Phytochemistry, Vol. 21, No. 3, pp. 761–766, 1982.
Printed in Great Britain.

0031-9422/82/030761-06$03.00/0

ISOPONGAGLABOL AND 6-METHOXYISOPONGAGLABOL, TWO NEW HYDROXYFURANOFLAVONES FROM *PONGAMIA GLABRA*

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(*Received* 8 *May* 1981)

Key Word Index—*Pongamia glabra*; Leguminosae; flowers; furanoflavone; isopongaglabol, 6-methoxyisopongaglabol; 5-methoxy-3′,4′-methylenedioxyfurano(8,7–4″,5″)flavone; desmethoxykanugin; fisetin tetramethyl ether; ovalichromene B; cycloart-23-ene-3β,25-diol; friedelin; β-sitosterol-β-D-glucoside; 5-methoxyfurano(8,7-4″,5″)flavone; synthesis.

Abstract—Isopongaglabol and 6-methoxyisopongaglabol, two new hydroxyfuranoflavones, together with two furanoflavones 5-methoxyfurano(8,7-4″,5″)flavone and 5-methoxy-3′,4′-methylenedioxyfurano(8,7-4″,5″)flavone, two simple flavones, desmethoxykanugin and fisetin tetramethyl ether, a chromenoflavanone, ovalichromene B, two triterpenes, cycloart-23-ene-3β,25-diol and friedelin, and β-sitosterol-β-D-glucoside were isolated from the petrol and $CHCl_3$ extracts of the flowers of *Pongamia glabra*. The structures of isopongaglabol and 6-methoxyisopongaglabol have been established as 4′-hydroxyfurano(8,7-4″,5″)flavone and 4′-hydroxy-6-methoxyfurano(8,7–4″,5″)flavone, respectively, on the basis of the spectral evidence and they have been confirmed by synthesis.

INTRODUCTION

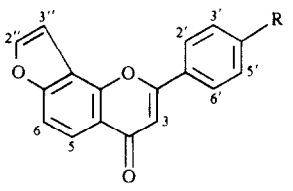
In a recent paper [1] we reported the isolation and characterization of a new hydroxyfuranoflavone, pongaglabol, and 10 other components of the flowers of *Pongamia glabra*. A careful investigation on the remaining fractions of the extracts resulted in the isolation of two more new hydroxyfuranoflavones along with one other furanoflavone, two simple flavones, one chromenoflavanone, two triterpenes and a sterol glucoside. In addition to the above 20 constituents 5-methoxyfurano(8,7-4″,5″)flavone was also isolated from another sample of the flowers. The isolation of the constituents not encountered earlier [1], elucidation of the structures of the new hydroxyfuranoflavones and their synthesis are discussed in this paper.

RESULTS AND DISCUSSION

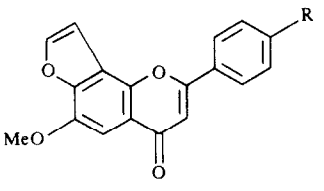
Extensive chromatography of the remaining fractions of the petrol and $CHCl_3$ extracts of the flowers of *P. glabra* [1] afforded a mixture of two new hydroxyfuranoflavones, designated isopongaglabol (**1**) and 6-methoxyisopongaglabol (**2**) (PG-R) in addition to one other furanoflavone, 5-methoxy-3′,4′-methylenedioxyfurano(8,7-4″,5″)flavone (**9**), two simple flavones desmethoxykanugin (**10**) and fisetin tetramethyl ether (**11**), one chromenoflavanone ovalichromene B (**12**) (second natural occurrence), two triterpenes cycloart-23-ene-3β, 25-diol (**13**) and friedelin and β-sitosterol-β-D-glucoside. While working on another sample of the flowers in order to isolate lanceolatin B (**5**) and kanjone (**6**) required for the synthesis of isopongaglabol (**1**) and 6-methoxyisopongaglabol (**2**) respectively, one additional furanoflavone characterized as 5-methoxyfurano(8,7-4″,5″)flavone (≡ pongaglabol methyl ether [1]) (**8**) was also isolated.

