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TWO FLAVONOIDS FROM *TEPHROSIA PURPUREA*

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Abstract—Purpurenone, a new β-hydroxychalcone, (+)-purpurin, a diastereoisomer of (−)-purpurin, dehydroisoderricin, and (−)-maackiain have been isolated from the roots of *Tephrosia purpurea* in addition to the earlier reported flavonoids [1, 2] Pseudosemiglabrin was obtained in admixture with (−)-semiglabrin

INTRODUCTION

In continuation of our studies on the flavonoids of the roots of *Tephrosia purpurea* [1, 2], we report here further examination of the petrol soluble fraction of the chloroform extract The residue when chromatographed over silica gel and the fractions further purified yielded four pure compounds together with a mixture of semiglabrin and pseudosemiglabrin (identified by HRMS and ^{13}C NMR data)

RESULTS AND DISCUSSION

The first new compound, $C_{21}H_{20}O_4$ (M^+ at *m/z* 336), named purpurenone, showed λ_{max} at 244, 252 nm and ν_{max} at 1595 cm^{-1} and colour reactions similar to those of pongamol (a β-hydroxychalcone) [1] The resonating signals in the ^1H NMR spectrum (see Table 1) (δ values, $CDCl_3$, 90 MHz) at 3 77 (*s*, 3H, OMe), 7 09 (*s*, 1H, olefinic proton), 7 42 (*m*, 3H, H-3, H-4, H-5), 7 9 (*m*, 2H, H-2, H-6) and two *ortho* coupled doublets at 7 55 and 6 58 with a separation of 9 Hz for H-5 and H-6, are definitely indicative of the structural resemblance of this compound to pongamol The remaining signals in the ^1H NMR showed the presence of 2,2-dimethylchromene ring system and they are at 1 42 (*s*, 6H, *gem*-dimethyl), 5 62 (*d*, 1H, J = 10 Hz, H-8′) and 6 6 (*d*, 1H, J = 10 Hz, H-7′) From the above data structure **1** can be assigned to purpurenone and the mass fragmentation is in agreement The recently reported praecansone B [3] differs from **1** in having an extra 6′-methoxyl and hence **1** may be described as 6′-demethoxypraecansone B

The second new compound (**2**), mp 145–146°, $[\alpha]_D$ +20°, $C_{23}H_{22}O_6$ (M^+ at *m/z* 394) showed λ_{max} 280, 312 (sh) nm and ν_{max} 1685 cm^{-1} indicative of a flavanone nucleus Its higher molecular weight by 2 mu than that of (−)-semiglabrin [4] and the typical ^1H NMR signal pattern at δ5 5 (*d*, *d*, 1H, J = 5, 9 Hz) and at δ2 8 (*m*, 2H) corresponding to H-2 and H-3 (*cis*) and H-3 (*trans*), respectively of the flavanone nucleus suggested that this could be the flavanone corresponding to semiglabrin, viz (−)-purpurin (**2a**) recently reported from the seeds of *Tephrosia purpurea* [5] The dextrorotation for **2** is quite unexpected as all the other isolated optically active flavonoids of *T purpurea* showed laevorotation Indeed **2** resembled (−)-purpurin in all its properties except the optical rotation and chemical shift difference of H-4″ (see Table 2) This led us to conclude that **2** must be (+)-purpurin

Our attempts to effect deacetylation under mild alkaline conditions resulted in the formation of a product (**2b**), mp 203–205° whose optical rotation (+ 157°) is much elevated The disappearance of the IR bands at 1735 and 1685 cm^{-1} and the appearance of new bands at 3500 and 1645 cm^{-1}, and similar changes in the ^1H NMR spectrum of **2b** (Table 1) with two well defined one proton doublets at δ6 49 (J = 15 Hz) and at 7 91 (J = 15 Hz) assignable to chalcone *trans* protons is clearly suggestive that **2** has undergone deacetylation followed by ring opening of the flavanone to give the chalcone **2b**

The higher positive optical rotation of the chalcone along with the chemical shift difference of H-4″ in (+)-purpurin from that of (−)-purpurin (**2a**) led us to propose

