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HIGHLY OXYGENATED FLAVONOID AGLYCONES FROM *GUTIERREZIA GRANDIS*

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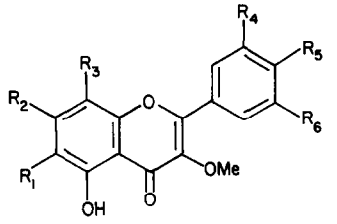
Key Word Index—*Gutierrezia grandis*; Compositae; Astereae; highly oxygenated flavonol 3-*O*-methyl ethers; unusual B-ring oxygenation; brickellin; sarothrin; permethylation.

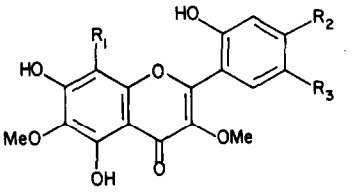
Abstract—Twelve known and nine new highly oxygenated flavonoid aglycones, some of which exhibit 2′-oxygenation, were isolated from *Gutierrezia grandis*.

INTRODUCTION

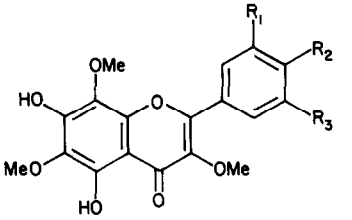
Following the recent major systematic revision of the '*Gutierrezia–Xanthocephalum* complex' [1–4], which more than doubled the number of species assigned to the North American section of *Gutierrezia*, flavonoid studies were undertaken to clarify the validity of the taxonomic realignments. Previous chemical investigations of this group are too scant in terms of flavonoids to be useful for chemotaxonomic purposes [5–8]. Our preliminary investigations have shown each member of the genus to contain an array of flavonoid aglycones, as well as some glycosides. We report here an unusual group of 21 flavonoid aglycones from *G. grandis* S. P. Blake, a woody species of Lanes' revised *Gutierrezia* occurring in the montane region between Saltillo and Monterrey in northern Mexico. The nine new compounds (**1–9**) are all flavonol 3-*O*-methyl ethers: 5,7,3′,4′,5′-pentahydroxy-3,6,8-trimethoxyflavone; 5,7-dihydroxy-3,6,8,3′,4′,5′-hexamethoxyflavone; 5,7,4′-trihydroxy-3,6,8,3′,5′-pentamethoxyflavone; 5,7,3′-trihydroxy-3,6,8,4′-tetramethoxyflavone; 5,7,3′,5′-tetrahydroxy-3,8,4′-trimethoxyflavone; 5,7,2′,4′-tetrahydroxy-3,6,5′-trimethoxyflavone; 5,7,2′,4′-tetrahydroxy-3,6,8,5′-tetramethoxyflavone; 5,7,2′,5′-tetrahydroxy-3,6,4′-trimethoxyflavone and 5,7,2′,5′-tetrahydroxy-3,6,8,4′-tetramethoxyflavone. In addition, 11 of the 12 known compounds (**10–21**) are also flavonol 3-*O*-methyl ethers: 5,3′,5′-trihydroxy-3,6,7,8,4′-pentamethoxyflavone [9]; 5,7,4′-trihydroxy-3,6,8-trimethoxyflavone (sarothrin) [10]; 5,7,3′-trihydroxy-3,6,4′-trimethoxyflavone (centaureidin) [11]; 5,7,4′-trihydroxy-3,8,3′-trimethoxyflavone [11]; 5,7,4′-trihydroxy-3,6-dimethoxyflavone [11]; 5,7,3′,4′-tetrahydroxy-3,6-dimethoxyflavone



	R_1	R_2	R_3	R_4	R_5	R_6
5	H	OH	OMe	OH	OMe	OH
10	OMe	OMe	OMe	OH	OMe	OH
12	OMe	OH	H	OH	OMe	H
13	H	OH	OMe	OMe	OH	H
14	OMe	OH	H	H	OH	H
15	OMe	OH	H	OH	OH	H
16	H	OH	OMe	OH	OH	H
17	OMe	OH	OMe	OH	OH	H
18	H	OH	H	OH	OMe	OH
19	OMe	OH	H	OH	OMe	OH
20	OMe	OH	OMe	OH	OMe	OH
21	OMe	OH	OMe	OH	OH	H (3-H)