PG-R, a light-yellow crystalline solid, isolated from the $CHCl_3$ extract of the flowers gave a brown colour with the Shinoda test and an elongated TLC spot exhibiting in UV light a deep blue fluorescence in its lower part and light blue fluorescence in its upper part indicating that it is a mixture of two furanoflavones. Although PG-R gave no colour with $FeCl_3$, the presence of phenolic hydroxyl groups in one or both of its components was apparent from a bathochromic shift of its UV absorption maxima with dilute alkali and the presence of a broad band at 3600–2000 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of PG-R in DMSO-d_6 clearly indicated it to be a mixture of two 4′-oxygenated furanoflavones (*ca* ratio 3:1) of which the minor one contained one methoxy group in the molecule. The mass spectrum of PG-R exhibited major peaks at *m/z* 308, 278, 250, 190, 175, 162, 160, 132, 125, 119 and 118 of which the peaks at *m/z* 190 (ion *a*), 175 (*a*–Me) and 162 (ion *b*) indicate that the methoxy group of the methoxyfuranoflavone component (M^+ 308) of PG-R is present in ring A. Attempted separation of the components of PG-R by fractional crystallizations and prep. TLC met with failure. The components of PG-R were separated as their methyl ethers by careful prep. TLC.

Isopongaglabol methyl ether, $C_{18}H_{12}O_4$, the ether of the major component of PG-R has been assigned the structure **3** from spectral and synthetic evidence. It showed λ_{max}^{EtOH} nm (log ε): 220 (4.55), 249 (sh, 4.15), 264 (4.20) and 319 (4.46) and characteristic ν_{max}^{KBr} cm^{-1}:



1 R = OH
3 R = OMe
5 R = H



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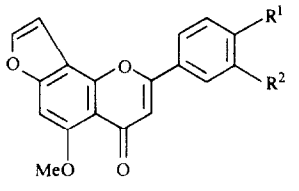
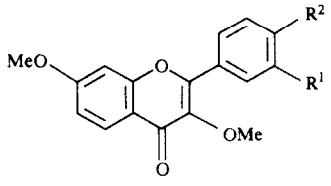
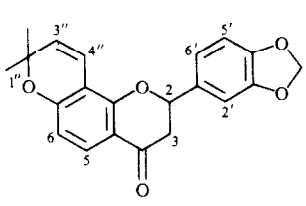
4 R = OMe
6 R = H
7 R = OCH_2Ph



8 $R^1 = R^2 = H$
9 R^1, R^2 = —O—CH_2—O—



10 R^1, R^2 = —O—CH_2—O—
11 $R^1 = R^2$ = OMe



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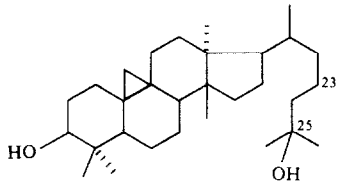

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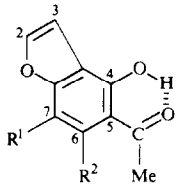
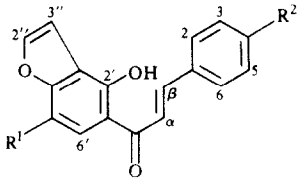
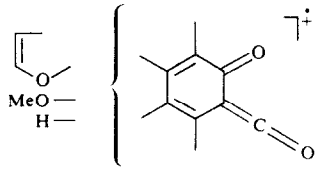


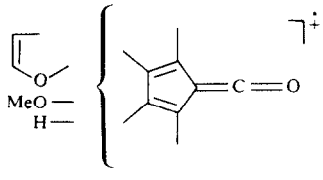
14 $R^1 = R^2 = H$
15 R^1 = OMe, $R^2 = H$
16 $R^1 = H$, R^2 = OMe



