8-Substituted Flavonoids and 3'-Substituted 7-Oxygenated Chalcones from *Tephrosia purpurea*

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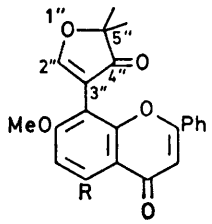
The isolation and characterisation of ten unusual and closely related flavonoids from the roots of *T. purpurea* are reported. Three of these compounds are new natural products and they all contain an isopentenyl derived unit attached to C-8 (in the flavones) or the corresponding C-3' (in the chalcones), suggesting that they are derived from a common biosynthetic precursor. The ^{1}H and ^{13}C n.m.r. spectra of use in structure elucidation are reported.

8-SUBSTITUTED isoflavonoids such as toxicarol isoflavone [1] and rotenoids [2] are well known. Recently compounds such as arthroxin,[3] obtusifolin [4] and constituents of 'dragons blood' resin,[5] have been shown to be flavonoids substituted at C-8 with complex substituents. Of particular interest from the point of view of the present paper are tachrosin (1),[6] isolated from *T. polystachyoides*, the very recently characterised apollinine (2) from *T. apollinea*,[7] and semiglabrin (3) and semiglabrinol (4) from *T. semiglabraa*.

Our continuing phytochemical investigation [8] of the roots of *T. purpurea* (Leguminosae) has resulted in the isolation of three new natural products to which we assign structures (5), (6), and (7). In addition we have also isolated and independently characterised the butenolide (2) and the known compounds (3), (4),[9] and (8)—(11),[10–13] to which (5), (6), and (7) may be related biosynthetically.

The structures of compounds (2), (3), and (4) (Table 1) were established on the basis of their n.m.r. and mass spectra, as outlined below. The structures assigned to these compounds on the basis of their chemical trans-



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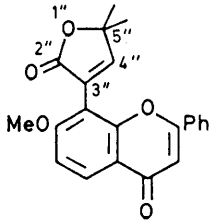

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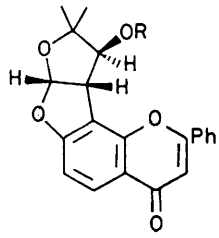

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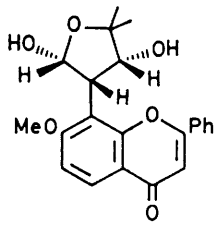

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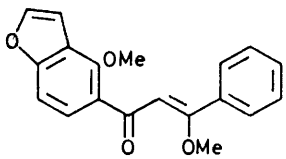

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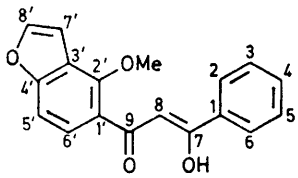

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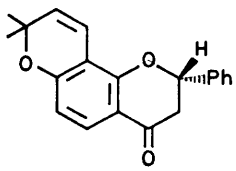

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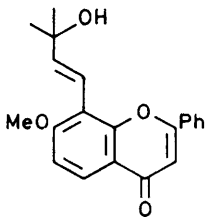

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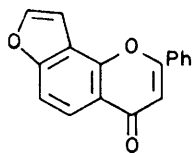

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TABLE 1

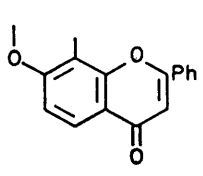
Compounds isolated from *T. purpurea*

		Yield (mg)	M.p. (°C)	$[\alpha]_D$(°)	Ref.
(2) Apollinine	$C_{22}H_{18}O_5$	144	261—262	0	7
(3) Semiglabrin	$C_{23}H_{20}O_6$	95	254—255	−273	9
(4) Semiglabrinol	$C_{21}H_{18}O_5$	120	245—247	−270	9
(5) Tephroglabrin	$C_{22}H_{18}O_5$	70	226—228	0	9
(6) Tepurindiol	$C_{22}H_{22}O_6$	20	195—197	−48	
(7) *O*-Methylpongamol	$C_{19}H_{16}O_4$	3200			
(8) Pongamol	$C_{18}H_{14}O_4$	4500	127—129		10
(9) Isolonchocarpin	$C_{20}H_{18}O_3$	200	108—110	−93	8, 11
(10) Lanceolatin A	$C_{21}H_{20}O_4$	1200	187—189		12
(11) Lanceolatin B	$C_{17}H_{10}O_3$	2600	127/147.9		13

formations and spectral properties are identical to those given for apollinine (2), semiglabrin (3), and semiglabrinol (4).