	R_1	R_2	R_3
6	H	OH	OMe
7	OMe	OH	OMe
8	H	OMe	OH
9	OMe	OMe	OH



	R_1	R_2	R_3
11	H	OH	H
1	OH	OH	OH
2	OMe	OMe	OMe
3	OMe	OH	OMe
4	OH	OMe	H

Table 1. Mass spectral data for flavonoid aglycones

Flavonoid	$[M]^+$	$[M-15]^+$	$[M-17]^+$	$[M-31]^+$	$[A_1-15]^+$	$[A_1-43]^+$	$[B_2]^+$	$[B_6]^+$	$[B_6-15]^+$
Sarothrin, 5,7,4′-OH-3,6,8,-OMe	360 (70%)	345 (100%)	—	—	197 (7%)	169 (5%)	121 (12%)	—	—
1, 5,7,3′,4′,5′-OH-3,6,8-OMe	392 (99%)	377 (100%)	—	—	197 (20%)	169 (15%)	153 (28%)	—	—
2, 5,7-OH-3,6,3′,4′,5′-OMe	434 (94%)	419 (100%)	—	—	—	—	—	—	—
3, 5,7,4′-OH-3,6,8,3′,5′-OMe	420 (93%)	405 (100%)	—	—	197 (7%)	169 (6%)	181 (9%)	—	—
4, 5,7,3′-OH-3,6,8,4′-OMe	390 (95%)	375 (100%)	—	—	197 (16%)	169 (14%)	151 (26%)	—	—
5, 5,7,3′,5′-OH-3,8,4′-OMe	376 (97%)	361 (100%)	—	—	167 (22%)	139 (33%)	167	—	—
6, 5,7,2′,4′-OH-3,6,5′-OMe	376 (100%)	361 (71%)	359 (27%)	345 (50%)	167 (20%)	139 (10%)	167	194 (27%)	179 (43%)
7, 5,7,2′,4′-OH-3,6,8,5′-OMe	406 (100%)	391 (53%)	389 (9%)	375 (17%)	197 (63%)	169 (21%)	167 (13%)	194 (70%)	179 (47%)
8, 5,7,2′,5′-OH-3,6,4′-OMe	376 (100%)	361 (35%)	359 (38%)	345 (68%)	167 (26%)	139 (11%)	167	194 (32%)	179 (51%)
9, 5,7,2′,5′-OH-3,6,8,4′-OMe	406 (100%)	391 (44%)	389 (15%)	375 (30%)	197 (60%)	169 (39%)	167 (26%)	194 (70%)	179 (60%)

(axillarin) [11]; 5,7,3',4'-tetrahydroxy-3,8-dimethoxyflavone [12]; 5,7,3',4'-tetrahydroxy-3,6,8-trimethoxyflavone [13]; 5,7,3',5'-tetrahydroxy-3,4'-dimethoxyflavone [14]; 5,7,3',5'-tetrahydroxy-3,6,4'-trimethoxyflavone [15] and 5,7,3',5'-tetrahydroxy-3,6,8,4'-tetramethoxyflavone [9]. The remaining known compound is 5,7,3',4'-tetrahydroxy-6,8-dimethoxyflavone [12].

RESULTS AND DISCUSSION

The dried and ground leaves of *Gutierrezia grandis* were extracted with aqueous methanol and the concentrated syrup was partitioned successively with hexane, methylene dichloride and ethyl acetate according to standard procedures [16]. Flavonoid aglycones (21) were obtained from the methylene dichloride partition, including nine new compounds. Identification of the new compounds was based on mass spectral, UV and ^{1}H NMR data (Tables 1–4).

The spectral data for **1–4** were compared with those for the known compound sarothrin [10] (5,7,4'-trihydroxy-3,6,8-trimethoxyflavone, **11**) as shown in Tables 1, 3 and 4. Since the A- and C-ring substitution patterns of sarothrin and **1–4** appeared to be identical based on mass spectral, UV and ^{1}H NMR data (see Tables 1, 3 and 4), the analysis of **1–4** was centred on the B-ring. Compound **1** showed a $[M]^+$ of *m/z* 392 (99%) indicating a flavonoid aglycone with five hydroxyl and three methoxyl substituents. Since the sarothrin A- and C-ring patterns account for three methoxyls and two hydroxyls, the remaining three hydroxyls must be in the B-ring. The colour on paper under UV light (purple) and with ammonia (yellow-green) and NA spray (orange) indicated that the compound contained a 3',4'-dihydroxyl. The UV absorption spectra also supported the *ortho*-dihydroxyl system. Moreover, the large hypsochromic shift (−67 nm) in band I in the presence of aluminium chloride–hydrochloric acid relative to band I in the aluminium chloride spectrum favoured three adjacent hydroxyls, such as found in myricetin-type B-rings. The mass spectral fragment $[B_2]^+$ at *m/z* 153 (28%) further indicated three hydroxyls in the B-ring. ^{1}H NMR showed a two-proton singlet at δ7.42, characteristic of a 2',6'-hydrogen and, thus confirmed the 3',4',5'-trihydroxy B-ring in **1**.

