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THE MAJOR FLAVONOIDS OF THE SEED OF *TEPHROSIA APOLLINEA*

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Key Word Index—*Tephrosia apollinea*; Leguminosae; 7-oxygenated flavones; semiglabrin; pseudosemiglabrin; glabratephrin; glabratephrinol; apollinine; lanceolatin-A; ^{13}C NMR; chemotaxonomy.

Abstract—A total of six complex 7-oxygenated-8-prenylflavones have been isolated from the seeds of *Tephrosia apollinea* and identified as the diastereoisomers (−)-semiglabrin and (−)-pseudosemiglabrin, (+)-glabratephrin, (+)-glabratephrinol, appollinine (7-methoxy-8-[3″-(2″,5″-dihydro-5″,5″-dimethyl-2″-oxofuryl)]-flavone and lanceolatin-A. The use of ^{13}C NMR in the structure elucidation of flavones of this type is discussed. The potential chemotaxonomic value of *Tephrosia* flavones of the type isolated from *T. apollinea* is explored.

INTRODUCTION

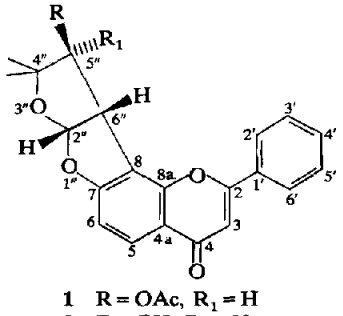
Tephrosia Pers. (Leguminosae–Papilionoideae) is a large tropical and sub-tropical genus estimated to contain about three hundred species [1, 2]. Chemical studies on a number of taxa have revealed rotenoids [3–5] and a range of isoflavones [6, 7], flavanones/chalcones [8, 9], flavonols [10, 11] and flavones [12–19]. Prominent among the latter is a group of 5,7-oxygenated [12–16] and 7-oxygenated [17–19] compounds characterized by the occurrence of a C-8 prenyl unit which has, in many cases, undergone a complex process of further substitution and cyclization [20].

The taxon *T. apollinea* (Del.) Link occurs through north-east Africa across to the Indian sub-continent; its status as a distinct species seems to be rather doubtful and it is probably best regarded as a segregate of the paleotropical polymorphic species *T. purpurea* (L.) Pers. (Polhill, R. M., personal communication). Indian populations of *T. purpurea* have been reported to contain a number of rotenoids [4]. The taxon *T. semiglabra* Sond., which is widespread throughout South Africa [21], can be regarded as another segregate of *T. purpurea* representing a separate line of development from the same core as *T. apollinea* (Polhill, R. M., personal communication). Recent phytochemical studies on this plant [18, 19] have yielded three novel 7-oxygenated-8-prenylflavones, semiglabrin (**1**), semiglabrinol (**2**) and glabratephrin (**5**).

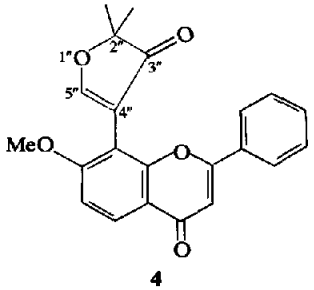
With the exception of a negative report concerning the occurrence of the amino acid canavanine in the seed [22], there does not appear to be any information available on the constituents of *T. apollinea*. An investigation of the flavonoid constituents of this taxon and their relationship to those of *T. purpurea* and *T. semiglabra* would be of obvious chemosystematic interest. We now wish to report the results of such a study in which a total of six flavonoids, several of them novel, have been isolated and identified. Information is presented, for the first time, on the ^{13}C NMR spectra of *Tephrosia* flavonoids.