Semiglabrin (3) and semiglabrinol (4) are closely related in that acetylation of (4) yields (3) whilst hydrolysis of (3) gives (4) showing that the same basic skeleton is present in each case. Compounds (3) and (4) lose acetic acid and water respectively in the mass spectrometer to give a base peak at *m/e* 332.1052 ($C_{21}H_{16}O_4$), after which the mass spectra are virtually indistinguishable. They also give rise to a significant peak at *m/e* 102 corresponding to $PhC{\equiv}CH^{+\bullet}$, a fragment commonly observed in the mass spectra of flavones with unsubstituted B rings.[14]

The correspondence between some of the ^{13}C n.m.r. signals of (3) and (4) and those of 7-methoxyflavone (Table 3),[15] together with the presence of two *ortho* coupled protons in the ^1H n.m.r. spectrum (Table 2), leaves little doubt that (3) and (4) both contain the part structure (12). This part structure accounts for all of the low field signals in the ^{13}C n.m.r. spectrum of (4) and indicates that it contains no further unsaturation in the form of carbonyl or alkene groupings. The presence of a *gem*-dimethyl group is indicated by two singlets (3 H each) at τ 8.58 and 9.08 in the ^1H n.m.r. spectrum of (4) and by the presence of only one aliphatic quaternary carbon atom at 88.4 p.p.m. in the ^{13}C n.m.r. spectrum. Two of the remaining protons are clearly coupled to one another and their chemical shift (τ 3.47 and 5.78) suggests that one of them is attached to a carbon atom bearing two oxygen atoms,[16] while the other is probably benzylic as in (13). The third proton in this system appears as a broad singlet at τ 5.78 and is moved downfield to τ 4.40 on acetylation. Decoupling experiments on the acetate (3) reveal a small (1—1.5 Hz) coupling between this signal and the signal at τ 5.76, leading to part structure (13) for this part of the molecule.



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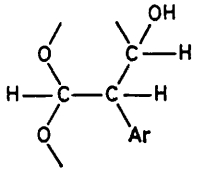
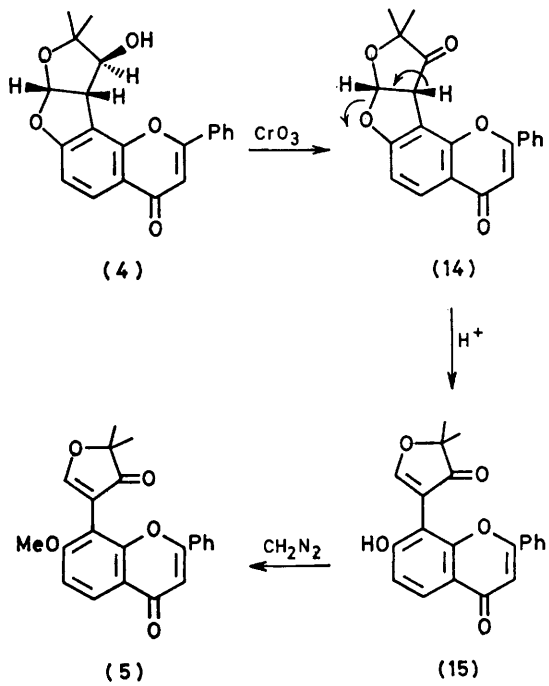


(13)

Combining these various pieces of information leads to structures (3) and (4) for semiglabrin and semiglabrinol, which are in complete accord with the structures previously assigned to these compounds.[9] The relative stereochemistry of (3) and (4) follows from the small coupling constant observed between H-3″ and H-4″, which is consistent with the dihedral angle of *ca.* 115° present in the assigned structures. We have confirmed the structures of (3) and (4) by their conversion into semiglabrinone (14), isosemiglabrinone (15) and tephroglabrin (5) as outlined below.

The ^1H and ^{13}C n.m.r. spectra of compound (2) indicate that it is an 8-substituted 7-methoxyflavone. Its lack of optical activity and the fact that the two methyl groups of the gem dimethyl grouping are equivalent in both the ^1H and ^{13}C n.m.r. spectra (Tables 2 and 3) indicate that, in common with tachrosin (1), tephroglabrin (5) and isosemiglabrinone (15), it contains a planar ring attached to C-8 of the flavone. The ^{13}C n.m.r. and i.r. spectra confirm that it is a γ-lactone



SCHEME 1

TABLE 2

^{1}H N.m.r. spectra of flavones [a,b]