The mass spectrum of **2** exhibited a $[M]^+$ at *m/z* 434 (94%), suggesting an aglycone with two hydroxyl and six methoxyl substituents and, based on the structure of sarothrin, three methoxyls and no hydroxyl substituents are present in the B-ring. The purple colour on paper under UV light changed little with ammonia and NA, supporting the absence of B-ring hydroxyls. The mass spectral fragment $[B_2]^+$ at *m/z* 195 (5%) further substantiated the presence of three B-ring methoxyls. ^{1}H NMR showed only a two-proton singlet at δ7.43, characteristic of 2',6'-protons, thus confirming the B-ring pattern as 3',4',5'-trimethoxy.

The mass spectrum of **3** exhibited a $[M]^+$ at *m/z* 420 (93%) in accord with a flavonoid aglycone bearing five methoxyl and three hydroxyl substituents and, comparison with sarothrin established a B-ring with two methoxyl and one hydroxyl substituent. A mass spectral $[B_2]^+$ fragment at *m/z* 181 (9%) supported this type of B-ring. Compound**3** appeared purple on paper under UV, with the spot turning to yellow after exposure to both ammonia and NA, indicating a 4'-hydroxyl and confirming the absence of *ortho*-dihydroxyls in the B-ring. A 4'-hydroxyl was further supported by the sodium methoxide UV absorption for band I, which gave a bathochromic shift of 63 nm with an increase in intensity relative to band I in methanol. Finally, in the ^{1}H NMR spectrum, a two-proton singlet at δ7.47 for 2',6'-protons allowed assignment of the B-ring as 3',5'-dimethoxy-4'-hydroxy.

Compound **4** gave a $[M]^+$ of *m/z* 390 (91%) indicating a flavonoid with three hydroxyl and four methoxyl groups. Thus, based on sarothrin, the B-ring must contain one hydroxyl and one methoxyl. A mass spectral fragment for $[B_2]^+$ at *m/z* 151 (26%) supported this substitution pattern. Moreover, **4** appeared purple on paper under UV light and showed no change when exposed to ammonia and NA, indicating no 4'-hydroxyl and no B-ring *ortho*-dihydroxyls. ^{1}H NMR showed B-ring signals at δ6.90 (1H, *d*, *J* = 9 Hz), 7.72 (1H, *dd*, *J* = 2.5, 9 Hz) and 7.65 (1H, *d*, *J* = 2.5 Hz) corresponding to protons at the 5',6'- and 2'-positions, respectively. Thus, the B-ring pattern was established as 3'-hydroxy-4'-methoxy.

^{1}H NMR of **5** clearly established skeletal protons in at least two rings. The mass spectrum of **5** showed a $[M]^+$ at *m/z* 376 (97%), indicating a flavonoid aglycone with three methoxyl and four hydroxyl groups. The compound appeared as a purple spot on paper under UV light and no colour change was observed with ammonia and only a slight change to yellow-brown with NA, indicating a 5-hydroxyl and 4'-methoxyl. UV absorption spectra [sodium methoxide band III, 345 nm (sh)] also indicated a 7-hydroxyl group. Band I in the aluminium chloride UV spectrum appeared at 415 nm (+77 nm relative to band I in methanol) and, in aluminium chloride–hydrochloric acid a strong shoulder for band I appeared at 410 nm