Table 1 ^1H NMR spectra of chalcone derivatives*

Position of proton	1	2b
8	7 09 (*s*)	6 49 (*d*, J = 15)
7	—	7 91 (*d*, J = 15)
5′	7 66 (*d*, J = 9)	7 86 (*d*, J = 8)
6′	6 6 (*d*, J = 9)	7 44 (*d*, J = 8)
2/6	7 9 (*m*, 2H)	7 64 (*m*, 2H)
3/4/5	7 42 (*m*, 3H)	7 44 (*m*, 3H)
7′	6 58 (*d*, J = 10)	—
8′	5 62 (*d*, J = 10)	—
2″	—	6 5 (*s*)
3″	—	4 33 (*br s*)
4″	—	4 03 (*br d*, J = 7)
OH	15 9 (enolic)	13 5 (phenolic)
ArOMe	3 77 (*s*)	—
Me_2	1 42 (*s*, 6H)	1 06 (*s*), 1 39 (*s*)

*All values given in δ, J values in Hz, spectra run in $CDCl_3$

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Table 2 ^{1}H NMR spectra of flavanones and flavones*

	2	3	3a	4	4a
H-2	5 5 (*d*, *d*, *J* = 6, 9)	5 46 (*d*, *d*, *J* = 6, 9)	5 46 (*d*, *d*, *J* = 6, 9)	—	—
3	2 8 (*m*, 2H)	2 94 (*m*, 2H)	2 94 (*m*)	6 70 (*s*)	6 62 (*s*)
5	7 75 (*d*, *J* = 9)	7 84 (*d*, *J* = 9)	7 44 (*d*, *J* = 8)	8 02 (*d*, *J* = 8)	—
6	6 44 (*d*, *J* = 9)	6 64 (*d*, *J* = 9)	6 64 (*d*, *J* = 8)	6 96 (*d*, *J* = 8)	6 49 (*s*)
2′,3′,4′ 5′,6′	7 35 (*m*, 5H)	7 25 (*m*, 5H)	7 45 (*m*, 5H)	7 4 (*m*, 2H) 7 85 (*m*, 3H)	7 92 (*m*, 5H)
1″	—	7 34 (*d*, *J* = 16)	1 0–1 8 (*m*)	7 35 (*d*, *J* = 16)	7 31 (*d*, *J* = 17)
2″	6 35 (*d*, *J* = 6)	6 75 (*d*, *J* = 16)		6 84 (*d*, *J* = 16)	6 89 (*d*, *J* = 17)
3″	3 95 (*d*, *J* = 6)	—		—	—
4″	5 46 (*br s*)	4 96 (*m*, 2H)	0 89 (*d*, *J* = 6)	5 12 (*br s*)	5 12 (*s*)
5″	—	1 92 (*s*, 3H)		2 02 (*s*)	2 08 (*s*)
OMe	—	3 88 (*s*)	3 88 (*s*)	3 94 (*s*)	3 92 (*s*)
OAc	2 01 (*s*)				
Me_2	1 18 (*s*), 1 01 (*s*)		0 89 (*d*, *J* = 6)		

