3,4-dimethoxy substitution pattern in the aromatic part of the molecule, and also to the 11,13-dioxygenated cyclophanes of *M. gale*. Further studies on the stereochemistry and spectroscopy of these unusual substances are in progress.

EXPERIMENTAL

Mps are uncorr. and optical rotations were measured in 10 cm cells.

A crude myricanol extract from *M. nagi* [2] (275 mg) was purified by prep-TLC (Merck Fertigplatten GF_{254} 0.2 mm, eluent C_6M_6–Me_2CO, 19:1). This extract yielded myricanone (**3**), R_f 0.8, 35 mg, and myricanol (**2**), R_f 0.55, 207 mg, both with R_f values and spectral data in accordance with authentic samples. In addition, another more polar substance (**7**) R_f 0.3, 19 mg, was isolated. This substance was further purified by repeated TLC and crystallization from MeOH–H_2O (4:1), yielding colourless microcrystals, mp 239.5–240°, $[\alpha]_D^{20}$ −36° (*c* 0.31, $CHCl_3$), $[\alpha]_{546}^{20}$ −51°, $[\alpha]_{436}^{20}$ −225°, $[\alpha]_{365}^{20}$ *ca* −1100°. UV λ_{max}^{MeOH} nm (log ε): 281 *sh* (4.01), 262 (4.24), 224 (4.23). IR ν cm^{-1}: KBr 3350, 2930, 2860, 1664 (*s*), 1612, 1573 (*s*), 1495, 1453 (*s*), 1409 (*s*), 1348 (*s*), 1226 (*s*), 1167, 1103, 1060, 1048, 1005, 973, 930, 918, 894, 829. ^1H NMR (100 MHz, $CDCl_3$): δ 1.4–3.8 (several overlapping *m*, 10H), 3.49 (1H, *s*, disapp. with D_2O), 3.92 (3H, *s*), 4.01 (3H, *s*), 4.14 (1H, *m*), 6.0 (1H, *br s*, disapp. with D_2O), 6.94 (1H, *s*), 7.04 (1H, *d*, J = 8 Hz), 7.89 (1H, *dd*, J = 2 and 8 Hz), 8.07 (1H, *d*, J = 2 Hz), 8.48 (1H, *s*, disapp. with D_2O). ^{13}C NMR (25.1 MHz, $CDCl_3$): δ 22.7, 25.3 (2 peaks), 38.1, 48.9, 61.3 (2 peaks), 71.0, 118.0, 121.7, 123.0, 124.1, 128.4, 128.5, 140.0, 148.3, 157.8. MS (IP 70 eV, *m/e* (%)): 372 (100, M^+), 355 (8, M^+-17), 343 (7, M^+-29), 329 (13, M^+-43), 323 (4, M^+-49), 301 (6, M^+-71), 287 (4, M^+-85), 271 (4, M^+-101), 259 (8, M^+-113), 258 (8, M^+-114), 143 (13), 115 (5). No metastable peaks were observed. M^+ obs. 372.1573 as calc. for $C_{21}H_{24}O_6$.

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THREE NEW FLAVONOIDS FROM *TEPHROSIA PRAECANS*

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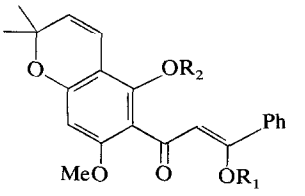
Key Word Index—*Tephrosia praecans*; Leguminosae; β-hydroxy- and β-methoxychalcones; chromenoflavone; chromenoflavanone.

In continuation of our study on the flavonoids and rotenoids of Leguminosae [1], we examined *Tephrosia praecans*. The oily residue obtained from $CHCl_3$ extraction of the seeds gave by chromatography on Si gel four pure compounds together with a mixture of tephrosin and 12a-hydroxyrotenone.