17 $R^1 = H$, R^2 = OMe
18 $R^1 = R^2$ = OMe
19 R^1 = OMe, $R^2 = OCH_2Ph$



a



b

1655 (γ-pyrone CO), 1072 (benzofuran) and 820 (*p*-disubstituted benzene). The structure was established from its ^{1}H NMR spectrum (80 MHz, $CDCl_3$) signals at δ3.93 (3H, *s*, 4′-OCH_3), 6.81 (1H, *s*, H-3), 7.06 (2H, pattern resembled a pair of triplets [2], $J_{3',2'} = J_{5',6'} =$ 9 Hz and $J_{3',5'} = 2.1$ or 3.1 Hz, H-3′ and H-5′), 7.21 (1H, *dd*, $J_{3'',2''} = 2.1$ Hz and $J_{3'',6} = 0.9$ Hz, H-3″), 7.56 (1H, *dd*, $J_{6,5} = 9$ Hz and $J_{6,3''} = 0.9$ Hz, H-6), 7.78 (1H, *d*, $J_{2'',3''} = 2.1$ Hz, H-2″), 7.93 (2H, pattern resembled a pair of triplets [2], $J_{2',3'} = J_{6',5'} = 9$ Hz and $J_{2',6'} = 3.1$ or 2.1 Hz, H-2′ and H-6′) and 8.17 (1H, *d*, $J_{5,6} = 9$ Hz, H-5). The mass spectrum showed M^+ at *m/z* 292 as the base peak and other important peaks at *m/z* (rel. int.) 264 $[M-CO]^+$ (6.4%), 160 [M–$MeOC_6H_4C$ ≡

$CH]^+$ (77.3) and 132 $[MeOC_6H_4C \equiv CH]^+$ and or $[160-CO]^+$ (64.3). The structure of **3** of the methyl ether was confirmed by synthesis from lanceolatin B (**5**) involving the route **5** → **14** → **17** → **3** (see Experimental). The structure **1** for isopongaglabol is apparent from that of **3**. On demethylation with BBr_3, **3** furnished **1**. On acetylation (Ac_2O–pyridine) **1** formed an acetate, mp 258°.

The structure of the methyl ether of the minor component of PG-R, $C_{19}H_{14}O_5$, was established as 6-methoxyisopongaglabol methyl ether (**4**) from spectral and synthetic evidence. The UV and IR spectra of this compound resembled closely those of isopongaglabol methyl ether [λ_{max}^{EtOH} nm (log ϵ): 220 (4.52), 247 (sh, 4.12), 266.5 (4.24) and 323 (4.49); ν_{max}^{KBr} cm^{-1}: 1648, 1080 and 830]. The ^1H NMR spectrum (200 MHz, $CDCl_3$) exhibited signals at δ3.92 (3H, *s*, 4′–OC<u>H</u>$_3$), 4.12 (3H, *s*, 6–OC<u>H</u>$_3$), 6.82 (1H, *s*, H–3), 7.08 (2H, pattern resembled a pair of triplets [2], $J_{3',2'} = J_{5',6'} = 9$ Hz and $J_{3',5'} = 2.1$ or 3.1 Hz, H-3′ and H-5′), 7.24 (1H, *d*, $J_{3'',2''} = 2.2$ Hz, H-3″), 7.57 (1H, *s*, H-5), 7.82 (1H, *d*, $J_{2'',3''} = 2.2$ Hz, H-2″) and 7.95 (2H, pattern resembled a pair of triplets [2], $J_{2',3'} = J_{6',5'} = 9$ Hz and $J_{2',6'} = 3.1$ or 2.1 Hz, H-2′ and H-6′). The mass spectrum showed peaks at *m/z* (rel. int.) 322 [Me^+] (100), 190 $[M-OC_6H_3C \equiv CH]^+$ (40.2), 175 [190–Me]$^+$ (4.1), 162 (11.2), 147 (11.3), 132 (9.2) and 119 (16.4). The structure **4** received confirmation from its unambiguous synthesis from kanjone (**6**) via the route **6** → **15** → **18** → **4** (see Experimental). Thus, the structure of the minor furanoflavone of PG-R having the methoxy group in ring A (cf. mass spectrum of PG-R as stated earlier) as 6-methoxyisopongaglabol (**2**) follows from the structures of the furanoflavones **3** and **4** isolated from the methylated PG-R. The synthesis of **2** was achieved following the route **15** → **19** → **7** → **2**. Treatment of 4′-benzyloxyfurano(8,7–4″,5″)flavone (**7**) with H_2 in presence of 10% Pd-C for 15 mins (when the starting material disappeared completely) furnished a mixture of **2** and its 2″,3″-dihydro derivative (as evident from ^1H NMR and mass spectra) in the *ca* ratio 3:1 (^1H NMR). The mixture could not be resolved by prep. TLC and/or fractional crystallization. However, under similar conditions ethyl-6-benzyloxy-4-methoxycoumarone-2-carboxylate was reported [3] to undergo debenzylation without any hydrogenation of the furan double bond.