*All values given in δ, *J* values are given in Hz Spectra run in $CDCl_3$

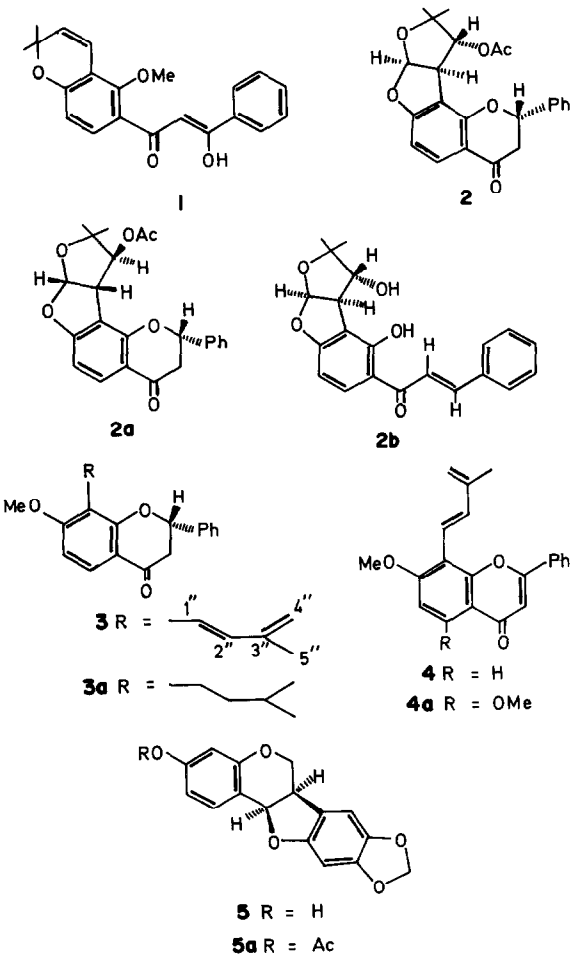

Table 3 ^{13}C NMR of flavonoids*

C	(+)-purpurin (2)	semiglabrin†	pseudo-semiglabrin‡
2	79 79	162 86	162 86
3	44 77	107 68	107 59
4	189 79	177 41	177 54
5	128 51	128 84	128 70
6	112 40	112 43	111 80
7	165 44	163 74	164 60
8	112 86	112 43	111 51
4a	115 94	118 40	118 71
8a	158 10	153 26	153 85
1′	138 88	131 64	131 75
2′,6′	125 71	126 36	126 21
3′,5′	128 77	129 14	129 04
4′	130 43	131 54	131 39
2″	105 04	109 02	108 94
3″	52 39	52 83	47 97
4″	80 37	80 24	76 86
5″	87 65	87 80	84 65
Me_2	27 46	27 47	27 61
	23 09	23 21	23 15
OAc	169 51	169 60	169 81
	20 72	20 78	20 02

*Chemical shifts in ppm downfield from TMS

†See ref [2]

‡Spectrum obtained by subtraction analysis of mixture of isomers

the diastereoisomeric structure, **2**, for (+)-purpurin in which the configuration at C-2 is unaltered ^{13}C NMR data for (+)-purpurin is presented in Table 3

The third component, mp 110–112°, $[\alpha]_D$ −141° λ_{max} 282, 310 (sh) nm, ν_{max} 1675 cm^{-1} showed a typical ^{1}H NMR signal pattern at δ2 94 (*m*, 2H, H-3α and H-3β) and 5 46 (*d*, *d*, 1H, *J* = 6, 9 Hz, H-2) of a flavanone nucleus The ^{1}H NMR spectrum (Table 2) further showed the presence of an unsubstituted C_6H_5, one methoxyl, one isoprenyl and two *ortho*-coupled aromatic protons centred at δ7 84 and 6 64 with a separation of 8 Hz which were ascribed to the protons at C-5 and C-6, respectively in the A-ring From the above data structure **3** can be

assigned to the compound The MS showed a prominent molecular ion peak at m/z 320 ($C_{21}H_{20}O_3$) The presence of fragment ions at m/z 279 $[M-C_3H_5]^+$, 175 (RDA from m/z 279), and 104 are in conformity with the structure assigned

As **3** was found to be rather unstable, it was subjected to catalytic hydrogenation using Pd–C as catalyst The product **3a** exhibited well defined signals in its ^{1}H NMR spectrum (see Table 2) at δ0 89 (*d*, 6H, J = 6 Hz, 2Me), and δ1 0–1 8 (*m*, 5H, 2H-1″, 2H-2″, H-3″) indicating that the isoprenyl group at C-8 was completely hydrogenated The MS showed a clear molecular ion at m/z 324 analysing for $C_{21}H_{24}O_3$ Comparison of the ^{1}H NMR spectrum of **3a** with the original flavanone (**3**) and with the spectra of anhydrolanceolatin A (**4**) and anhydrotephrostachin (**4a**) [6, 7] (Table 2) leads to the conclusion that **3** is the flavanone corresponding to anhydrolanceolatin A This structure was recently assigned for a flavanone, dehydroisoderricin, isolated from a *Tephrosia* species not fully identified [8]