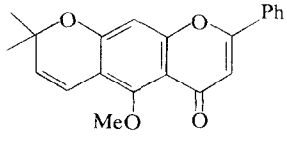
The main component, $C_{23}H_{24}O_5$ (M^+ at *m/e* 380), named praecansone A, showed λ_{max} at 284 nm and ν_{max} at 1660 cm^{-1}. The ^1H NMR spectrum gave evidence of a dimethylchromene ring, three methoxyl groups, two aromatic/olefinic protons and a C_6H_6 conjugated to a double bond. From the above data structure **1** can be assigned to praecansone A and the mass fragmentation is in agreement. Further confirmation



	R_1	R_2
1	Me	Me
2	H	Me
6	H	H

was obtained by alkaline degradation giving benzoic acid and methyl isoevodionol [2]. Catalytic hydrogenation (PtO_2) of praecansone A unusually yielded an octahydro derivative (M^+ at *m/e* 288) in which both the chromene and the unsubstituted aromatic ring are reduced, as indicated by the ^1H NMR, IR and MS data and in particular by the hypsochromic shift of the λ_{max}. Reduction of the aromatic ring by PtO_2 or Pd/C is quite rare in the literature [3, 4], but from other results in this laboratory it seems to happen in flavonoids with the sequence Ar—C=C—OR or Ar—C(OR)=C.

The second substance ($C_{22}H_{22}O_5$, M^+ at *m/e* 366, λ_{max} 270, 311 with inflection at 327 nm, ν_{max} 3550, 1660 cm^{-1}), named praecansone B, showed in the ^1H NMR spectrum only two methoxy groups, but one strongly chelated hydroxyl (δ 15.7): therefore the structure **2** was attributed to it. The third compound isolated from *T. praecans* was recognized as a flavone by its UV spectrum and by the characteristic singlet at δ 6.66 in the ^1H NMR spectrum. The other signals in the ^1H NMR spectrum were attributed to an isolated aromatic proton, a methoxy group, a chromene and an unsubstituted aromatic B ring. The above data and the mass fragmentation are consistent with structure **3**, i.e. the angular isomer of isopongaflavone, previously synthesized [5] from 6-C-prenylchrysin by cyclodehydrogeration with DDQ and successive methylation. Finally, the fourth compound, mp 125–127°, was identified as the flavanone **4**, previously isolated in this laboratory from another *Tephrosia* sp.



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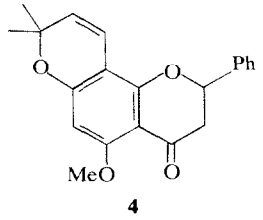
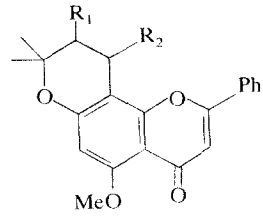


4

The finding of a β-methoxy- and a β-hydroxychalcone in the same plant together with the closely related flavone **3** and flavanone **4** implies a common biogenesis. β-Hydroxy- and α-hydroxychalcones have rarely been isolated from natural sources. The latter are considered [6] to be intermediates in the biosynthesis of mopanols and peltogynols: analogous β-hydroxychalkones may represent intermediates in the formation of flavones. The co-occurrence both in *Milletia ovalifolia* [7] and in *Pongamia glabra* [8] of the other two known β-hydroxychalcones, pongamol and ovalitenone, with the corresponding flavones supports this hypothesis. Having this in mind, we submitted praecansone A to treatment with $AlCl_3$, obtaining 3 compounds. The main one was identified as isopongaflavone **5** [5], (the angular isomer of **3**), while on the basis of the spectral data, the structures **6** and **7** were attributed to the other two products. Production of the



5 R_1, R_2 = H
7 R_1 = H, R_2 = OH

angular isomer **5**, rather than the linear isomer **3** present in the plant, may be due to the different reactivity of the two aromatic methoxy groups to $AlCl_3$ and to an enzymatic system, respectively.

EXPERIMENTAL

Plant material. Seeds of *Tephrosia praecans* (Leguminosae) collected (September 1977) in the National Botanic Garden (Kirstenbosh, Newland, South Africa). A voucher sample is deposited in the Herbarium of CCR under the cipher Muller 2670.

Extraction and separation. Seeds (102 g) were powdered and continuously extracted (15 hr) with hot MeOH and the extract evapd. Residue was dissolved in $CHCl_3$–H_2O and the organic layer separated and evapd (14 g). Crude oily residue was chromatographed on Si gel and the column eluted with C_6H_6 to give a mixture of triglycerides (~ 6 g). Elution with C_6H_6–EtOAc mixtures gave successively praecansone B (100 mg), praecansone A (3.3 g), sitosterol (50 mg), flavanone **4** (220 mg), flavone **5** (50 mg) and a mixture of tephrosin/12a-hydroxyrotenone (50 mg).