RESULTS AND DISCUSSION

Examination of the $CHCl_3$ extract of the defatted seeds of *T. apollinea* by TLC revealed the presence of a number of blue, blue-green and yellow fluorescent



1 R = OAc, R_1 = H
2 R = OH, R_1 = H
3 R = R_1 = O



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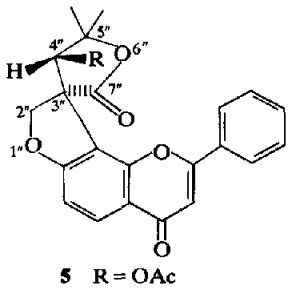


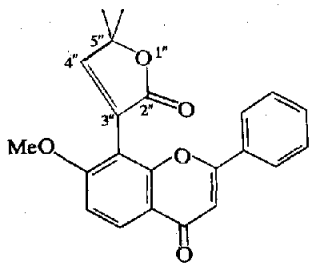
5 R = OAc
6 R = OH

compounds. Column chromatography of the concentrated extract over silica gel gave, on elution with petrol (bp 40–60°) containing increasing amounts of EtOAc, three blue fluorescent bands each of which yielded a pure crystalline compound. A fourth compound was obtained, in trace amounts, from the mother liquors remaining after crystallization of the major component of the third band, by repeated PLC. Further elution of the column with mixtures of $CHCl_3$ and MeOH yielded a fifth compound.

The initial component eluted from the column analysed for $C_{23}H_{20}O_6$. The ^1H NMR spectrum was typical of a 7-oxygenated flavone showing coupled resonances ($J = 9$ Hz) at approximately δ 6.9 and 8.1 for the C-6 and C-5 protons, respectively. A complete spectral analysis (UV, IR, ^1H NMR, MS, OR) gave data in close agreement with that previously published [18] for semiglabrin (**1**). The co-identity of the isolated compound with **1** was confirmed by its conversion to semiglabrinol (**2**), semiglabrinone (**3**) and tephroglabrin (**4**), all of which agreed closely with literature data [18]. ^{13}C NMR spectra were obtained for **1, 3** and **4** (see later).

The second major compound from the column analysed for $C_{24}H_{20}O_7$. Both the ^1H NMR and IR spectra were in close agreement with those published [19] for glabratephrin (**5**). The presence of an acetate group was confirmed by hydrolysis to the corresponding alcohol, glabratephrinol (**6**), with the anticipated shielding of the signal for the secondary alcohol C-4″ proton in the ^1H NMR spectrum. Subsequent reacetylation yielded the parent compound. This procedure also demonstrated the highly shielded nature of the acetate moiety of **5** (δ 1.63, cf. δ 2.20 in **1**). Spectral analysis of **6** also gave data in agreement with that published [19] although it was notable that the coupling observed in ^1H NMR spectrum between the 2″ protons and between the H and OH at 4″ by Vleggar *et al.* [19] was not apparent. Measurement of the OR of **5** gave a value of +185° compared with a value of −215° reported for the material from *T. semiglabra* [19]. It would appear therefore that the material obtained from *T. apollinea* is the enantiomer of that found in *T. semiglabra*. ^{13}C NMR of **5** and **6** are discussed later.

The major product of the third band from the column analysed for $C_{22}H_{18}O_5$. Bands at 1640 and 1740 cm^{-1} in the IR spectrum could be assigned to the flavone nucleus and an α,β-unsaturated furanone, respectively. A series of eight signals for aromatic protons together with a singlet at δ 3.96 in the ^1H NMR spectrum indicated a 7-methoxyflavone. The remaining seven protons were observed as two singlets: at δ 1.68 (6H) for *gem*-Me_2 and at δ 7.53 for an isolated olefinic proton. The position of the olefinic resonance is typical of the 4″ position of a furan-2-one [23] and less shielded than the 5″ position of furan-3-one which invariably yields signals resonating below δ 8.0 ([24, 25] and see structure 4). The absence of a signal for a proton α to the carbonyl indicates that the furan-2-one must be attached to the flavone through C-3″ and permits the assignment of structure **7** to the isolated compound. The structure assigned is supported by a comparison of the ^{13}C NMR spectra of **7** with those of **4** and **5**. This compound, which we have given the trivial name apollinine, does not appear to have been recorded previously.