The fourth compound was obtained in admixture with lanceolatin B [1] Acetylation of the mixture and column chromatography over silica gel gave **5** as its acetate (**5a**) (acetylmethyl protons signal at δ2 27) followed by unaffected lanceolatin B The ^{1}H NMR spectrum of the acetate (**5a**) suggested its pterocarpan nature by showing a series of signals of a complex four spin system in between δ3 5 and 5 5 The mp, optical rotation and spectral data of the acetate (**5a**) and its deacetylated product (**5**) were in close agreement with those reported for (−)-maackiain acetate and (−)-maackiain respectively [9, 10]

This is the first report of the isolation of maackiain from the Tephrosieae *sensu* Polhill Four other pterocarpans have been found in *Lonchocarpus* species [11] A biogenetically related coumestone was isolated from *Tephrosia villosa* [12] The isolation of a pterocarpan from *T purpurea* is of interest in spite of the absence of isoflavones (as also rotenoids) in the plant investigated by us

From the mother liquors of the fraction which yielded (−)-semiglabrin [2] another crystalline substance, mp 252–255° was obtained The ^{1}H and ^{13}C NMR data suggested that it is a mixture of closely related diastereoisomers (−)-semiglabrin and (−)-pseudosemiglabrin From Table 3 it can be observed that the chemical shift differences of 3″, 4″, 5″ carbon atoms are significant and these differences are perhaps caused by the difference in spatial arrangement of the acetate substituent

The co-occurrence of a β-hydroxychalcone (purpurenone) together with the closely related flavanone (isolonchocarpin) [1], and similarly dehydroisoderricin and lanceolatin A is of biogenetic interest [11] β-Hydroxy/methoxychalcones are rare and the present report of purpurenone adds a seventh member to the existing list, the others being *O*-methylpongamol [2], pongamol, melletenone, ovalitenone, praecansone A and praecansone B [11]

EXPERIMENTAL

UV spectra were run in $CHCl_3$ unless mentioned and IR spectra in KBr discs ^{1}H NMR spectra were run at 90 MHz or 100 MHz in $CDCl_3$ using TMS as int standard MS were obtained at 70 eV Optical rotations were taken in $CHCl_3$ Spots in TLC were visualized in UV light and with I_2 vapour

Isolation of compounds For extraction details and isolation and identification of pongamol, (−)-isolonchocarpin, *O*-methylpongamol, lanceolatin B and (−)-semiglabrin from the petrol soluble portion of the $CHCl_3$ extract of *Tephrosia purpurea* roots see earlier papers [1, 2] Further examination of some of the petrol soluble fractions yielded **1** (100 mg) from petrol–C_6H_6 (3 7), **2** (120 mg) from pure C_6H_6, **3** (150 mg) from petrol–C_6H_6 (1 3) The C_6H_6–$CHCl_3$ (3 1) fraction contained a mixture of **5** and lanceolatin B, which were separated after acetylation followed by chromatography over silica gel The acetate **5a** (155 mg) was eluted earlier with petrol–C_6H_6 (1 1) Semiglabrin and pseudosemiglabrin mixture was obtained from the mother liquor of the $CHCl_3$ eluate which yielded (−)-semiglabrin

Identification of the compounds Purpurenone (**1**) Oil $[\alpha]_D^{27}$ ±0° UV λ_{max} nm 244, 252 IR ν_{max} cm^{-1} 1595, 1065, 750 and 710 ^{1}H NMR (Table 1) MS m/z (%) 336 (23 4), 321 (100), 305 (91 1), 263 (51), 219 (9 4), 201 (7 8), 160 (19 8), 154 (16 1), 77 (98 4)