	(4) [c]	(3)	(14)	(15)	(5)	(6) [c]	(2)	(1)
3	3.25 (s)	3.28 (s)	3.26 (s)	3.21 (s)	3.31 (s)	3.17 (s)	3.32 (s)	3.38 (s)
5	*ca.* 1.8	1.85 (d, *J* 8)	*ca.* 1.8	1.89 (d, *J* 7)	1.81 (d, *J* 9)	2.00 (d, *J* 9)	1.82 (d, *J* 8)	
6	3.18 (d, *J* 9)	3.12 (d, *J* 8)	3.15 (d, *J* 9)	2.92 (d, *J* 7)	2.97 (d, *J* 9)	2.85 (d, *J* 9)	2.94 (d, *J* 8)	3.56 (s)
2′3′4′	2.0—2.2 (m, 2 H)	2.0—2.3 (m, 2 H)	1.8—2.0 (m, 2 H)	2.1—2.3 (m, 2 H)	2.2—2.4 (m, 2 H)	1.8—2.0 (m, 2 H)	2.2—2.35 (m, 2 H)	2.30 (m, 2 H)
5′6′	2.4—2.6 (m, 3 H)	2.4—2.7 (m, 3 H)	2.3—2.6 (m, 3 H)	2.3—2.6 (m, 3 H)	2.5—2.7 (m, 3 H)	2.4—2.6 (m, 3 H)	2.4—2.7 (m, 3 H)	2.57 (m, 3 H)
2″	3.47 (d, *J* 7)	3.42 (d, *J* 7)	3.25 (d, *J* 6)	1.04 (s)	1.64 (s)	4.38 (d, *J* 5)		1.74 (s)
3″	*ca.* 5.78	5.76 (d, *J* 7)	5.48 (d, *J* 6)			5.82 (dd, *J* 5, 10)		
4″	5.78 (d, *J* 6) [d]	4.40br (s)				5.60 (d, *J* 10) [f]	2.48 (s)	
Me_2	9.08 (s), 8.58 (s)	8.49 (s), 8.72 (s)	8.60 (s), 8.78 (s)	8.37 (s, 6 H)	8.46 (s, 6 H)	8.60 (s), 8.70 (s)	8.46 (s, 6 H)	8.46 (s)
OH	4.38 (d, *J* 6)					5.1, 3.9		
OAc		7.82 (s)						
OMe					6.11 (s)	6.05 (s)	6.07 (s)	6.10 (s)

[a] All values given in τ; *J* values in Hz. [b] Spectra run in $CDCl_3$ unless otherwise indicated. [c] Run in $CDCl_3$–$(CD_3)_2SO$ (3 : 1). [d] Broad singlet after D_2O exchange. [e] Run in $CDCl_3$–$(CD_3)_2SO$ (1 : 1). [f] After D_2O exchange.

TABLE 3

^{13}C N.m.r. spectra [a,b]

	7-MeO flavone [d,15]	(4) [c]	(3)	(14)	(15)	(5)	(2)	(1)
2	162.6	162.1	162.9	163.1	163.2	161.3	160.6	116.1
3	107.2	106.9	107.8	107.4	108.0	107.4	105.0	108.8
4	177.4	177.1	177.4	177.4	177.9	178.1	174.4	177.8
5	126.7	127.4	128.9	129.1	126.3	126.5	125.3	161.3
6	114.0	112.8	112.4	109.1	117.7	109.4	108.5	91.8
7	163.7	163.5	163.8	163.8	160.9	163.7	159.8	161.5
8	100.2	114.5	112.4	109.3	110.9	109.4	115.7	98.4
9	157.7	153.0	153.3	153.5	154.8	155.1	152.5	156.8
10	117.6	118.2	118.8	119.2	117.7	118.3	121.0	109.1
1′	131.6	131.4	131.6	131.6	132.2	132.3	129.7	131.8
2′6′	125.8	126.2	126.4	126.5	126.8	127.1	124.3	126.2
3′5′	128.7	129.0	129.1	129.1	129.4	128.8	127.1	128.8
4′	131.1	131.4	131.6	131.7	131.6	131.4	129.7	131.1
2″		108.6	109.6	108.9	178.5	175.8	168.1	175.9
3″		54.8	52.9	50.5	104.7	106.1	106.4	109.5
4″		80.0	80.5	209.8	208.6	204.0	159.3	204.6
5″		88.4	87.8	82.5	89.3	88.2	83.0	88.0
Me_2		23.2, 27.4	23.2, 27.5	24.2, 27.1	23.2	23.0	23.5	23.0
OAc			169.6, 20.8					
OMe	55.9					56.4		56.3

[a] Chemical shifts in p.p.m. downfield from $SiMe_4$. [b] All spectra in $CDCl_3$ unless otherwise indicated. [c] Run in $CDCl_3$–$(CD_3)_2SO$ (3 : 1). [d] Run in $(CD_3)_2SO$.

(168.1 p.p.m. and 1 740 cm^{-1}) and the ^{1}H n.m.r. spectrum confirms the presence of an olefinic hydrogen β to the carbonyl group. Hence structure (2) is assigned to this compound which is therefore identical with apollinine.[7] It is unusual in that it represents the first example of a natural product containing a butenolide unit attached to a flavone.

Tephroglabrin (5) has not been previously reported as a natural product but has been prepared by treating semiglabrinone (14) with methyl iodide and dry K_2CO_3.[7] In our hands Jones' oxidation of semiglabrinol (4) leads initially to semiglabrinone (14), which on contact with silica gel or on treatment with acid, isomerises to iso-semiglabrinone (15). This compound, in addition to

being optically inactive and having two equivalent methyl groups, is soluble in the cold in aqueous alkali and has a carbonyl stretching frequency of 1 700 cm^{-1}. The ^1H n.m.r. spectrum confirms that it is an αβ unsaturated ketone since the two aliphatic protons H-2″ and H-3″ in (14) are replaced in (15) by an olefinic proton giving rise to a singlet at τ 1.04, and similar changes are also observed in the ^{13}C n.m.r. spectrum. Methylation of isosemiglabrinone with diazomethane in ether affords tephroglabrin (5), identical in all respects with the natural product.