Table 2. Mass spectral (permethylated) data for flavonoid aglycones

Flavonoids	$[M]^+$	$[M-15]^+$	$[M-31]^+$	$[A_1-15]^+$	$[A_1-43]^+$	$[B_2]^+$
Brickellin (permethylated)	432	417	401	195	167	195
5,6',6,7,2',3',4'-OMe	(30%)	(100%)	(59%)	(6%)	(11%)	(6%)
6 (permethylated),	432	417	401	195	167	195
5,7,2',4',3,6,5'-OMe	(35%)	(100%)	(74%)	(3%)	4%)	(3%)
7 (permethylated),	462	447	431	225	197	195
5,7,2',4',3,6,8,6'-OMe	(33%)	(100%)	(43%)	(16%)	(13%)	(12%)
8 (permethylated),	432	417	401	195	167	195
5,7,2',5',3,6,4'-OMe	(21%)	(61%)	(32%)	(15%)	(14%)	(15%)
9 (permethylated),	462	447	431	225	197	195
5,7,2',5',3,6,8,4'-OMe	(22%)	(56%)	(24%)	(6%)	(12%)	(12%)

Table 3. UV data (λ_{max}^{MeOH} nm) for flavonoid aglycones

Flavonoid	MeOH	NaOMe	$AlCl_3$	$AlCl_3$–HCl	NaOAc	NaOAc–H_3BO_3
Sarothrin, 5,7,4′-OH-3,6,8-OMe	278, 338	282, 335, 406	285, 313, 366, 415	290, 313, 360, 415	283, 320 sh, 340 sh, 400	280, 332
1, 5,7,3′,4′,5′-OH-3,6,8-OMe	260 sh, 274, 362	275, 400 (dec.)	281, 325, 442	285, 316, 375, 420 sh	281, 335, 405	267, 392
2, 5,7-OH-3,6,3′,4′,5′-OMe	281, 333	283, 310 sh, 381	290, 310 sh, 362	285, 310 sh, 358	285, 310 sh, 375	281, 333
3, 5,7,4′-OH-3,6,8,3′,5′-OMe	256, 270, 355	260, 280 sh, 345 sh, 418	261 sh, 282, 320 sh, 382	288, 286, 317 sh, 370	280 sh, 302 sh, 380	279, 348
4, 5,7,3′-OH-3,6,8,4′-OMe	258, 278, 350	278, 310 sh, 400	271, 288, 308 sh, 375, 420 sh	265, 290, 308 sh, 365, 420 sh	280, 315 sh, 380	280, 343
5, 5,7,3′,5′-OH-3,8,4′-OMe	275, 338	278, 320, 390	281, 300 sh, 352, 410 sh	283, 305 sh, 350, 410 sh	281, 310 sh, 388	275, 350
6, 5,7,2′,4′-OH-3,6,5′-OMe	260, 305 sh, 350	270, 305, 405	272, 320, 400	272, 320, 380	268, 325 sh, 388	262, 350
7, 5,7,2′,4′-OH-3,6,8,5′-OMe	268, 355	280, 338, 416	280, 325, 370 sh, 405	280, 325 sh, 370, 405 sh	278, 330 sh, 394	271, 356
8, 5,7,2′,5′-OH-3,6,4′-OMe	260, 305 sh, 350	267, 345 (dec.)	272, 325, 370	274, 322, 370	265, 355	262, 350
9, 5,7,2′,5′-OH-3,6,8,4′-OMe	264, 350	268, 350 (dec)	278, 328, 375 sh, 400	278, 328, 370, 400 sh	273, 350	264, 350

Table 4. ^{1}H NMR data for flavonoid aglycones (δ-scale in ppm, TMS as int. standard)