The furanoflavone **9** was identified from its UV, IR, ^1H NMR and mass spectral features and its alkaline hydrolysis to 5-acetyl-4-hydroxy-6-methoxycoumarone (**16**), mp 85° [4]. The flavonoids **10**, **11**, **12** and the triterpene **13** were identified from their UV, IR, ^1H NMR and mass spectral data. The furanoflavone **8** was identical to pongaglabol methyl ether [1] in all respects. Friedelin and β-sitosterol-β-D-glucoside were identified by direct comparison with the authentic samples.

EXPERIMENTAL

Mps: uncorr.; IR: KBr; UV: 95% EtOH; ^1H NMR, δ-values in ppm downfield from TMS; MS: 70 eV; Si gel for chromatography, spot visualized in UV light and on exposure to I_2.

The chromatography of the $CHCl_3$ extract of the flowers (2 kg) of *P. glabra* Vent. (fraction C of ref. [1]) over Si gel was continued.

5-Methoxy-3′,4′-methylenedioxy(8,7-4″,5″)*flavone* (**9**). The residue obtained from the later $CHCl_3$–MeOH (97.5:2.5) eluate fractions on rechromatography over Si gel followed by crystallization from $CHCl_3$–petrol furnished 5-methoxy-3′,4′-methylenedioxy(8,7–4″,5″)flavone (**9**) as colourless needles, mp 262–263° (lit. 263–264° [5], 268–269° [6]), λ_{max}^{EtOH} nm (log ϵ): 230 (4.58), 246 (4.46), 274 (4.21) and 330.5 (4.34); ν_{max}^{KBr} cm^{-1}: 1643 (γ-pyrone CO), 1600, 1452, 1323, 1253, 1155, 1065 (benzofuran), 1027, 920 and 835; ^1H NMR (90 MHz, DMSO-d_6): δ3.91 (3H, *s*, –OC<u>H</u>$_3$), 6.18 (2H, *s*, –OC<u>H</u>$_2$O–), 6.87 (1H, *s*, H-3), 7.13 (1H, *dd*, $J_{5',6'} = 9$ Hz and $J_{5',2'} = 1$ Hz, H-5′), 7.33 (1H, *d*, $J_{6,3''} = 1$ Hz, H-6), 7.51 (1H, *dd*, $J_{3'',2''} = 2$ Hz, $J_{3'',6} = 1$ Hz, H-3″), 7.73 (1H, *brs*, H-2′), 7.78 (1H, *dd*, $J_{6',5'} = 9$ Hz and $J_{6',2'} = 2$ Hz, H-6′) and 8.09 (1H, $J_{2'',3''} = 2$ Hz, H-2″); MS: *m/z* (rel. int.) 336 (M^+, 58.3), 335 (31), 319 (9.5), 318 (6.2), 307 (47.6), 290 (52.4), 190 (22.6), 175 (50), 160 (66.7), 147 (80), 146 (100), 145 (45.2), 132 (26.2), 119 (28.6) and 104 (19).

PG-R[≡ *mixture of isopongaglabol* (**1**) *and 6-methoxyisopongaglabol* (**2**)]. The black gummy residue obtained by concn of the early $CHCl_3$–MeOH (19:1) fractions on repeated chromatography over Si gel followed by crystallization from EtOH afforded PG-R as light yellow needles, mp 280–285°; λ_{max}^{EtOH} nm: 221, 263.5 and 323; $\lambda_{max}^{EtOH+KOH}$ nm: 224, 241, 312.5 and 390; ν_{max}^{KBr} cm^{-1}: 3600–2000, 1632, 1565, 1450, 1367, 1253, 1180, 1075, 835, 818 and 750.

β-Sitosterol-β-D-glucoside. The brown jelly-like residue from the $CHCl_3$–MeOH (9:1) fractions on rechromatography over Si gel afforded β-sitosterol-β-D-glucoside as a colourless amorphous solid, mp 265°; acetate, mp 168°; identical in all respects (mmp, co-TLC and IR) with authentic sample.