The ^1H and ^{13}C n.m.r. spectra of tepurindiol (6) show it to be a 7-methoxyflavone substituted at C-8. This accounts for all of the low field ^{13}C n.m.r. signals. The ^1H n.m.r. spectrum contains two signals at τ 3.9 and 5.1 (see Table 2) which are removed by D_2O exchange. This process also greatly simplifies the signals at τ 4.38 and 5.60, which then appear as two doublets (*J* 5 and 10 Hz), both coupled to H-3″. This observation suggests that the two hydroxy-groups are attached to C-2″ and C-4″ and, together with the presence of an aromatic methoxy-group at τ 6.05 and two non-equivalent methyl groups at τ 8.60 and 8.70, leads to structure (6) for this compound. It does not show a molecular ion in its mass spectrum but gives instead a peak at *m/e* 364.1311 ($C_{22}H_{20}O_5$) corresponding to ($M - H_2O$). Other peaks are observed at *m/e* 349 ($M - H_2O$ — Me) and *m/e* 346 ($M - 2H_2O$) while the base peak occurs at *m/e* 365 and corresponds to the fragment ion (16). The flexibility of the five-membered ring together with uncertainties regarding its conformation makes it rather difficult to establish the precise stereochemistry of tepurindiol. However the large coupling constant (10 Hz) between H-3″ and H-4″ would be consistent with the configuration and conformation shown in (17) and is, therefore, taken to indicate that the configuration at C-4″ is probably as shown.

The sixth compound was rapidly shown to be one of the two β-methoxychalcones (7) or (18), since on treatment with alcoholic HCl it afforded pongamol (8). Indeed

TABLE 4

^1H N.m.r. spectra of β-methoxychalcones and 1,3-diketones [a,b]

	(8)	(19) [18]	(7)	(18) [c]	(20) [18]	$PhCOCH_3$ [17]	$PhC(Me)=CH_2$ [17]
8	2.85 (s, 2 H)	3.72 (s)	3.72 (s)	3.62 (s)	3.77 (s)		
5′	2.12 (d, *J* 9)						
6′	2.72 (d, *J* 9)	3.93 (s)			4.01 (s)		
2/6	2.02 (m, 2 H)	2.20 (m, 2 H)	2.3—3.2 (m)	2.3—3.2 (m)	2.30 (m, 2 H)	2.1 (m, 2 H)	2.5—2.8 (m)
3/4/5	2.50 (m, 3 H)	2.67 (m, 3 H)		and	2.70 (m, 3 H)	2.4—2.7	
7′	2.40 (d, *J* 2)	3.60 (d, *J* 10)		2.1 (m)	3.67 (d, *J* 10)	(m, 3 H)	
8′	3.02 (d, *J* 2)	4.63 (d, *J* 10)			4.70 (d, *J* 10)		
OH	−6.95br (s)	−5.7br (s)					
ROMe			6.15 (s)	6.11 (s)	6.23 (s)		
ArOMe	5.89 (s)	6.27 (s)	5.94 (s)	6.05 (s)	6.40 (s)		
Me_2		8.60 (s)			8.63 (s)		

[a] All values given in τ; *J* values in Hz. [b] Spectra run in $CDCl_3$. [c] Spectrum obtained by subtraction from mixture of (7) and (18).

TABLE 5

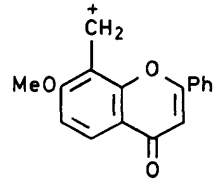
^{13}C N.m.r. spectra of pongamol derivatives [a,b]

	(8)	(7)	$PhCH=CH_2$ [19]	Δ^1	Δ^2	(18) [c]	$PhCOCH_3$ [d]	Δ^2	Δ^1
7	184.28	170.57				189.95			
8	97.90	103.21				99.72			
9	186.10	191.04				169.33			
6′	126.50	126.76				126.08			
5′	105.28	105.13				105.14			
4′	152.78	152.81				151.22			
3′	122.18	?				121.13			
2′	158.73	158.22				157.40			
1′	119.58	119.13				118.48			
1	135.70	135.48	137.6	−2.12	1.62	139.76	137.1	2.66	2.16
2/6	128.63	128.95	126.1	2.85	0.75	128.19	128.2	−0.01	2.09
3/5	127.11	127.63	128.3	−0.67	−0.77	127.99	128.4	−0.41	−0.31
4	132.14	129.61	127.6	2.01	−3.29	131.84	132.9	−1.06	4.24
8′	144.83	144.63				144.10			
7′	107.03	106.45				105.98			
ROMe		56.39				56.36			
ArOMe	61.10	61.28				60.22			

$\Delta^1 = \delta - \delta PhCH=CH_2$
$\Delta^2 = \delta - \delta PhCOCH_3$

All values given in p.p.m. downfield from $SiMe_4$. [b] Spectra run in $CDCl_3$. [c] Spectrum obtained by subtraction from mixture of compounds (7) and (18). [d] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' John Wiley and Sons, New York, 1972, No. 288.