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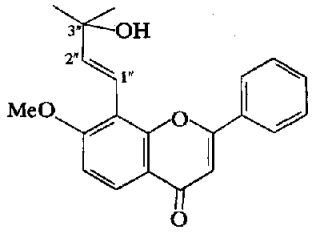

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The minor compound, isolated in small amounts from the mother liquors which had previously yielded apollinine, also analysed for $C_{22}H_{18}O_5$. Its physical and spectral characteristics were identical to those found previously for glabratephrinol (**6**) obtained by the hydrolysis of **5**. It remains uncertain as to whether **6** is a true natural product or an artefact derived from **5**. However the apparent absence of **2**, which with the major constituent **1** makes up a comparable pair of compounds, would tend to suggest that the appreciable amounts of **6** obtained strongly indicate its natural occurrence.

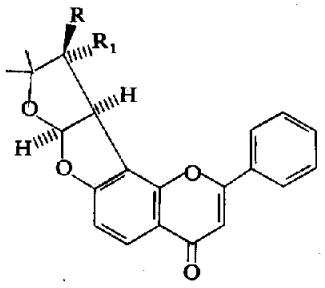
The final compound eluted from the column analysed for $C_{21}H_{20}O_4$. The ^1H NMR spectrum suggested a 7-methoxyflavone with seven of the nine remaining protons occurring as *gem*-Me_2 and OH substituents. The two remaining protons were found as an AB quartet ($J = 17$ Hz) centred at δ 6.87 and 6.93. These data, and all other spectral data obtained, were in close agreement with that previously reported [17] for lanceolatin-A (**8**), a constituent of the stem of *T. lanceolata* Gamb.

From a separate Et_2O extraction of a small quantity of seeds a further crystalline compound was obtained. This material analysed for $C_{23}H_{20}O_6$ and was in most respects identical to semiglabrin (**1**) although the OR (−384°) was somewhat elevated. However, significant differences were observed in the ^1H NMR resonances for the protons of the bifurano and acetate moieties (Table 1). The appearance of additional coupling between 5″ and 6″ protons was in close agreement with observations made by Smalberger *et al.* [18] regarding differences in the ^1H NMR spectra of methyl semiglabrinate and methyl pseudosemiglabrinate, stereoisomers of a decomposition product of **1**. The isolated compound must therefore be the corresponding stereoisomer of **1** and can be assigned the structure **9** and the trivial name of pseudosemiglabrin. The highly shielded resonance position of the acetate substituent of **9** (δ 1.51) is comparable to that observed in **5** and contrasts markedly with the more typical value of δ 2.22 observed in **1**. This shielding is considered to be caused by spatial interaction of the acetate with

Table 1. Comparison of chemical shift values (δ) of the protons of semiglabrin (**1**) and pseudosemiglabrin (**9**)

	2',4',6'-H	3',5'-H	3-H	5-H	6-H	2"-H	3"-H	5"-H	5"Ac	4"-Me_2
1	7.50–7.63	7.88–8.00	6.80	8.18	6.96	6.67	4.32	5.68	2.22	1.11,1.33
	m	*m*	*s*	*d*	*d*	*d*	*d*	*s*	*s*	*s*
J(Hz)				8	8	7	7			
9	7.52–7.61	7.80–7.95	6.78	8.19	6.96	6.53	4.63	5.60	1.51	1.16, 1.40
	m	*m*	*s*	*d*	*d*	*d*	*dd*	*d*	*s*	*s* *s*
J(Hz)				8	8	7	7/8	8		

heterocyclic ring systems in **5** and **9**. Oxidation of **9** gave pseudosemiglabrinone (**10**) similar in all respects to **3**.



9 R = OAc, R_1 = H
10 R = R_1 = O

^{13}C *NMR*

During the course of this study ^{13}C NMR spectra were obtained for compounds **1**, **3**, **4**, **5**, **6** and **7**. Assignments for the resonances of both the flavonoid nucleus and the C-7/C-8 substituent(s) are given in Table 2.