Praecansone A (**1**). Oil (Found: C, 69.82; H, 6.05. $C_{23}H_{24}O_5$ requires: C, 69.68; H, 6.10%). UV λ_{max} nm (log ε): 284 (4.18). IR ν_{max}, cm^{-1}: 1660. ^1H NMR (CCl_4): δ 7.70 (2H, *m*), 7.30 (3H, *m*), 6.33 (1H, *d*, *J* = 10 Hz), 6.23 (1H, *s*), 5.99 (1H, *s*), 5.30 (1H, *d*, *J* = 10 Hz), 3.70 (3H, *s*), 3.60 (6H, *s*), 1.37 (6H, *s*). MS *m/e* (%): 380 (6), 365 (42, M-15), 351 (21), 349 (100, M-31), 336 (18), 319 (15), 263 (9), 255 (7), 217 (10, $C_{12}H_9O_4$), 205 (7), 167 (15), 123 (21), 105 (52, C_6H_5—C≡O$^+$), 91 (8), 77 (50).

Alkaline degradation of praecansone A. Praecansone A (370 mg) in ethanolic KOH (5%) was refluxed for 7 hr. Standard work-up and chromatographic separation gave praecansone B (40 mg), methyl isoevodionol (130 mg, mp and mmp 76–7°, lit. [2] 76.5–77°) and benzoic acid (70 mg).

Catalytic hydrogenation of praecansone A. Praecansone A (100 mg) in MeOH was hydrogenated over Pt (from 100 mg PtO_2). Standard work-up and purification of Si gel afforded an oily octahydro derivative. UV λ_{max} nm (log ε): 256 (4.05). IR ν_{max} cm^{-1}: 1680. ^1H NMR (CCl_4): δ 5.96 (1H, *s*), 5.52 (1H, *s*), 3.63 (6H, *s*), 3.58 (3H, *s*), 2.6 (2H, *t*, *J* = 7 Hz), 1.90–1.4 (7H, *m*), 1.28 (6H, *s*), 1.30–1.0 (6H, *m*). MS *m/e* (%): 388 (5), 357 (100, M-31), 305 (50, M-C_6H_{11}), 301 (10, M-56), 286 (7), 275 (5), 273 (4), 265 (5), 249 (40, M-83-56), 235 (8), 231 (6), 219 (8), 217 (7), 205 (10), 191 (15), 189 (8), 157 (8); m* 328.4 (388→357), m* 253.8 (357→301) and m* 203.2 (305→249).

Praecansone B (**2**). Oil. UV λ_{max} nm (log ε): 270 (4.44), 311 (4.31) with inflection at 327; +$AlCl_3$, 341. IR ν_{max}, cm^{-1}: 3550, 1600. ^1H NMR (CCl_4): δ 15.7 (1H, *br s*), 7.80 (2H, *m*), 7.33 (3H, *m*), 6.40 (1H, *d*, *J* = 10 Hz), 6.28 (1H, *s*), 6.07 (1H, *s*), 5.37 (1H, *d*, *J* = 10 Hz), 3.73 (6H, *s*), 1.40 (6H, *s*). MS, *m/e* (%): 366 (19), 351 (100, M-15), 335 (M-31),

305 (10), 247 (M-C_6H_5—CO—CH_2), 231 (12), 217 (21), 205 (61), 203 (13), 190 (8), 175 (8), 160 (10), 115 (10), 105 (75, C_6H_5—C≡O^+), 103 (9), 91 (17), 77 (78).

Flavone **3**. Mp 177–80° (MeOH), lit. [5] 182–83° (EtOH). UV λ_{max} nm (log ε): 275 (4.35), 316 (4.04). IR ν_{max}, cm^{-1}: 1640. ^1H NMR ($CDCl_3$): δ 7.80 (2H, *m*), 7.43 (3H *m*), 6.7 (1H, *d*, $J = 7$ Hz), 6.65 (1H, *s*), 6.58 (1H *s*), 3.88 (3H, *s*), 1.43 (6H, *s*). MS *m/e* (%): 334 (27), 319 (57, M-15), 305 (8), 291 (14), 290 (11), 289 (9), 217 (24, RDA of M-15), 208 (47), 202 (14), 187 (14), 165 (15), 159 (9), 146 (14), 145 (9), 115 (22), 105 (44, C_6H_5—C≡O^+), 102 (38, C_6H_5—C≡CH^+), 91 (76), 77 (100).