methylation of pongamol with diazomethane afforded a mixture of (7) and (18). The n.m.r. spectra of these compounds were broadly similar but showed a number of significant differences. Firstly the ^{1}H n.m.r. spectrum of the natural isomer (see Table 4) contains no signals below τ 2.3 whereas the spectrum of the unnatural isomer contains a multiplet at τ 2.1 typical of the *ortho* hydrogens



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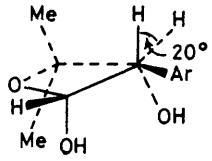
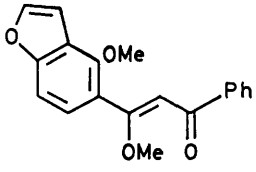


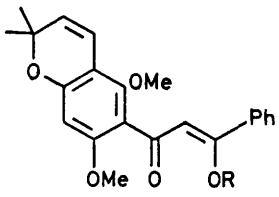
(17)

of a PhCO group (*cf.* $PhCOCH_3$).[17] This suggests that the naturally occurring isomer has structure (7). This conclusion is confirmed by comparing the ^{13}C chemical shifts of the phenyl ring of (7) and (18) with those of styrene and acetophenone (see Table 5). Thus C-4 resonates at 129.61 in the spectrum of the naturally occurring enol ether (7) but at 131.84 in the spectrum of its isomer (18). The same carbon atom appears at 127.6 and 132.9 in the spectra of styrene and acetophenone respectively. As shown in Table 5 reversing the structures of the two enol ethers would lead to significantly greater chemical-shift differences in each case. The naturally occurring β-methoxychalcone is therefore assigned structure (7).

There are also interesting differences in the mass spectra of the two compounds (see Experimental section). In particular the base peak in the mass spectrum of the synthetic isomer (18) occurs at *m/e* 277.0863 and corresponds to loss of CH_3O from the molecular ion. This in itself is unusual and can be most readily accounted for by the process depicted in Scheme 2. This, in turn, supports the above structural assignment since a similar mechanism cannot be drawn starting

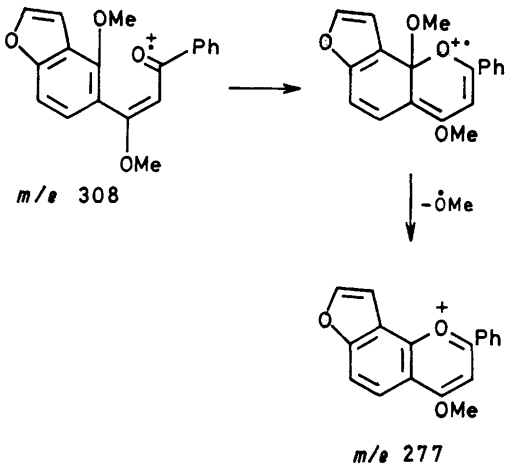


(18)



(19) R = H
(20) R = Me

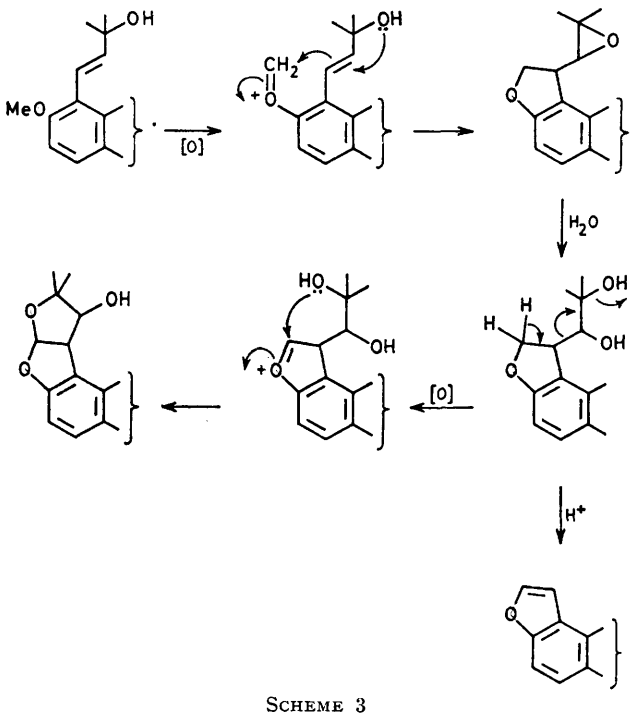
from the naturally occurring isomer (7). Indeed the observation of an intense (M − 31) peak in the mass spectrum of praecansone A (20) [18] along with the clear indication of a PhCO group in its ^{1}H n.m.r. spectrum (Table 4) suggests that the isomeric structure (not shown) may be more appropriate for this compound.