In comparison with resonance data published previously for 7-hydroxyflavone [26] and 7-methoxyflavone [27] the carbon resonances of the B-ring appeared little affected by the substituents. In most cases this was also true of C-2, C-3, C-4, C-4a and C-5 of the benzopyran moiety. In contrast pronounced shielding, of the order of 3–5 ppm, was observed at C-6 and at C-8a whilst at C-8 there was deshielding of between 5 and 9 ppm. As would be anticipated, carbons of the A and C rings showed greater variability in response to the differing C-7/C-8 substituents than did the relatively isolated B-ring carbons. A comparison of spectra obtained for glabratephrin (**5**) and glabratephrinol (**6**) showed a marked shielding at C-8a, C-2 and C-3 in the latter. This phenomenon was also observed for the C-3 proton in the ^1H NMR spectra (δ 6.80 in **5**; 6.33 in **6**) and is thought to indicate a strong steric interaction between the acetate and pyrone ring. This interaction is also responsible for the highly shielded resonance observed for the acetate in the ^1H NMR spectrum of **5**. Interpretation of ^1H NMR data would suggest a comparable situation in pseudosemiglabrin (**9**) but not in semiglabrin (**1**).

Table 2. ^{13}C NMR spectra of *Tephrosia* flavonoids and their derivatives

Carbon No.	**1**	**3**	**5**	**6**	**4**	**7**
2	162.3	163.4	162.4	163.9	161.8	161.6
3	108.1*d*	107.6*d*	107.3*d*	105.8*d*	107.6*d*	107.2*d*
4	177.8	177.8	176.8	178.5	178.4	177.5
4a	119.2	119.5	118.7	118.4	118.6	117.8
5	129.4*d*	129.4*d*	130.0*d*	129.8*d*	127.4*d*	128.0*d*
6	109.3*d*	109.2*d**	109.0*d*	109.3*d*	109.5*d*	109.3*d*
7	163.3	164.2	165.9	167.1	164.0	163.0
8	110.0	109.3	112.0	113.0	109.7	114.2
8a	153.7	153.9	153.7	158.1	155.1	158.0
1'	132.0	132.0	131.2	131.7	132.6	131.8
2',6'	126.7*d*	126.9*d*	126.1*d*	126.6*d*	126.9*d*	126.1*d*
3',5'	129.4*d*	129.4*d*	129.0*d*	129.1*d*	129.2*d*	128.9*d*
4'	132.0*d*	132.0*d*	131.7*d*	131.8*d*	131.7*d*	131.4*d*
7–OMe	—	—	—	—	56.6*q*	56.5*q*
2"	112.7*d*	109.5*d**	81.4*t*	81.8*t*	88.5	170.5
3"	—	—	58.9	61.6	204.5	124.0
4"	88.0	82.8	80.2*d*	81.2*d*	106.5	159.9*d*
5"	80.6*d*	210.3	85.2	87.9	176.4*d*	84.9
6"	53.0*d*	50.9*d*	—	—	—	—
7"	—	—	172.4	176.2	—	—
gem-Me_2	27.5*q*	27.2*q*	28.5*q*	28.5*q*	23.1*q*	25.8*q*
	23.2*q*	24.3*q*	22.2*q*	22.5*q*		
Ac	170.0		168.6			
	20.8*q*	—	19.7*q*	—	—	—

*Interchangeable signals; *d* = doublet, *t* = triplet, *q* = quartet. All spectra run in $CDCl_3$.

The non-flavonoid parts of the six compounds studied also gave ^{13}C resonances that could be assigned without ambiguity. In semiglabrin (**1**) the three tertiary carbons observed at 112.7, 80.6 and 53.0 ppm can be attributed to C-2″, C-5″ and C-6″, respectively. The C-4″ *gem*-Me_2 system occurred as a singlet at 88.0 ppm with the two Me substituents resonating at 27.5 and 23.2 ppm. The acetate group at C-5″ gave typical resonances [26]. Oxidation of **1** to **3** had a shielding effect of between 2.1 and 5.3 ppm on C-2″, C-4″ and C-6″ with the new C-5″ carbonyl group resonating at 210.3 ppm.

