *A. annua* (12) and *A. ludoviciana* (10), respectively. Finally, 5,3′-dihydroxy-3,6,7,4′-tetramethoxyflavone (casticin) has been identified in *A. annua* (13).

Compounds **2**, **3** and **4** on demethylation gave rise to 6-hydroxyapigenin which co-chromatographed with an authentic sample. All three compounds exhibited fragmentation patterns characteristic of 6-methoxyflavones (5,6) (see Table 2). The UV data were in agreement with the presence of a free 4′-hydroxyl group in compounds **2** and **4** as shown by the strong increase in band I with NaOMe, while **3** showed a diminished peak confirming a substituted 4′-hydroxyl group. A careful examination of



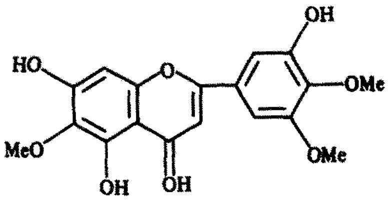
1 Casticin





		R^1	R^2	R^3
2	Hispidulin	OMe	H	H
3	Pectolinarigenin	OMe	H	Me
4	Cirsimaritin	OMe	Me	H

		R^1	R^2	R^3	R^4
5	Jaceosidin	OMe	H	Me	H
6	Eupatilin	OMe	H	Me	Me
7	Cirsilineol	OMe	Me	Me	H



8

Table 1. The distribution of flavonoids isolated from *Artemisia judaica*, *A. monosperma* and *A. herba-alba*

Compound	Presence and relative quantity in*			R_f (X100)†			
	A. judaica	*A. monosperma*	*A. herba-alba*	BAW	H_2O	HOAc	PhOH
Quercetin 3-glucoside	—	+	+	47	12	45	49
Quercetin 3-rutinoside	—	++	+	32	30	60	42
Quercetin 5-glucoside	—	++	—	20	1	9	32
Isorhamnetin 5-glucoside	—	++	—	27	2	12	72
Patuletin 3-glucoside	—	+	+	40	13	46	60
Patuletin 3-rutinoside	—	+++	+++	26	36	62	54
Apigenin 7-glucoside	+	—	—	56	4	23	83
Apigenin 7-glucuronide	++	—	—	48	9	13	32
Apigenin 4′-glucoside	+	—	—	53	3	23	88
Apigenin 7-gentiobioside	+	—	—	40	8	37	75
Apigenin 7-diglucuronide	++	—	—	26	12	34	21
Apigenin 7-rutinoside	+	—	—	41	9	39	79
Acacetin 7-glucoside	—	+	—	35	11	44	81
Acacetin 7-rutinoside	—	+	—	17	54	79	73
Luteolin 3′-glucoside	+	—	—	48	2	11	63
Luteolin 4′-glucoside	+	—	—	54	3	20	62
Luteolin 7-gentiobioside	+	—	—	25	3	19	46
Luteolin 7,3′-diglucoside	+	—	—	30	13	25	55
Chrysoeriol 7-glucoside	++	—	—	43	2	15	87
Chrysoeriol 7-glucuronide	+++	—	—	24	4	14	46
Chrysoeriol 4′-glucoside	++	—	—	55	4	28	86
Chrysoeriol 7-gentiobioside	+	—	—	34	5	16	39
Chrysoeriol 7-diglucuronide	++	—	—	14	16	27	19