Friedelin. During CC of the petrol-soluble portion of the petrol extract (fraction A [1]) of the flowers of *P. glabra* over Si gel (60–120 mesh), the early petrol–C_6H_6 (1:1) fractions afforded a light yellow waxy solid. This solid, showing one major spot in TLC, was chromatographed twice over Si gel and then crystallized from $CHCl_3$–petrol to afforded friedelin as colourless needles, mp 254°, $[\alpha]_D^{30}$ − 11.9° ($CHCl_3$; *c* 0.066), identical in all respects with authentic sample (mmp, co-TLC and IR).

Ovalichromene B (**12**). The mother liquors after crystallization of ovalitenone [1], showing two spots on TLC, were combined and subjected to rechromatography over Si gel using petrol–C_6H_6 (1:2) as eluent. The earlier fractions afforded ovalitenone and later ones ovalichromene B (**12**). Ovalichromene B crystallized from $CHCl_3$–petrol as colourless needles, mp 176° (lit. [7] 182°), $[\alpha]_D^{30}$ − 116.6° ($CHCl_3$; *c* 0.10) (lit. [7] − 91.6°); light pink colouration with Mg/HCl; λ_{max}^{EtOH} nm (log ϵ): 240 (4.38), 249 (4.37), 269 (4.43) and 313 (3.92); ν_{max}^{KBr} cm^{-1}: 1680, 1643, 1592, 1578, 1440, 1390 and 1375 (–C(Me)$_2$), 1328, 1278, 1095, 1041, 927, 815 and 735; ^1H NMR (80 MHz, $CDCl_3$) δ 1.44 and 1.45 [each 3H, *s*, –C(C<u>H</u>$_3$)$_2$], 2.73 [1H, *dd*, $J_{3(eq),3(ax)} = 16.8$ Hz and $J_{3(eq),2} = 4.8$ Hz, H-3(eq)], 3.02 [1H, *dd*, $J_{3(ax),3(eq)} = 16.8$ Hz and $J_{3(ax),2} = 11.1$ Hz, H-3(ax)], 5.38 [1H, *dd*, $J_{2,3(ax)} = 11.1$ Hz and $J_{2,3(eq)} = 4.8$ Hz, H-2], 5.57 (1H, *d*, $J_{3'',4''} = 9.9$ Hz, H-3″), 6.00 (2H, *s*, –OC<u>H</u>$_2$O–), 6.50 (1H, *dd*, $J_{6,5} = 8.2$ Hz and $J_{6,4''} = 0.6$ Hz, H-6), 6.65 (1H, *dd*, $J_{4'',3''} = 9.9$ Hz and $J_{4'',6} = 0.6$ Hz, H-4″), 6.78–7.02 (3H, *m*, like that of 1,2,4-trichlorobenzene [8], H-2′, H-5′ and H-6′) and 7.74 (1H, *d*, $J = 8.2$ Hz, H-5); MS: *m/z* (rel. int.) 350 (M^+, 100), 335 (80), 202 (12.6), 187 (86.6), 174 (4.3), 159 (9.8), 148 (31.5), 147 (25.2) and 131 (7.8).

Desmethoxykanugin (**10**). The concentrate of the mother

liquors after crystallization of lanceolatin B (**5**) [1] exhibiting TLC spots for lanceolatin B and another major component was subjected to repeated crystallizations from EtOAc–petrol. First two crops of crystals were mixtures of lanceolatin B and desmethoxykanugin and pure desmethoxykanugin was obtained in the third crop as fine colourless needles, mp 146°, pink with Mg–HCl.

Fisetin tetramethyl ether (**11**). The concentrate of the mother liquors after crystallization of pinnatin [1] exhibited two major spots on TLC. It was chromatographed repeatedly over Si gel using $CHCl_3$–MeOH (99:1) as eluent. The early fractions afforded fisetin tetramethyl ether (**11**) and the later ones pinnatin. Fisetin tetramethyl ether crystallized from EtOAc–petrol as colourless needles, mp 147–148°, pink with Mg–HCl.