Flavanone **4**. Mmp [6] 125–27° (MeOH). $[\alpha]_D^{24} - 40°$ (*c* 0.85, $CHCl_3$). ^1H NMR (CCl_4): δ 7.33 (5H, *br s*), 6.50 (1H, *d*, $J = 10$ Hz), 5.85 (1H, *s*), 5.35 (1H, part X of ABX), 5.30 (1H, *d*, $J = 10$ Hz), 3.73 (3H, *s*), 2.70 (2H, part AB of ABX), 1.38 (6H, *s*).

Treatment of praecansone A with $AlCl_3$. Praecansone A (200 mg) in $CHCl_3$ was stirred for 1.5 hr with $AlCl_3$ (200 mg). Filtration and evapn gave a crude product which was chromatographed on Si gel column, eluted with $CHCl_3$–MeOH, 97/3. β-Diketone **6** (20 mg), isopongaflavone **5** (60 mg), an unidentified compound (7 mg), and flavone **7** (90 mg) were eluted successively. In other experiments the ratio of the compounds eluted varies, the main component being **5** and **7**.

β-Diketone **6**. Mp 105–7° from CH_2Cl_2–petrol. UV λ_{max} nm (log ε): 272 (4.20), 372 (3.91) with inflection at 295 (3.98): + NaOMe, 392: + $AlCl_3$, 402. IR ν_{max}, cm^{-1}: 3550, 1600. ^1H NMR (CCl_4): δ 14.70 (1H, *s*), 12.80 (1H *s*), 7.80 (2H *m*), 7.40 (3H, *m*), 7.18 (1H, *s*), 6.58 (1H, *d*, $J = 10$ Hz), 5.78 (1H, *s*), 5.28 (1H, *d*, $J = 10$ Hz), 3.90 (3H, *s*), 1.40 (6H, *s*). MS *m/e* (%): 352 (45), 337 (60, M-15), 232 (7, M-120), 217 (100, M-15-120), 202 (7), 191 (26), 179 (7), 105 (32, C_6H_5—C≡O^+), 77 (17).

Isopongaflavone **5**. Mp 206–8° (CH_2Cl_2–heptane), lit. [5] 215–16° (EtOH). UV λ_{max}, nm (log ε): 269 (4.07), 335 (3.10). IR ν_{max} cm^{-1} ($CHCl_3$): 1635, 1385, 1375, 1030. ^1H NMR ($CDCl_3$): δ 7.80 (2H, *m*), 7.43 (3H, *m*), 6.8 (1H, *d*, $J = 10$ Hz), 6.60 (1H, *s*), 6.28 (1H, *s*), 5.57 (1H, *d*, $J = 10$ Hz), 3.90 (3H, *s*), 1.42 (6H, *s*). MS, *m/e* (%): 334 (100), 319 (73), 305 (15), 290 (12), 289 (11), 217 (91), 202 (19), 187 (9), 167 (6), 159 (5), 153 (6), 146 (6), 145 (5), 144 (7), 105 (5), 102 (6), 77 (4).

Flavone **7**. Mp 242–44° from CH_2Cl_2. UV λ_{max} nm (log ε): 268 (4.11) 310 (3.91). IR ν_{max} cm^{-1} ($CHCl_3$): 3400, 1640, 1385, 1365, 1030. ^1H NMR ($CDCl_3$): δ 7.80 (2H, *m*), 7.40 (3H, *m*), 6.45 (1H, *s*), 6.15 (1H, *s*), 5.22 (1H, *t*, $J = 4.5$ Hz), 3.75 (3H, *s*), 2.16 (2H, *m*), 1.56 (3H, *s*), 1.45 (3H, *s*). MS *m/e* (%): 352 (36), 334 (46), 319 (100), 305 (44), 296 (16), 295 (10), 290 (9), 289 (7), 267 (11), 217 (38), 202 (9), 194 (6), 187 (6), 153 (5), 136 (6), 105 (9), 102 (10), 77 (15). With $POCl_3$–Py flavone **7** gave isopongaflavone **5**. With Ac_2O–Py it gave a monoacetate, mp 194–95° (CH_2Cl_2–heptane), ^1H NMR ($CDCl_3$): δ 7.80 (2H, *m*), 7.43 (3H, *m*), 6.70 (1H, *s*), 6.35 (1H, *t*, $J = 4$ Hz), 6.30 (1H, *s*), 3.93 (3H, *s*), 2.25 (2H, *d*, $J = 4$ Hz), 1.98 (3H, *s*), 1.50 (3H, *s*), 1.26 (3H, *s*).

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