Table 1. *continued*

Compound	Presence and relative quantity in*			R_f (X100)†			
	A. judaica	*A. monosperma*	*A. herba-alba*	BAW	H_2O	HOAc	PhOH
Chrysoeriol 7-rutinoside	+	—	—	33	5	30	70
Chrysoeriol 7,4′-diglucoside	—	—		17	24	45	33
Isovitexin	—	—	+	50	18	56	79
Vicenin-2	+	+	tr	31	21	53	61
Lucenin-2	+	+	—	8	15	46	33
Schaftoside	+	—	+	34	20	51	73
Isoschaftoside	+	—	+	29	15	40	71
Neoschaftoside	+	—	—	38	19	52	74
Neoisoschaftoside	+	—	—	30	6	27	71
				Polyamide‡		Silica gel‡	
				TMM	BPMM	CAF	BPF
5,3′-Dihydroxy-3,6,7,4′-tetramethoxyflavone (casticin)	+++	—	—	83	45	92	69
5,7,4′-trihydroxyflavone (apigenin)	+	+	+	8	1	63	48
5,7-Dihydroxy-4′-methoxyflavone (acacetin)	tr	tr	tr	56	13	85	70
5,7,4′-Trihydroxy-6-methoxyflavone (hispidulin)	+	+	+	31	4	78	51
5,7-Dihydroxy-6,4′-dimethoxyflavone (pectolinarigenin)	+	—	—	70	29	91	57
5,4′-Dihydroxy-6,7-dimethoxyflavone (cirsimaritin)	++	++	++	65	17	85	56
5,7,3′,4′-Tetrahydroxyflavone (luteolin)	+	+	+	6	1	44	19
5,7,4′-Trihydroxy-3′-methoxyflavone (chrysoeriol)	+	—	—	27	2	67	45
5,7,4′-Trihydroxy-6,3′-dimethoxyflavone (jaceosidin)	—	+	+	47	6	84	54
5,7-Dihydroxy-6,3′,4′-trimethoxyflavone (eupatilin)	+	—	—	75	30	91	65
5,4′-Dihydroxy-6,7,3′-trimethoxyflavone (cirsilineol)	++	++	++	76	26	88	60
5,4,3′-trihydroxy-6,4′,5′-trimethoxy-flavone	—	—	+	51	7	77	56

*+++ = major, ++ = strong, + = weak, tr = trace, — = absent.

†BAW, *n*-butanol–acetic acid–water (4:1:5); HOAc, 15% acetic acid; PhoH, phenol–Water (4:1).

‡TMM, toluene–methylethyl ketone–methanol (12:5:3): BFMM, benzene–petrol (60–80) methylethyl ketone–methanol (60:60:7:7); CAF, chloroform–acetone–formic acid (9:2:1); in BPF, benzene–pyridine–formic acid (36:9:5).

the NaOAc and NaOMe spectra revealed a free 7-hydroxyl group in **2** and **3**. Compound **4** co-chromatographed with an authentic sample cirsimaritin. Hispidulin **2** was reported to be present in *A. frigida* (2) and *A. compestris* (14), while cirsimaritin is more common being detected in *A. scoparia* (11), *A. mesatlantica* (15) and *A. capillaris*(16). Pectolinarigenin **3** has been reported from *Brickellia* species (17, 18), also in the Compositae but the present study is its first report in *Artemisia* species.

Compounds **5**, **6** and **7** on demethylation all gave the same product, the R_f values of which corresponded to 6-hydroxyluteolin. All three compounds exhibited fragmentation patterns characteristic of 6-methoxyflavones (see Table 2). The UV data in the presence of NaOMe indicated a free 4′-hydroxyl group for **5** and **7** and a substituted group in the case of **6**. The small peak at 335 with NaOMe indicated a free 7-hydroxyl group in **5**. The free 7-hydroxyl group in **6** was indicated by the similar spectra of both NaOMe and NaOAc complexes. This was also true of compound **3**, and is indicative of a 7-hydroxyl-4′-methoxyl grouping (19). Compounds **5**, **6** and **7** co-chromatographed with authentic samples of jaceosidin, eupatilin and cirsilineol, respectively. Eupafolin (6-methoxyluteolin) and its methylated derivatives are frequent constituents of *Artemisia* species [3, 20]. Jaceosidin (**5**) was reported in *A. arctican* [21] and *A. ludoviciana* [10]. Eupatilin (**6**) was identified in *A. frigida* [2] and *A. ludoviciana* [10] while the more common cirsilineol [7] was detected in *A. herba-alba* [22], *A. mesatlantica* [15], *A. monosperma* [23] and *A. capillaris* [16].