In glabratephrinol (**5**) the *gem*-Me_2 signals were found at 85.2 for C-5″ with the Me resonances 2 ppm more widely separated from one another than in **1**. The C-4″ resonance at 80.2 ppm agreed closely with the equivalent C-5″ resonance in **1**. The C-2″ and C-3″ resonances of the dihydrofuran ring occurred at 81.4 and 58.9 ppm, respectively, whilst the 174.2 ppm signal agreed with the literature data for the carbonyl of furan-2-ones [28]. Conversion of **5** to **6** caused appreciable deshielding of all carbons of the bi-furan skeleton but, as previously noted, had more pronounced effects on the C-ring of the flavone.

Of the six signals in the ^{13}C NMR spectrum of tephroglabrin (**4**) remaining after assignment of the flavonoid nucleus, that at 56.6 ppm can be attributed to the C-7 OMe and those at 88.5 and 23.1 ppm to C-2″ and equivalent Me resonances of a *gem*-Me_2 group. The carbonyl resonance at 204.5 ppm was of the same order as the analogous signal for C-5″ in **3**. The very highly deshielded doublet centred at 176.4 ppm must be assigned to C-5″ where there is direct attachment to O and a position β to the carbonyl. The remaining singlet at 106.5 ppm must, because of its relative shielding, be placed at C-4″, α to the carbonyl. Signals for OMe and C-Me_2 systems in apollinine (**7**) were comparable to those of **4**. In this case, however, the carbonyl resonance was found at 170.5, similar to that of the C-7″ signal in **5**. The olefinic carbon doublet, in this case influenced only by its position β to the carbonyl, was found at the relatively less deshielded position (cf. **4**) of 159.9 ppm.

DISCUSSION

T. apollinea yields appreciable quantities of a wide range of flavonoids of a type at present unique to, but seemingly quite common in, *Tephrosia*. As might have been anticipated from current hypotheses (Polhill, R. M., personal communication) concerning the phylogeny of this taxon the major constituents appear to be most closely allied to those reported from *T. semiglabra*. However, on the basis of our present knowledge there do appear to be very appreciable differences between the metabolic processes shaping the C-7/C-8 substituents in these taxa as is demonstrated by the isolation of enantiomers of **5** and by the occurrence of **7** in *T. apollinea*. The relationship between **5** and **7** is an interesting one in that it is possible to envisage them as products of a linear pathway leading from one to the other or as representing divergent pathways from a common precursor.

To date flavonoids have been studied in only a few taxa of *Tephrosia*. It is already apparent however that *C*-prenyl substituted flavonoids will prove to be quite common in the genus and are likely to receive attention as potential taxonomic markers. At present it appears possible to recognise three series among the *C*-prenyl flavonoids, the first two of which are represented by single taxa: (a) *C*-6-prenyl. The isoflavone elongatin from *T. elongata* E. Mey. [7]. (b) *C*-6/*C*-8-prenyl. The flavanones lupinifoline and lupinifolinol from *T. lupinifolia* Burch. [8]. (c) *C*-8-prenyl. This group contains the bulk of the *Tephrosia* flavonoids. All compounds of this group are characterized by an unsubstituted B-ring and are oxygenated in the A-ring at C-5 and C-7, or at C-7 only. So far the two oxygenation patterns appear mutually exclusive. In many cases the C-8 prenyl substituent has undergone a series of modifications of which those reported here for *T. apollinea* are typical. The patterns of modification found in the C-7/C-8 substituent appear to have occurred in parallel in the two flavonoid series (Table 3). The problem of deciding the relative weighting to be assigned to the oxygenation pattern of the flavonoid and to the cyclization processes undergone in the formation of the C-7/C-8 substituent remains to be resolved.

EXPERIMENTAL

UV spectra were run in EtOH and IR spectra as KCl discs. ^1H NMR spectra were run at 90 MHz in $CDCl_3$ using TMS as internal standard. ^{13}C NMR spectra were run at 25.1 MHz using the same solvent and standard and employing the FT mode. MS were obtained at 70 eV. Mps are uncorr. Petrol refers to the bp 40–60° fraction unless otherwise stated.

Plant material. Seeds and roots of *Tephrosia apollinea* (Del.) Link were collected from plants growing in the outskirts of Khartoum in November 1977. A voucher specimen has been deposited at the herbarium of the University of Khartoum.