Cycloart-23-ene-3β-25-diol (**13**). The concentrate of the mother liquor obtained after crystallization of kanugin [1] showed a TLC spot which became prominent on keeping the developed plate in I_2 vapour for 20 min in addition to the spot due to kanugin. Repeated chromatography of this concentrate over Si gel afforded cycloart-23-ene-3β,25-diol (**13**), crystallizing from $CHCl_3$–petrol as colourless needles, mp 198–199° (lit. [9] 200–204°); $[\alpha]_D^{30}+41.6°$ ($CHCl_3$; *c* 0.09); positive Liebermann–Burchardt test; IR and ^1H NMR spectral features are similar to those reported earlier; MS: *m/z* (rel. int.): 442 (M^+, 8.8), 427 (7.3), 424 (61.8), 409 (51.5), 406 (8.8), 391 (13.2), 381 (14.7), 355 (3.2), 343 (14.7), 337 (10.3), 325 (14.7), 315 (13.2), 302 (51.5), 297 (14.9), 284 (13.2), 269 (19.1), 255 (27.9), 203 (66.2), 175 (50) and 109 (100)—characteristic of cycloartene skeleton [10]. On acetylation (Ac_2O–pyridine, room temp., 24 hr) **13** furnished 3β-acetoxycycloart-23-ene-25-ol, mp 150° (lit. [9] 148–150°), $[\alpha]_D^{30}+44.6°$ ($CHCl_3$; *c* 0.066), M^+ 484.

Investigation of second sample of flowers: isolation of 5-methoxyfurano(8,7–4″,5″)flavone (≡ pongaglabol methyl ether [1]) (**8**). Dried and powdered flowers (4 kg) were extracted with petrol and $CHCl_3$ successively, each for 40 hr. The concentrates of the two extracts were mixed and chromatographed over Si gel (60–120 mesh). The concentrate of the early $CHCl_3$–MeOH (97.5:2.5) eluate fractions on rechromatography over Si gel followed by crystallization from EtOAc–petrol afforded 5-methoxyfurano(8,7–4″,5″)flavone (**8**), mp 181° (lit. 180–181° [5], 185° [6]) identical in all respects (mmp, co-TLC and IR) with pongaglabol methyl ether. The concentrate of the mother liquor after crystallization of **8** was chromatographed over Si gel. The solid thus obtained was found to be a mixture of **8** and pinnatin [1] in the ratio of *ca* 12:1 (^1H NMR). The yields were (mg/100 g dry wt), PG-R 2·2, **8** 7·5, **9** 1·0, **10** 3·5, **11** 1·6, **12** 2·5, **13** 0·4, fiedelin 0·3, β-sitosterol-β-D-glucoside 45.

Methylation of PG-R: isolation of isopongaglabol methyl ether (**3**) *and 6-methoxyisopongaglabol methyl ether* (**4**). PG-R (36 mg) was dissolved in MeOH–Et_2O (1:2), cooled and to the cold soln CH_2N_2–Et_2O was added. The reaction mixture was kept 18 hr at room temp. and then the solvent was removed to afford the methylation product as a solid. The methylation product was subjected to prep. TLC over Si gel G using $CHCl_3$–MeOH (49:1). The upper portions of the spots were carefully removed and the component eluted from the absorbent with $CHCl_3$–MeOH (19:1). Another prep. TLC of the component followed by crystallization from $CHCl_3$–MeOH afforded isopongaglabol methyl ether (**3**) as colourless neeldes (18 mg), mp 218°; ν_{max}^{KBr} cm^{-1}: 1655, 1610, 1515, 1405, 1365, 1272, 1190, 1145, 1072, 1025, 832, 820 and 742.

The lower portions of the spots were also removed and the component eluted from the Si gel with $CHCl_3$–MeOH (19:1). The component was then subjected to repeated (×4) prep. TLC and crystallized from $CHCl_3$–MeOH to afford 6-methoxyisopongaglabol methyl ether (**4**) as colourless needles (7 mg), mp 225–226°; ν_{max}^{KBr} cm^{-1}: 1648, 1615, 1515, 1490, 1378, 1272, 1198, 1159, 1080, 1035, 830 and 750.