Flavone **8** exhibited a molecular ion at m/z 360 with a strong fragment at m/z 345 characteristic of 6-methoxyflavones. Other fragments suggested the presence of two hydroxyl and one methoxyl group in ring A, and one

Table 2. Mass spectral data for the methylated flavonoids isolated

Compound	M+	$[M-H]^+$	$[M-Me]^+$	$[M-18]^+$	$[M-CO]^+$	$[M-HCO]^+$
1. 5,3′-dihydroxy-3,6,7,4′-tetramethoxyflavone	374 (100)	373 (30)	359 (70)	356 (31)	346 (6)	345 (11)
Acacetin 5,7-dihydroxy-4′-methoxyflavone	284 (100)	283 (10)	— —	— —	256 (9)	— —
2. 5,7,4′-trihydroxy-6-methoxyflavone	300 (100)	299 (9)	285 (69)	282 (38)	272 (9)	271 (12)
3. 5,7-dihydroxy-6,4′-dimethoxyflavone	314 (100)	313 (10)	299 (73)	296 (41)	286 (10)	285 (43)
4. 5,4′-dihydroxy-6,7-dimethoxyflavone	314 (100)	313 (22)	299 (98)	296 (3)	286 (4)	285 (23)
5. 5,7,4′-trihydroxy-6,3′-dimethoxyflavone	330 (100)	329 (1)	315 (74)	312 (55)	302 (1)	301 (7)
6. 5,7-dihydroxy-6,3′,4′-trimethoxyflavone	334 (100)	343 (8)	329 (68)	326 (44)	316 (3)	315 (9)
7. 5,4′-dihydroxy-6,7,3′-trimethoxyflavone	344 (100)	343 (12)	329 (67)	326 (37)	316 (2)	315 (13)
8. 5,7,3′-trihydroxy-6,4′,5′-trimethoxyflavone	360 (100)	— —	345 (74)	342 (62)	332 (1)	331 (7)

Table 3. UV spectral data of methylated flavonoids isolated from *Artemisia judaica*, *A. monosperma* and *A. herba-alba*

Compound	MeOH	NaOMe	$AlCl_3$	$AlCl_3$ + HCl	NaOAc	NaOAc + H_3BO_3
1. 5,3′-dihydroxy-3,6,7,4′-tetramethoxyflavone	254 sh	274	263	261	274	254 sh
	272	312 sh	280 sh	283	313	272
	345	374	300 sh	297 sh	371	347
			372	362		
			410 sh	400 sh		
2. 5,7,4′-trihydroxy-6-methoxyflavone	273	275	263 sh	260 sh	274	254
	335	327	279 sh	280 sh	297 sh	337
		393	303	300 sh	308 sh	
			360	352	370	
			390 sh	390 sh		
3. 5,7-dihydroxy-6,4′-dimethoxyflavone	275	275	261	260	257	276
	330	295 sh	277 sh	280 sh	296 sh	333
		307 sh	302	300	308 sh	
		367	355	349	365	
4. 5,4′-dihydroxy-6,7-dimethoxyflavone	285	287	263 sh	262 sh	278	280
	332	370	285 sh	285 sh	335	333
			302	300	388 sh	
			364	354		
5. 5,7,4′-trihydroxy-6,3′-dimethoxyflavone	252 sh	262	259	257	274	274
	273	277 sh	280	283 sh	320	345
	343	334	298	295	374	
		405	372	362		
6. 5,7-dihydroxy 6,3′,4′-trimethoxyflavone	275	275	258	255	276	275
	339	310	285	290	315	340
		371	295 sh	358	365	
			367			
7. 5,4′-dihydroxy-6,7,3′-trimethoxyflavone	253 sh	273	260	258	273	253 sh
	275	305 sh	282	288	347	275
	342	386	297 sh	362	405 sh	342
			373			
8. 5,7,3′-trihydroxy-6,4′,5′-trimethoxyflavone	274	268 sh	280	282 sh	275	275
	332	274	300	298	305 sh	333
		305	358	348	365	
		372				

from *Artemisia judaica*, *A. monosperma and A. herba-alba*

$[M-CoMe]^+$	$[A_1-Me]^+$	$[A_1-MeCo]^+$	$[A_1-MeCo-Co]^+$	$[B_1]^+$	$[B_2]^+$
331	—	153	—	148	151
(40)	—	(9)	—	(9)	(6)
241	152	124	—	132	135
(11)	(7)	(20)	—	(12)	(9)
257	167	139	111	118	121
(48)	(16)	(15)	(2)	(12)	(7)
271	167	139	111	132	135
(43)	(14)	(13)	(2)	(8)	(7)
271	181	153	125	118	121
(29)	(20)	(41)	(5)	(11)	(9)
387	167	139	111	148	151
(59)	(20)	(24)	(1)	(7)	(6)
301	167	139	111	162	165
(38)	(11)	(12)	(1)	(5)	(4)
301	181	153	125	148	151
(33)	(5)	(10)	(2)	(10)	(2)
317	167	139	111	178	181
(49)	(13)	(15)	(1)	(2)	(3)