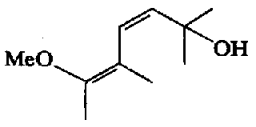
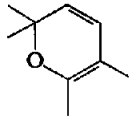
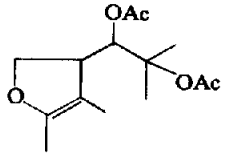
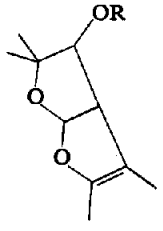
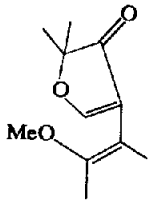
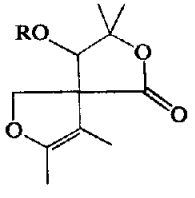
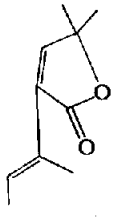
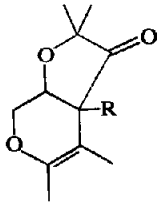
Isolation of compounds. Ground seeds (950 g) were defatted with petrol and then extracted in a Soxhlet with $CHCl_3$. Concn of the $CHCl_3$ extract yielded a brown oil (63 g). A portion of this oil (15 g) was subjected to column chromatography over Si gel. Elution with petrol–EtOAc (3:2) gave **1** (680 mg) followed by **5** (535 mg). Elution with petrol–EtOAc (3:7) gave **7** (138 mg). Prep. TLC of the mother liquors from which **7** crystallized (Si gel G, solvent C_6H_6–EtOAc, 8:3) yielded **6** (78 mg). Further elution of the column with $CHCl_3$–Me_2CO (9:1) and subsequent PLC (Si gel G, solvent C_6H_6–EtOAc, 19:5) gave **8** (211 mg). Direct extraction of a second sample of seeds (10 g) from the same source with Et_2O gave a ppt. which on repeated recrystallization gave **9** (61 mg). Similar analyses of the powdered root revealed the presence of all the above compounds in approximately the same proportions.

Identification of isolated compounds. (−)-*Semiglabrin* (**1**). Needles from $CHCl_3$–MeOH, mp 253–256° (lit. [18] 176–178°). $[\alpha]_D^{24}$ −293° (*c* 0.42, $CHCl_3$) (lit. [18] −369°). Found: M^+ 392.1256; $C_{23}H_{20}O_6$ requires: 392.1260. UV λ_{max} nm: 249, 257, 310. IR ν_{max} cm^{-1}: 1735, 1645. ^1H NMR (Table 1). ^{13}C NMR: (Table 2). MS *m/e* (%): 392 (22), 332 (100), 317 (32), 303 (13), 289 (22), 263 (18).

Semiglabrinol (**2**). **1** (324 mg) was dissolved in the minimum amount of 0.1% KOH in EtOH and allowed to stand for 24 hr. The mixture was diluted with H_2O and extrd with $CHCl_3$ to yield **2**, mp 260–262° (lit. [18] 273–275°). Identical in all respects (UV, IR, ^1H NMR, MS) to **2** [18].

Semiglabrinone (**3**). **2** (240 mg) was dissolved in Me_2CO

Table 3. C-8 prenylated flavonoids of *Tephrosia*

C-7/C-8 substituents	5/7-Oxygenated flavonoids	7-Oxygenated flavonoids
	(*cis*)-Tephrostachin *T. polystachyoides* E. Mey. [14]	(*trans*)-Lanceolatin-A *T. lanceolata* [17] *T. apollinea*
	Obovatin*, obovatin Me ether* *T. obovata* Merr. [9]	
	(+)-Polystachin *T. polystachyoides* [16]	
	(+)-Multijugin (R = Ac) (+)-Multijuginol (R = H) *T. multijuga* Young [15]	(−)-Semiglabrin (R = Ac) *T. semiglabra* [18] *T. apollinea* (−)-*Pseudosemiglabrin* (R = Ac) *T. apollinea* (−)-Semiglabrinol (R = H) *T. semiglabra* [18]
	Tachrosin *T. polystachyoides* [12]	
		(−)-Glabratephrin (R = Ac) *T. semiglabra* [19] (+)-glabratephrin (+)-Glabratephrinol (R = H) *T. apollinea*
		Apollinine *T. apollinea*
	(−)-Stachyoidin (R = H) (−)-Tephrodin (R = OAc) *T. polystachyoides* [13]	

*Flavanone nucleus; otherwise always a flavone nucleus.