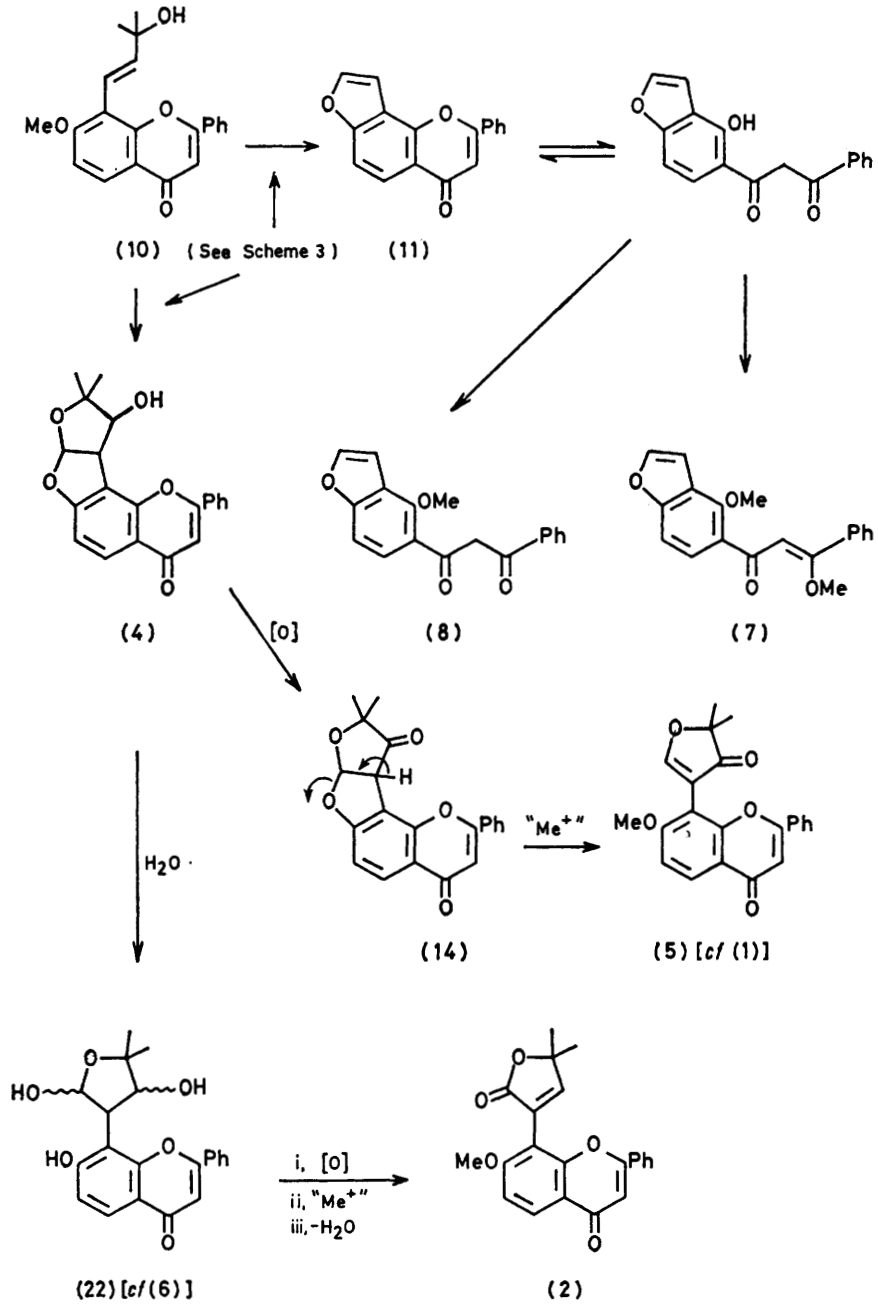
SCHEME 2

The four remaining compounds (8)—(11) were identified by comparison of their physical and spectral data with those reported in the literature [10-13] and by comparison with authentic samples.

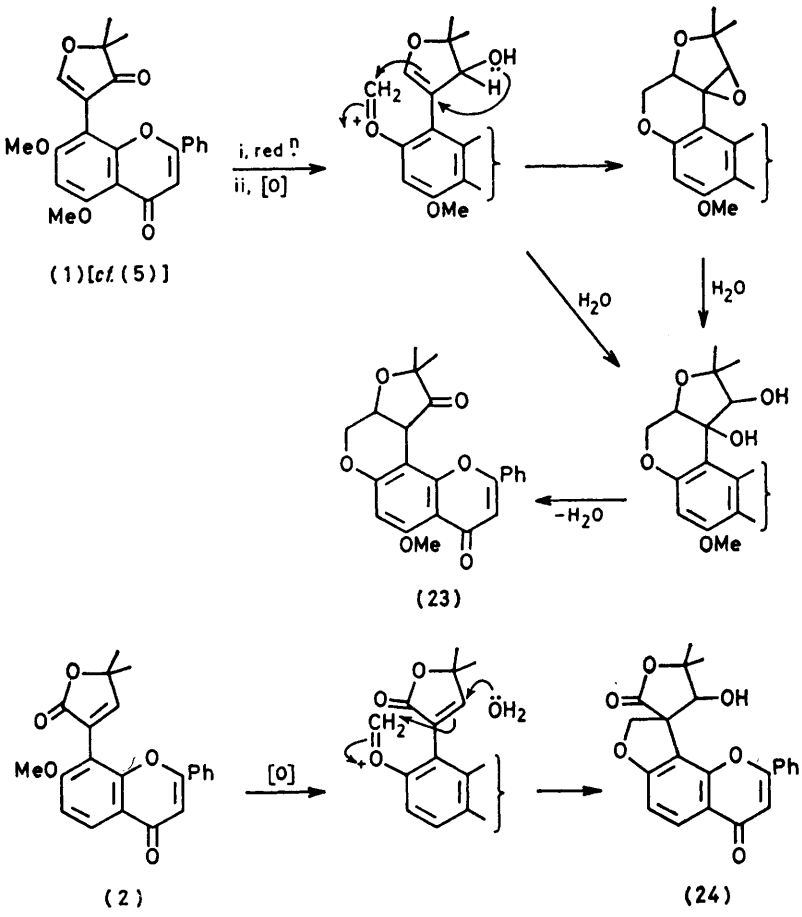
It would appear that the complex substituents at C-8 arise from the ability of *Tephrosia* species to oxidise a 7-OMe group to a $-\overset{+}{O}=CH_2$ group (see Scheme 3), in the same way that closely related species of Leguminosae oxidise the 2′-OMe group of isoflavonoids to yield rotenoids.[20] A pattern that explains the various C-8 substituents in *T. purpurea* and *T. apollinea* is shown in Scheme 4. In *T. polystachoides* this process is taken even further and the carbon of yet another 7-OMe group is incorporated into the additional rings attached to C-7 and C-8 (see Scheme 5).