hydroxyl and two methoxyl groups in ring B (Table 2). The UV data of **8** was identical to that reported in the literature for 5,7,3′-trihydroxy-6,4′,5′-trimethoxyflavone, which is quite different from its isomer 5,7,4′-trihydroxy-6,3′,5′-trimethoxyflavone [24]. Furthermore, it co-chromatographed with an authentic sample. 5,7,3′-Trihydroxy-6,4′,5′-trimethoxyflavone has been reported to be present in *A. frigida* [24] and *A. ludoviciana* [10].

Little has been reported on *C*-glycosides of *Artemisia*, with only isovitexin, vicenin-2 and an isomer of the latter being isolated from *A. transiliensis* [25]. Recently the *C*-glycosides of *A. monosperma* and *A. herba-alba* were identified as isovitexin, vicenin-2 (6,8-di-*C*-glucosyl-apigenin), lucenin-2 (6,8-di-*C*-glucosylluteolin), schaftoside (6-*C*-glucosyl-8-*C*-α-arabinosylapigenin) and isoschaftoside (6-*C*-α-arabinosyl-8-*C*-glucosylapigenin) [1]. In the present study, the *C*-glycosides of *A. judaica* were identified as vicenin-2, schaftoside, isoschaftoside, neoschaftoside (6-*C*-glucosyl-8-*C*-β-arabinosylapigenin) and neoisochaftoside (6-*C*-β-arabinosyl-8-*C*-glucosyl-apigenin) (Saleh, N. A. M. and Chopin, J., unpublished results) (Table 1).

Few detailed studies on the flavonoid *O*-glycosides of *Artemisia* have been reported [26]. The 3-glucosides and 3-rutinosides of kaempferol, quercetin, isorhamnetin and patuletin were reported in *A. vulgaris*, *A. dracunculus* and *A. absinthium* [7], and *A. monosperma* and *A. herba-alba* [1]. The 7-glucosides of apigenin and luteolin were identified in *A. japonica* [27], luteolin 7-glucoside in *A. tridentata* [3] and acacetin 7-glucoside and 7-rutinoside in *A. monosperma* [1]. In the present study 17 *O*-glycosides were isolated from *Artemisia judaica* (Table 1): six apigenin, four luteolin and seven chrysoeriol glycosides (see Experimental for details of characterization). The major glycosylation patterns being in position 7 and to a lesser extent positions 3′ and 4′. The major glycoside was chrysoeriol 7-glucuronide.

EXPERIMENTAL

Material. Fresh plant material was collected as follows: *Artemisia judaica* L. was collected in August 1984, 5 km west of St. Cathrine, Sinai; *A. monosperma* Del. was collected in June 1985, 50 km from Cairo on the Cairo–Ismailia road; *A. herba-alba* Asso. was collected in August 1984, Mt. Moses, St. Cathrine, Sinai. Samples were authenticated by Prof. Dr L. Boulos, NRC, and voucher specimens are deposited at the herbarium, NRC.