(50 ml) and titrated with Jones' reagent. Work-up of the reaction mixture gave **3** (210 mg) as needles, mp 157–161° (lit. [18] 159–161°). Found: M^+ 348.0987; $C_{21}H_{16}O_5$ requires: 348.0998. UV and IR as lit. [18]. ^1H NMR: δ 1.22, 1.41 (6H, 2×*s*, 5″-Me_2), 4.52 (1H, *d*, *J* = 6 Hz, 6″-H), 6.76 (1H, *d*, *J* = 6 Hz, 2″-H), 6.77 (1H, *s*, 3-H), 6.97 (1H, *d*, *J* = 9 Hz, 6-H), 7.50–7.60 (3H, *m*, 2′,4′,6′-H), 8.06–8.16 (2H, *m*, 3′,5′-H), 8.13 (1H, *d*, *J* = 9 Hz, 5-H). ^{13}C NMR: (Table 2). MS *m/e* (%): 348 (53), 332 (11), 262 (87), 160 (100).

Tephroglabrin (**4**). **3** (190 mg) was dissolved in dry Me_2CO (40 ml) and MeI (1.5 ml) and dry K_2CO_3 (2 g) added. The mixture was refluxed for 3 hr, filtered and extd with $CHCl_3$ to give **4** (146 mg) as needles from C_6H_6–petrol, mp 243–246° (lit. [18] 232–233°). Found: M^+ 362.1162; $C_{22}H_{18}O_5$ requires: 362.1154. UV and IR as lit. [18]. ^1H NMR: δ 1.58 (6H, *s*, 2″-Me_2), 3.92 (3H, *s*, 7-OMe), 6.72 (1H, *s*, 3-H), 7.06 (1H, *d*, *J* = 9 Hz, 6-H), 7.39–7.50 (3H, *m*, 2′,4′,6′-H), 7.70–7.83 (2H, *m*, 3′,5′-H), 8.21 (1H, *d*, *J* = 9 Hz, 5-H), 8.38 (1H, *s*, 5″-H). ^{13}C NMR: (Table 2). MS: *m/e* (%) 362 (100), 347 (71), 305 (13), 276 (33).

(+)-*Glabratephrin* (**5**). Plates from $CHCl_3$–MeOH, mp 234–237° (lit. for (−)-**5** [18] 227–228°). $[\alpha]_D^{24}$ +185° (*c* 0.73, $CHCl_3$). Found: M^+ 420.1220; $C_{24}H_{20}O_7$ requires: 420.1209. UV λ_{max} nm: 245, 255, 308. IR ν_{max} cm^{-1}: 1770, 1745, 1640. ^1H NMR: δ 1.52, 1.57, 1.62 (9H, 3×*s*, 5″-Me_2 and 4″-Ac), 5.01 (2H, *s*, 2″-CH_2), 5.45 (1H, *s*, 4″-H), 6.79 (1H, *s*, 3-H), 7.00 (1H, *s*, *J* = 9 Hz, 6-H), 7.51–7.63 (3H, *m*, 2′,4′,6′-H), 7.86–8.00 (2H, *m*, 3′,5′-H), 8.24 (1H, *d*, *J* = 9 Hz, 5-H). ^{13}C NMR: (Table 2). MS: *m/e* (%) 420 (86), 317 (100), 316 (67), 305 (19), 291 (18), 263 (43), 161 (20).