SCHEME 3



SCHEME 4



(1)[*cf.* (5)] (23) (2) (24)

SCHEME 5

EXPERIMENTAL

^1H and ^{13}C n.m.r. spectra were recorded on Varian HA 100 and XL 100 instruments respectively, using tetramethylsilane as internal standard. Mass spectra were recorded on an A.E.I. MS9 double focusing instrument. The m.p.s of the extractives are recorded in Table 1, their ^1H n.m.r. in Tables 2 and 4 and their ^{13}C n.m.r. in Tables 3 and 5.

Extraction of Roots of T. purpurea.—The roots were collected from plants growing around Visakhapatnam. The powered roots (3.2 kg) were extracted with hot chloroform and the extracts evaporated to give a brown resinous semi-solid material (140 g) which was subdivided into petroleum-soluble (65 g) and benzene-soluble (75 g) fractions. Chromatography of the petroleum-soluble fraction over silica gel afforded four compounds: pongamol (8), isolonchocarpin (9), lanceolatin A (10) and lanceolatin B (11). The isolation and identification of these compounds has been reported earlier.[8]

Extensive chromatography of the benzene-soluble fraction over silica gel gave pongamol (8), lanceolatin A (10), and lanceolatin B (11) in addition to six compounds whose identification is described below.

Identification of β-*Methoxychalcone* (7).—This compound was eluted with pure benzene and obtained as a yellow oil (3.2 g) (Found: M^+, 308.1049. $C_{19}H_{16}O_4$ requires 308.1049), $\lambda_{max.}$ ($CHCl_3$) 242 and 352 nm; $\nu_{max.}$ (KBr) 1 660 cm^{-1}; *m/e* 308(8%), 291(11), 264(19), 263(100), 176(13), 175(87), 161(29), 160(30), 151(12), 149(11), 145(11), 117(10), and 105(63). Accurate mass measurements: 263.0707 ($C_{17}H_{11}O_3$), 175.0395 ($C_{10}H_7O_3$), and 161.0594 ($C_{10}H_9O_2$).

Demethylation of β-*Methoxychalcone* (7).—The compound (50 mg) was dissolved in ethanol and treated with two drops of concentrated aqueous HCl. The mixture was heated to 85 °C for 4—5 min and set aside to cool. White crystals separated and were recrystallised from chloroform to give rhombic crystals, m.p. 127—129 °C, identical with pongamol (8),[8] *m/e* 294(13%), 264(29), 263(100), 176(11), 175(95), 160(24), 148(11), and 105(32).

Methylation of Pongamol (8).—Pongamol (100 mg) in dry ether (5 ml) was treated with CH_2N_2–Et_2O at 0 °C for 24 h. The product was obtained as a yellow oil and shown to be a mixture of the two isomeric β-methoxychalcones (7) and (18), *m/e* 308(5%), 291(13), 278(17), 277(100), 263(32), 175(43), 161(23), 160(24), and 105(42). Accurate mass measurements: *m/e* 308.1049 ($C_{19}H_{16}O_4$) and 277.0863 ($C_{18}H_{13}O_3$).

Identification of Semiglabrin (3).—This compound was eluted with benzene–chloroform (1 : 1) and recrystallised from chloroform–hexane to give needles (95 mg), m.p. 254—255 °C (lit.,[7] 253—256 °C), $[\alpha]_D^{30}$ −273°, $\lambda_{max.}$ ($CHCl_3$) 212(4.72), 246sh.(4.58), 256(4.59), and 308(4.62) nm; $\nu_{max.}$ (KBr) 1 735 cm^{-1} (Found: M^+, 392.1264. $C_{23}H_{20}O_6$ requires 392.1260). Accurate mass measurements: 332.1052 ($C_{21}H_{16}O_4$), 317.0817 ($C_{20}H_{13}O_4$), 289.0865 ($C_{19}H_{13}O_3$), 263.0708 ($C_{17}H_{11}O_3$), and 230.0577 ($C_{13}H_{10}O_4$).