Methods. Plant material (leaf and stem) was extracted with 70% EtOH. The concd extracts were purified by polyamide CC. Flavonoid glycoside fractions were further purified on sephadex LH-20. Aglycone fractions were subjected to prep. TLC on polyamide plates followed by separation on Sephadex LH-20. Aglycones were identified by demethylation with pyridinium chloride (autoclaved in a sealed tube to avoid oxidation), co-chromatography with authentic samples (Table 1), MS (Table 2) and UV spectral data (Table 3). Pure glycosides were investigated and their structures determined according to standard methods (19, 28, 29). The *C*-glycosides co-chromatographed with authentic samples on reversed-phase HPLC with a Lichrosorb RP18(10 μm) column (1, 30). *O*-Glycosides were subjected to strong and mild acid hydrolysis, enzymic hydrolysis, H_2O_2 oxidation of (31) and UV analysis. Most well known glycosides were co-chromatographed with authentic samples (see Table 1 for R_f values). 7-Diglycosides, 7,3′- and 7,4′-diglycosides gave the corresponding 7-monoglycosides on mild acid hydrolysis. H_2O_2 oxidation (31) which is normally used for flavonol 3-glycosides was found to apply to flavone 7-glycosides, but with lower yields. This gave rise to gentiobiose and rutinose in the case of 7-gentiobiosides and 7-rutinosides, respectively. UV data for some uncommon glycosides (λ_{max}, nm): (1) apigenin 4′-glucoside MeOH 268, 322; NaOMe 277, 295 sh, 365; $AlCl_3$ 257 sh, 277, 300, 340, 382; $AlCl_3$–HCl 255 sh, 279, 297, 334, 380; NaOAc 273, 295 sh, 348; NaOAc–H_3BO_3 270, 300 sh, 327 (2) apigenin 7-gentiobioside: MeOH 267, 330; NaOMe 273, 298 sh, 345 sh, 384; $AlCl_3$ 272, 299, 340, 380; $AlCl_3$-HCl 273, 298, 336, 380; NaOAc 255 sh, 267, 335, 400 sh; NaOAc-H_3BO_3 267, 333 (3) apigenin 7-diglucuronide MeOH 267, 330; NaOMe 275, 302 sh, 352 sh, 393; $AlCl_3$–HCl 274, 298, 337, 378; NaOAc 255 sh, 267, 334, 400 sh; NaOAc–H_3BO_3 267, 332 (4) luteolin 3′-glucoside MeOH 271, 278 sh, 335; NaOMe 282, 287 sh, 325 sh, 397; $AlCl_3$ 272, 278 sh, 300 sh, 347, 385; $AlCl_3$–HCl 272, 278 sh, 300 sh, 342, 385; NaOAc 271, 278 sh, 392; NaOAc–H_3BO_3 271, 278 sh, 345, 400 sh (5) luteolin 4′-glucoside MeOH 269, 287 sh, 333; NaOMe 267, 300 sh, 371; $AlCl_3$ 257 sh, 276, 293 sh, 350, 385;

$AlCl_3$–HCl 255 sh, 278, 293 sh, 342, 380; NaOAc 272, 318 sh, 355; NaOAc–H_3BO_3 269, 335 (6) luteolin 7-gentiobioside MeOH 255, 265 sh, 349; NaOMe 275, 408; $AlCl_3$ 272, 295 sh, 413; $AlCl_3$–HCl 268, 295 sh, 353, 386; NaOAc 260, 267 sh, 370, 400; NaOAc–H_3BO_3 258, 372 (7) luteolin 7,3'-diglucoside MeOH 255 sh, 269, 337; NaOMe 279, 394; $AlCl_3$ 274, 302 sh, 352, 387 sh; $AlCl_3$–HCl 275, 300 sh, 344, 384 sh; NaOAc 270, 280 sh, 309 sh, 352; NaOAc–H_3BO_3 269, 345 (8) Chrysoeriol 4'-glucoside MeOH 272, 333; NaOMe 278, 310 sh, 366; $AlCl_3$ 258, 278, 295, 353, 388; $AlCl_3$–HCl 255, 280, 293 sh, 343, 385; NaOAc 277, 313, 355; NaOAc-H_3BO_3 270, 333 (9) chrysoeriol 7-gentiobioside MeOH 249, 268, 343; NaOMe 265, 277 sh, 295 sh, 392; $AlCl_3$ 262, 273, 295, 358, 388; $AlCl_3$–HCl 260, 273, 295, 353, 385; NaOAc 250, 267, 345, 415 sh; NaOAc–H_3BO_3 250, 267, 345 (10) chrysoeriol 7-diglucuronide MeOH 248, 268, 348; NaOMe 263, 280 sh, 405; $AlCl_3$ 258 sh, 276, 300 sh, 356, 386; $AlCl_3$–HCl 356 sh, 276, 300 sh, 354, 386; NaOAc 248, 265, 348; NaOAc-H_3BO_3 248, 269, 347 (11) chrysoeriol 7,4'-diglucoside MeOH 270, 330; NaOMe 287, 330 sh, 387; $AlCl_3$ 255 sh, 275, 295, 343, 387; $AlCl_3$–HCl 255 sh, 277, 295, 337, 382; NaOAc 247 sh, 270, 330; NaOAc–$H_3BO_3$247 sh, 270, 330.

Acknowledgements—This work was supported by National Research Centre Grant No. 1/4/1/85. The authors thank Dr M. Linscheid, Institut für Spektrochemie, Dortmund, F.R.G. for mass measurements. They are also grateful to Prof. Dr. J. Chopin and Miss G. Dellamonica, Université Claude Bernard, Lyon, France, for HPLC measurements.