	H-3		H-6		H-8		H-2′		H-3′		H-4′		H-5′		H-6′	
	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6	CCl_4	C_6D_6
Sarothrin, 5,7,4′-OH-3,6,8-OMe	3.83	3.81	3.70	3.68	3.86	3.66	8.03	8.20	6.87	6.92	—	—	6.87	6.92	8.03	8.20
1, 5,7,3′,4′,5′-OH-3,6,8-OMe	3.90	3.86	3.73	3.63	3.90	3.74	7.42	7.77	—	—	—	—	—	—	7.42	7.77
2, 5,7-OH-3,6,3′,4′,5′-OMe	3.88	3.85	3.72	3.83	3.82	3.66	7.43	7.54	3.93	3.13	3.88	3.64	3.93	3.53	7.43	7.54
3, 5,7,4′-OH-3,6,8,3′,5′-OMe	3.91	3.83	3.73	3.66	3.91	3.66	7.47	7.62	3.90	3.12	—	—	3.90	3.52	7.47	7.62
4, 5,7,3′-OH-3,6,8,4′-OMe	3.90	3.88	3.72	3.75	3.84	3.68	7.65	8.02	—	—	3.90	3.35	6.90	6.63	7.72	7.95
5, 5,7,3′,5′-OH-3,8,4′-OMe	3.80	3.82	6.12	6.50	3.86	3.72	7.33	7.70	—	—	3.86	3.70	—	—	7.33	7.70
6, 5,7,2′,4′-OH-3,6,5′-OMe	3.80	3.83	3.74	3.62	6.34	6.70	—	—	6.44	6.72	—	—	3.74	3.33	6.88	6.93
7, 5,7,2′,4′-OH-3,6,8,5′-OMe	3.84	3.82	3.76	3.70	3.84	3.66	—	—	6.36	6.67	—	—	3.76	3.35	6.91	6.91
8, 5,7,2′,5′-OH-3,6,5′-OMe	3.82	3.86	3.73	3.62	6.44	6.66	—	—	6.34	6.40	3.73	3.30	—	—	6.88	7.16
9, 5,7,2′,5′-OH-3,6,8,4′-OMe	3.83	3.86	3.75	3.64	3.83	3.71	—	—	6.35	6.38	3.75	3.33	—	—	6.88	7.13

(+72 nm relative to band I in methanol). These large shifts are in accord with an 8-methoxyl rather than at 6-methoxyl group [17]. Furthermore, the mass spectrum of **5** showed a $[M-15]^+$ at m/z 361 (100%) thus supporting an A-ring with an 8-methoxyl. In the ^1H NMR spectrum, H-6 appeared, as expected, at δ6.14 in carbon tetrachloride. Thus, the above data confirmed a 5,7-dihydroxy-8-methoxy A-ring. An additional ^1H NMR signal appeared as a two-proton singlet at δ7.33, for equivalent protons at 2′ and 6′. Thus, C-3 must contain a methoxyl group (i.e. no signal for H-3 and purple colour on paper under UV). The appropriate UV data also indicated the lack of *ortho*-dihydroxyls in the B-ring (aluminium chloride, aluminium chloride–hydrochloric acid spectra, band I). All relevant spectral data were compared with those of sarothrin and **19** (5,7,3′,5′-tetrahydroxy-3,6,4′-trimethoxyflavone), which exhibited a ^1H NMR two-proton singlet at δ7.2 for the 2′,6′-protons and a one-proton singlet at δ6.5, as expected, for H-8. Thus, the structure of **5** was established as 5,7,3′,5′-tetrahydroxy-3,8,4′-trimethoxyflavone.

Compounds **6–9** form a group of new 3-*O*-methyl ethers quite similar in oxygenation pattern to brickellin [18], which was recently revised to 5,2′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone on the basis of synthesis [19]. Indeed, upon permethylation **6** exhibited the same mass spectrum as that of the permethylated derivative of brickellin (Table 2), thus establishing the oxygenation pattern of **6**. Underivatized **6** gave a $[M]^+$ at m/z 376 (100%) for a flavonol aglycone bearing four hydroxyls and three methoxyls. A fragment $[M_1-15]^+$ at m/z 361 (71%), and $[A_1-15]^+$ and $[B_2]^+$ both at m/z 167 (20%) favoured an A-ring with two hydroxyls and a 6-methoxyl. The compound appeared purple when viewed on paper under UV light and changed to yellow-green when fumed with ammonia and sprayed with NA. These results indicated hydroxylation at positions 5 and 4′ and no *ortho*-dihydroxyls in the B-ring and, thus, established that, as in brickellin, **6** must have 3- and 5′-methoxyls. ^1H NMR showed a one-proton singlet at δ6.44, corresponding to H-8. Additional ^1H NMR singlets for one proton at δ6.88 and 6.34 indicated two *para*-protons in the B-ring, since **6** and brickellin give the same permethylated derivative. Mass spectral fragments $[M-17]^+$ at m/z 359 (27%), $[M-31]^+$ at m/z 345 (50%) and $[B_6]^+$ at m/z 194 (27%) [21, 22], and $[B_6-15]^+$ at m/z 179 (43%) indicated a 2′-hydroxyl and, therefore, the remaining hydroxyl at the 7 position. Thus, **6** is 5,7,2′,4′-tetrahydroxy-3,6,5′-trimethoxyflavone.