Demethylation of isopongaglabol methyl ether (**3**): *isopongaglabol* (**1**). To a soln of isopongaglabol methyl ether (12 mg) in CH_2Cl_2 (10 ml) BBr_3 (0.1 ml) was added and the mixture was kept at room temp. for 24 hr. The complex was then decomposed by pouring into ice (~30 g). The mixture was warmed at 100° for 30 min and then filtered. Crystallization of the residue from $CHCl_3$–EtOH afforded isopongaglabol (**1**) (R_f comparable to that of PG-R) as almost colourless needles (8 mg), mp 335°; λ_{max}^{EtOH} nm (log ε): 221 (4.59), 248 (sh, 4.19), 263.5 (4.22) and 323 (4.45); $\lambda_{max}^{EtOH+KOH}$ nm (log ε): 224 (4.51), 241 (4.39), 312.5 (4.02) and 390 (4.59); ν_{max}^{KBr} cm^{-1}: 3100–2400, 1630, 1570, 1455, 1363, 1297, 1253, 1175, 1167, 1070, 830, 810 and 745; ^1H NMR (80 MHz, DMSO-d_6) δ 6.83 (1H, *s*, H-3), 6.88 (2H, pattern resembled a pair of triplets [2], $J_{3',2'} = J_{5',6'} = 9$ Hz and $J_{3',5'} =$ 2.0 or 3.1 Hz, H-3′ and H-5′), 7.50 (1H, *dd*, $J_{3'',2''} = 2.3$ Hz and $J_{3'',6} = 0.9$ Hz, H-3″), 7.63 (1H, *dd*, $J_{6,5} = 8.8$ Hz and $J_{6,3''} =$ 0.9 Hz, H-6), 7.89 (1H, *d*, $J_{5,6} = 8.8$ Hz, H-5), 8.00 (2H, pattern resembled a pair of triplets [2], $J_{2',3'} = J_{6',5'} = 9$ Hz and $J_{2',6'} = 3.1$ or 2.0 Hz, H-2′ and H-6′) and 8.14 (1H, *d*, $J_{2'',3''} =$ 2.3 Hz, H-2″); MS: *m/z* (rel. int.) 278 (M^+, 100), 250 (6.4), 249 (1.0), 160 (94.3), 132 (11.3)125 (17.7), 118 (13.5) and 104 (7).

Synthesis of isopongaglabol methyl ether (**3**) *and isopongaglabol* (**1**). *5-Acetyl-4-hydroxycoumarone* (**14**). Lanceolatin B (**5**) (300 mg) was added to a soln of KOH in EtOH (10 g in 100 ml) and the mixture refluxed for 5 hr. EtOH was removed by distillation, 100 ml H_2O added and the soln acidified with dil. HCl. The ppt formed was extracted with Et_2O. The Et_2O extract (~150 ml) was first extracted with 5% $NaHCO_3$ soln (4 × 50 ml) and then with 3% NaOH soln (4 × 30 ml). The combined NaOH extracts were acidified with dil. HCl and the ppt formed extracted with Et_2O. The light-yellow residue obtained after removal of solvent was chromatographed over Si gel. C_6H_6 elution afforded 5-acetyl-4-hydroxycoumarone (**14**), crystallizing from $CHCl_3$–petrol as almost colourless needles (67.5 mg), mp 95° (lit. [6] 95°); ν_{max}^{KBr} cm^{-1}: 1630, 1607, 1435, 1362, 1300, 1200, 1163, 1059, 818 and 782.

2′-Hydroxy-4-methoxyfurano(3′,4′–4″,5″)chalcone(**17**). To a soln of 5-acetyl-4-hydroxycoumarone (**14**) (50 mg) in a 20% aq. EtOH soln of KOH (30 ml), *p*-anisaldehyde (0.2 ml) was added and the reaction mixture heated at 100° for 5 min and then kept at room temp. for 24 hr. The reaction mixture was dil. with H_2O (100 ml), acidified with dil. HOAc and extracted with $CHCl_3$. The dark-red residue obtained after removal of $CHCl_3$ was chromatographed over Si gel. C_6H_6 elution afforded 2′-hydroxy-4-methoxyfurano(3′,4′–4″,5″) chalcone (**17**), crystallizing from $CHCl_3$–petrol as red needles (60 mg), mp 140°; λ_{max}^{EtOH} nm (log ε): 245 (4.34) and 362 (4.3); ν_{max}^{KBr} cm^{-1}: 1630, 1595, 1508, 1467, 1360, 1287, 1242, 1160, 1090, 1040, 820, 785 and 730; ^1H NMR (80 MHz, $CDCl_3$): δ 3.87 (3H, *s*, $-OCH_3$), 6.96 (2H, pattern resembled a pair of triplets [2], $J_{3,2} = J_{5,6} = 9$ Hz and $J_{3,5} = 2.0$ or 3.1 Hz, H-3 and H-5), 7.02 (1H, H-3″), 7.08 (1H, *dd*, $J_{5',6'} = 8.9$ Hz and $J_{5',3''} = 0.8$ Hz, H-5′), 7.54 (1H, *d*, $J_{\alpha,\beta} = 15.7$ Hz, H-α), 7.58 (1H, *d*, $J_{2',3'} = 2.2$ Hz, H-2″), 7.65 (2H, pattern resembled a pair of triplets [2], $J_{2,3} = J_{6,5} = 9$ Hz and $J_{2,6} = 3.1$ or 2.0 Hz, H-2 and H-6), 7.86 (1H, *d*, $J_{6',5'} = 8.9$ Hz, H-6′), 7.94 (1H, *d*, $J_{\beta,\alpha} = 15.7$ Hz, H-β) and 14.09 (1H, *s*, exchangeable with D_2O, chelated OH on C-2′).