Identification of Semiglabrinol (4).—This compound was eluted with chloroform–methanol (98 : 2) and recrystallised from chloroform–methanol to give plates (120 mg), m.p. 245—247 °C (lit.,[7] 260—262 °C), $[\alpha]_D^{29}$ −270°; $\lambda_{max.}$ ($CHCl_3$) 210(4.21), 243sh.(4.14), 255(4.15), and 308(4.11) nm. This compound was identical in all respects with the data reported for semiglabrinol [9] (Found: M^+, 350.1154. $C_{21}H_{18}O_5$ requires 350.1154).

Oxidation of Semiglabrinol (4).—Oxidation of semiglabrinol as described in the literature [9] gave semiglabrinone (14), m.p. 164—167 °C (lit.,[9] 159—161 °C), $[\alpha]_D^{30}$ −256, $\lambda_{max.}$ ($CHCl_3$) 214(4.75) ,248(4.63), and 308(4.67) nm; $\nu_{max.}$ (KBr) 1 760 and 1 640 cm^{-1} (Found: M^+, 348.0996 ($C_{21}H_{16}O_5$ requires 348.0998).

Identification of Tephroglabrin (5).—Eluted with benzene–chloroform (1 : 3) recrystallised from chloroform–hexane to give needles (70 mg), m.p. 226—228 °C (lit.,[9] 232—233 °C) (Found: M^+, 362.1154. $C_{22}H_{18}O_5$ requires 362.1154), $\lambda_{max.}$ ($CHCl_3$) 252, 286, and 310 nm; $\nu_{max.}$ (KBr) 1 695 and 1 630 cm^{-1}; *m/e* 362(100%), 348(10), 347(37), 319(10), 305(14), 291(19), 277(47), 276(34), 233(11), 217(13), 190(15), 189(81), 174(11), 145(16), 144(17), 116(12), 105(14), and 102(10).

Preparation of Isosemiglabrinone (15).—Treatment of semiglabrinone (14) with 10% alcoholic H_2SO_4 at 70—75 °C for 1 h gave isosemiglabrinone which was obtained as needles from chloroform–hexane, m.p. 238—240 °C (Found: M^+, 348.0995. $C_{21}H_{16}O$ requires 348.0998), $\lambda_{max.}$ ($CHCl_3$) 214(4.71), 248(4.70), 260(4.72), and 310(4.55) nm; $\nu_{max.}$ (KBr) 3 150, 1 700, 1 670, and 1 640 cm^{-1}; *m/e* 349(20%), 348(100), 333(44), 262(40), 203(22), 160(40), and 102(13). Accurate mass measurements: 262.0638 ($C_{17}H_{10}O_3$), 203.0345 ($C_{11}H_7O_4$), and 160.0163 ($C_9H_4O_3$).

Preparation of Tephroglabrin (5).—Methylation of isosemiglabrone (15) with CH_2N_2–Et_2O at 10—15 °C for 24 h afforded tephroglabrin which was obtained as needles from chloroform–hexane, m.p. 230—232 °C (lit.,[9] 232—233 °C). This sample was identical in all respects with the sample obtained from natural sources above.

Identification of Apollinine (2).—This compound was eluted with chloroform and recrystallised from chloroform–hexane to give plates (144 mg), m.p. 261—262 °C (lit.,[7] 274—276 °C), $\lambda_{max.}$ ($CHCl_3$) 214(4.73), 246(4.60), and 306(4.65) nm; $\nu_{max.}$ (KBr) 1 740, 1 645, and 1 635 cm^{-1} (Found: M^+, 362.1154. $C_{22}H_{18}O_5$ requires 362.1154). Accurate mass measurements: 291.1023 ($C_{19}H_{15}O_3$), 277.0861 ($C_{18}H_{13}O_3$), and 189.0548 ($C_{11}H_9O_3$).

Identification of Compound (6).—This compound was eluted with chloroform–methanol (9 : 1) and recrystallised from chloroform–hexane to give needles (20 mg), m.p. 195—197 °C, $\lambda_{max.}$ ($CHCl_3$) 212(3.68), 250sh.(3.58), 266(3.60), and 308(3.58) nm; $\nu_{max.}$ (KBr) 3 400, 1 635, and 1 595 cm^{-1}; $[\alpha]_D^{30}$ −48° (Found: $M - H_2O$ 364.1311. $C_{22}H_{20}O_5$ requires 364.1311), *m/e* 364(13%), 346(12), 321(27), 294(35), 279(14), 277(13), 266(24), 265(100), 219(12), 191(13), 189(17), 163(53), 133(24), and 105(24). Accurate mass measurements: 394.1065 ($C_{21}H_{17}O_5$), 346.1202 ($C_{22}H_{18}O_4$), 321.1129 ($C_{20}H_{17}O_4$), 294.0886 ($C_{18}H_{14}O_4$), and 265.0866 ($C_{17}H_{13}O_3$).

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