Compound **7** gave a $[M]^+$ at m/z 406 (100%) in accordance with a flavonoid aglycone with four hydroxyl and four methoxyl substituents. Indeed, comparison of mass spectral, ^1H NMR and UV data indicated the same substitution pattern as **6**, except for an extra 8-methoxyl. The data which confirmed this analysis were the absence of the ^1H NMR signal at δ6.44 and the appearance of a new three-proton singlet at δ3.84 with respect to **6**, and $[A-15]^+$ at m/z 197 (63%). Other data corresponded to those for **6**. Thus, **7** is 5,7,2′,4′-tetrahydroxy-3,6,8,5′-tetramethoxyflavone.

Compounds **8** and **9** showed many similarities to **6** and **7**, respectively. However, structural difference was reflected in the colour of **8** and **9** when viewed on paper under UV; **8** and **9** appeared purple but, unlike **6** and **7**, remained so with ammonia and NA. Permethylation of **8** and **9** was achieved using the diazomethane method rather than with Methelute, with which decomposition occurred. The permethylated derivatives of **8** and **9** gave mass spectra identical to those of **6** and **7**, respectively. The UV data indicated that **8** and **9** were the isomers of **6** and **7**, respectively, at the 4′- and 5′-positions, i.e. 4′-methoxyl and 5′-hydroxyl. The resulting unstable *para*-hydroxyl B-rings would account for the difficulty in derivatizing these compounds with Methelute. Therefore, **8** is 5,7,2′,5′-tetrahydroxy-3,6,4′-trimethoxyflavone and **9** is 5,7,2′,5′-tetrahydroxy-3,6,8,4′-tetramethoxyflavone.

EXPERIMENTAL

Plant material. Gutierrezia grandis was collected from the state of Neuvo Leon, Mexico, on Highway 40 between Monterrey and Saltillo on the road to Microondas Mariposa by Mark Leidig and Meredith Lane. Voucher specimens are on deposit in the University of Texas and Lundell Herbarium (Lane collection number 2589).

Isolation of flavonoids. Air-dried leaf material (1 kg) was exhaustively extracted in aq. MeOH, first in 85% concn followed by 50% concn. These two extracts were concd, combined and the aq. soln partitioned according to standard procedures [16]. Each partition was checked for flavonoids by 2D PC. The hexane and aq. fractions showed no evidence of flavonoids, whereas the CH_2Cl_2 and EtOAc fractions showed multiple purple spots on paper in UV. These two fractions were evaporated to dryness *in vacuo*; the CH_2Cl_2 portion yielding 61.4 g syrup and the EtOAc fraction 26.3 g.

The CH_2Cl_2 fraction was run on a short, large diameter column containing 500 g cellulose powder (Merck), eluted first with H_2O, then with 15% HOAc, and, finally, with 40% HOAc. All fractions fluorescing under UV light were combined and, after evaporation to dryness, yielded a total of 10.4 g dry wt.

The 10.4 g cleaned-up mixture was chromatographed on a Polyclar (Polyclar AT, GAF corp) column (1 × 10 cm) initiated with toluene and gradually increasing to pure MeOH in 10% increments. H_2O was then gradually introduced into the mobile phase in 10% increments until 100% H_2O was reached. All bands appearing purple under UV were collected separately. The first fraction containing flavonoid material was evaporated *in vacuo* and the residue chromatographed on a small silica gel column in CH_2Cl_2–MeCOEt (9:1). The material in the other bands was similarly dried and separated by PC, using 15% HOAc on Whatman 3 MM paper. Final purification of each compound for spectral analysis was by standard procedures [16] using 75% or 100% MeOH over Sephadex LH-20 columns.

General techniques. All UV spectra were recorded using standard procedures [16]. ^1H NMR spectra of the TMSi ethers of these flavonoids were recorded in both CCl_4 and C_6D_6 at 90 MHz and are reported in δ-values (ppm) relative to TMS as int. standard. MS data for both underivatized and permethylated samples were recorded by direct probe EIMS at 70 eV with a source temp. of 250–270°.

The A_1, B_1 and B_2 terminology for the fragments is according to ref. [20]. The B_ϵ ion was designated by authors. Permethylation was achieved using Methelute (Pierce) and/or CH_2N_2 produced by the reaction of *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine with KOH. Previously published spectral data are provided only for sarothrin and brickellin. All data for new compounds are presented in Tables 1–4.

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