(+)-*Glabratephrinol* (**6**). **5** (290 mg) was hydrolysed as previously described for **2** from **1**, to yield **6** (211 mg) as needles from EtOAc, mp 223–226° (lit. [19] 223–225°). Found: M^+ 378.1099; $C_{22}H_{16}O_6$ requires: 378.1103. UV and IR as lit. [19]. ^1H NMR: δ 1.57, 1.74 (6H, 2×*s*, 5″-Me_2), 4.53 (1H, *s*, 4″-H), 4.93 (2H, *s*, 2″-CH_2), 5.35 (1H, *s*, replaceable by D_2O, 4″-OH), 6.32 (1H, *s*, 3-H), 6.95 (1H, *d*, *J* = 9 Hz, 6-H), 7.28–7.42 (3H, *m*, 2′,4′,6′-H), 7.57–7.70 (2H, *m*, 3′,5′-H), 7.63 (1H, *d*, *J* = 9 Hz, 5-H). ^{13}C NMR: (Table 2). MS *m/e* (%): 378 (61), 291 (33), 263 (100), 189 (11), 161 (36). This material proved identical in all respects to a natural sample of glabratephrinol isolated from later eluates of the Si gel column.

Apollinine (**7**). Needles from $CHCl_3$–MeOH, mp 274–276°. Found: 362.1143; $C_{22}H_{18}O_5$ requires: 362.1154. UV λ_{max} nm: 244, 255, 312. IR $2\nu_{max}$ cm^{-1}: 1740, 1640, 1595, 1375, 1280. ^1H NMR: δ 1.67 (6H, *s*, 5″-Me_2), 3.96 (3H, *s*, 7-OMe), 6.76 (1H, *s*, 3-H), 7.10 (1H, *d*, *J* = 9 Hz, 6-H), 7.53 (1H, *s*, 4″-H), 7.43–7.55 (3H, *m* 2′,4′,6′-H), 7.73–7.86 (2H, *m*, 3′,5′-H), 8.26 (1H, *d*, *J* = 9 Hz, 5-H). ^{13}C NMR: (Table 2). MS *m/e* (%): 362 (100), 291 (34), 277 (34), 189 (99).

Lanceolatin-A (**8**). Needles from $CHCl_3$–MeOH, mp 189–191° (lit. [17] 187–189°). Found: M^+ 336.1371; $C_{21}H_{20}O_4$ requires 336.1361. UV and IR as lit. [17]. ^1H NMR: ($CDCl_3$/DMSO-d_6): δ 1.53 (6H, *s*, 3″-Me_2), 3.99 (3H, *s*, 7-OMe), 4.50 (1H, *s*, replaceable by D_2O, 3″-OH), 6.78 (1H, *s*, 3-H), 6.87, 6.93, (2H, AB*q*, *J* = 17 Hz, 1″,2″-H), 7.11 (1H, *d*, *J* = 9 Hz, 6-H), 7.50–7.60 (3H, *m*, 2′,4′,6′-H), 7.90–8.05 (2H, *m*, 3′,5′-H), 8.02 (1H, *d*, *J* = 9 Hz, 5-H). MS *m/e* (%): 336 (17), 317 (100), 303 (33), 287 (85), 265 (31), 263 (10).

Pseudosemiglabrin (**9**). Plates from Et_2O, mp 181–183°. $[\alpha]_D^{24}$ −384° (*c* 0.49 $CHCl_3$). Found: 392.1258; $C_{23}H_{20}O_6$ requires: 392.1260. UV and IR identical to **1**. ^1H NMR: (Table 1). MS as **1**.

Pseudosemiglabrinone (**10**). **9** (51 mg) treated with Jones' reagent and worked up as previously described under **3** gave **10** (42 mg) as needles, mp 186–190°. UV, IR and MS as **3**. ^1H NMR: 1.25, 1.42 (6H, 2×*s*, 4″-Me_2), 4.54 (1H, *d*, *J* = 6 Hz, 6″-H), 6.79 (1H, *s*, 3-H), 6.81 (1H, *d*, *J* = 6 Hz, 2″-H), 6.99 (1H, *d*, *J* = 9 Hz, 6-H), 7.50–7.63 (3H, *m*, 2′,4′,6′-H), 8.05–8.15 (2H, *m*, 3′,5′-H), 8.13 (1H, *d*, *J* = 9 Hz, 5-H).

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