REFERENCES

1. Saleh, N. A. M., El- Negoumy, S. I., Abd-Alla, M. F., Abou-Zaid, M. M., Dellamonica, G. and Chopin, J. (1985) *Phytochemistry* **24**, 201.
2. Liu, Y. -L. and Mabry, T. J. (1981) *Phytochemistry* **20**, 1389.
3. Brown, D., Asplund, R. O. and McMahon, V. A. (1975) *Phytochemistry* **14**, 1083.
4. Rodriguez, E., Carman, N. J., Vander-Velde, G., McReynolds, J. H., Mabry, T. J., Irwin, M. A. and Geissman, T. A. (1972) *Phytochemistry* **11**, 3509.
5. Kingston, D. G. I. (1971) *Tetrahedron* **27**, 2691.
6. Goudard, M., Favre-Bonvin, J., Lebreton, P. and Chopin, J. (1978) *Phytochemistry* **17**, 145.
7. Hoffmann, B. and Herrmann, K. (1982) *Z. Lebensm. Unters. Forsch.* **174**, 211.
8. Oganesyan, E. T., Smirnova, L. P., Dzhumyrko, S. F. and Kechatova, N. A. (1976) *Khim. Prir. Soedin* 599.
9. Barbera, O., Marco, J. A., Sanz, J. F. and Sanchez-Paraeda, J. (1986) *Phytochemistry* **25**, 2357.
10. Liu, Y. -L. and Mabry, T. J. (1982) *Phytochemistry* **21**, 209.
11. Chandrasekharan, I., Khan, H. A. and Ghanim, A. (1981) *Planta Med.* **43**, 310.
12. Djermanovic, M., Jokic, A., Mladenovic, S. and Stefanovic, M. (1975) *Phytochemistry* **14**, 1873.
13. Jermic, D., Stefanovic, M., Dokovic, D. and Milosavljevic, S. (1979) *Glas. Hem. Drus. Beograd* **44**, 615.
14. Hurabielle, M., Eberle, J. and Paris, M. (1982) *Planta Med.* **46**, 124.
15. Bouzid, N., Moulis, C. and Fouraste, I. (1982) *Planta Med.* **44**, 157.
16. Namba, T., Hattori, M., Takehana, Y., Tsunezuka, M., Tomimori, T., Kizu, H. and Miyaichi, Y. (1983) *Phytochemistry* **22**, 1057.
17. Mues, R., Timmermann, B. N., Ohno, N. and Mabry, T. J. (1979) *Phytochemistry* **18**, 1379.
18. Ulubelen, A., Timmermann, B. N. and Mabry, T. J. (1980) *Phytochemistry* **19**, 905.
19. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids.* Springer, Berlin.
20. Esteban, M. D., Collado, I. G., Macias, F. A., Massanet, G. M. and Luis, F. R. (1986) *Phytochemistry* **25**, 1502.
21. Herz, W., Bhat, S. V. and Santhanam, P. S. (1970) *Phytochemistry* **9**, 891.
22. Segal, R., Cohen, D., Sokoloff, S. and Zaitschek, D. V. (1973) *Lloydia* **36**, 103.
23. Khafagy, S. M., El-Ghazooly, M. G. and Metwally, A. M. (1979) *Pharmazie* **34**, 748.
24. Liu, Y. -L. and Mabry, T. J. (1981) *Phytochemistry* **20**, 309.
25. Chumbalov, T. R. and Fadeeva, O. V. (1970) *Khim. Prir. Soedin* 364.
26. Greger, H. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds) p. 899. Academic Press, London.
27. Kaneta, M., Hikichi, H., Endo, S. and Sugiyama, N. (1978) *Agric. Biol. Chem.* **42**, 475.
28. Harborne, J. B. (1967) *Comparative Biochemistry of the Flavonoids.* Academic Press.
29. Markham, K. R. (1982) *Techniques of Flavonoid Identification.* Academic Press, London.
30. Lardy, C., Bouillant, M. L. and Chopin, J. (1984) *J. Chromatogr.* **291**, 307.
31. Chandler, B. V. and Harper, K. A. (1961) *Aust. J. Chem.* **14**, 586.