(+)-*Purpurin* (**2**) Needles from petrol–$CHCl_3$, mp 145–146° (lit for (−)-purpurin [5] 145–147°) $[\alpha]_D^{27}$ +20 3° (*c* 1 05%) (lit for (−)-purpurin [5] −67 41°) UV λ_{max} nm 280, 312 (sh) IR ν_{max} cm^{-1} 1740, 1685, 1610, 1240, 750, 700, 560 ^{1}H NMR (Table 2) ^{13}C NMR (Table 3) MS m/z (%) 394 (14 5), 335 (19 1), 334 (72 7), 319 (21 8), 291 (19 1), 231 (22 0), 230 (100), 215 (18 2), 202 (40 9), 131 (20 9), 104 (54 5), 103 (36 4), 77 (36 4)

Treatment of (+)-purpurin with alkali (+)-Purpurin (**2**, 30 mg) was dissolved in a minimum of 0 2% KOH in EtOH and allowed to stand for 12 hr at room temp (28°) Addition of cold water to the mixture gave a ppt which cryst from $CHCl_3$–hexane to give yellow needles of (+)-deacetylisopurpurin (**2b**), mp 203–205° Brownish red colour with neutral $FeCl_3$ $[\alpha]_D^{27}$ +157 4° (*c* 1%) IR ν_{max} cm^{-1} 3500, 1645, 1610, 1570, 790, 760 ^{1}H NMR (Table 1) MS m/z (%) 352 (84), 334 (100), 319 (22 5), 291 (51), 265 (32), 263 (14), 230 (71), 215 (15), 187 (32), 177 (26), 149 (54), 131 (55), 104 (24), 103 (50), 77 (42 5), 28 (61)

(−)-*Dehydroisoderricin* (**3**) Yellow needles from C_6H_6, mp 110–112° (lit [8] 73–75°) UV λ_{max}^{MeOH} 239, 282, 310 (infl) IR ν_{max} cm^{-1} 1675, 1590, 1375, 1220, 1090, 750, 690 ^{1}H NMR (Table 2) MS m/z (%) 320 (64), 279 (33), 216 (12), 201 (48), 175 (63), 104 (25)

Hydrogenation of (−)-dehydroisoderricin (**3**) Catalytic hydrogenation of **3** in EtOAc in the usual way under a little positive pressure using Pd–C as catalyst gave 7-methoxy-8-isopentanyl flavanone (**3a**) ^{1}H NMR (Table 2) MS m/z (%) 324 (64), 322 (19), 268 (51), 267 (43), 218 (21), 190 (21), 163 (100), 136 (38), 133 (18), 103 (10), 77 (19)

(−)-*Maackiain acetate* (**5a**) Acetylation of the C_6H_6–$CHCl_3$ (3 1) fraction after column chromatography of the petrol soluble portion with Ac_2O and pyridine at room temp in the usual way and chromatography of the mixture afforded **5a** in the petrol–C_6H_6 (1 1) eluate Needles from C_6H_6–hexane, mp 175–177° (lit [9] 176–177 5°), $[\alpha]_D^{27}$ −181 8° (*c* 0 9%) (lit [9] −176°), identical in all respects (UV, IR, ^{1}H NMR, MS) to **5a** [9, 10]

(−)-*Maackiain* (**5**) The acetate (**5a**) (100 mg) in EtOH (5 ml) was heated under reflux with 25% NH_4OH (1 ml) for 15 min The product was isolated by dilution with H_2O and extraction with Et_2O Compound **5** (76 mg) cryst from C_6H_6 as needles, mp 165–167° (lit [9] 163–164°), $[\alpha]_D^{27}$ −240 6° (*c* 1%) (lit [9] −220°), identical in all respects (UV, IR, ^{1}H NMR and MS) to **5** [9, 10]

Pseudosemiglabrin + semiglabrin Needles from $CHCl_3$–hexane, mp 252–255° (Found M^+, 392 1264 $C_{23}H_{20}O_6$ requires 392 1260) OR and UV were similar to (−)-semiglabrin [2] ^{1}H NMR indicated signals similar to that of mixture of semiglabrin and pseudosemiglabrin [2, 6, 7] ^{13}C NMR (Table 3)

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