4'-Methoxyfurano(8,7–4'',5'')flavone or isopongaglabol methyl ether (**3**). 2'-Hydroxy-4-methoxyfurano(3',4'–4'',5'')chalcone (**17**) (45 mg) was refluxed in isoamyl alcohol (30 ml) with SeO_2 (100 mg) for 8 hr. The solvent was removed by distillation under red. pres. and the solid obtained chromatographed over Si gel. $CHCl_3$–MeOH (99:1) elution afforded 4'-methoxyfurano(4'',5''–8,7)flavone (**3**), crystallizing from $CHCl_3$–MeOH as colourless needles (36 mg), mp 218°, identical in all respects with the methyl ether of natural isopongaglabol (mmp, co-TLC and IR).

Isopongaglabol (**1**). Isopongaglabol methyl ether (**3**) (20 mg) was demethylated with BBr_3 in CH_2Cl_2 to obtain isopongaglabol (**1**) (14 mg).

Synthesis of 6-methoxyisopongaglabol methyl ether (**4**). *5-Acetyl-4-hydroxy-7-methoxycoumarone* (**15**). Kanjone (**6**) (300 mg) was converted to 5-acetyl-2-hydroxy-7-methoxycoumarone (**15**) following the procedure for the conversion of **5** to **14** described above. **15** crystallized from $CHCl_3$–petrol as light yellow needles (76 mg), mp 106–107° (lit. [11] 107°); ν_{max}^{KBr} cm^{-1}: 1632, 1603, 1478, 1362, 1310, 1200, 1175, 1057, 882, 786 and 753.

2'-Hydroxy-4,5'-dimethoxyfurano(3',4'–4'',5'')chalcone (**18**). 5-Acetyl-4-hydroxy-7-methoxycoumarone (**15**) was converted to 2'-hydroxy-4,5'-dimethoxyfurano(3',4'–4'',5'')chalcone (**18**) following the procedure for the conversion of **14** to **17** described above. **18** crystallized from $CHCl_3$–petrol as red needles (27 mg), mp 131°; λ_{max}^{EtOH} nm (log ϵ): 245 (4.4) and 360 (4.32); ν_{max}^{KBr} cm^{-1}: 1625, 1595, 1540, 1505, 1470, 1355, 1287, 1158, 1092, 1038, 823 and 802; ^1H NMR (80 MHz, $CDCl_3$): 3.87 (3H, *s*, $-OCH_3$ on C-4), 4.05 (3H, *s*, $-OCH_3$ on C-5'), 6.96 (2H, pattern resembled a pair of triplets [2], $J_{3,2} = J_{5,6} = 9$ Hz and $J_{3,5} = 2.1$ or 3 Hz, H-3 and H-5), 7.04 (1H, *d*, $J_{3'',2''} = 2.4$ Hz, H-3''), 7.22 (1H, *s*, H-6'), 7.46 (1H, *d*, $J_{\alpha,\beta} = 15.7$ Hz, H-α), 7.62 (1H, *d*, $J_{2'',3''} = 2.4$Hz, H-2''), 7.66 (2H, pattern resembled a pair of triplets [2], $J_{2,3} = J_{6,5} = 9$ Hz and $J_{2,6} = 3$ or 2.1 Hz, H-2 and H-6), 7.94 (1H, *d*, $J_{\beta,\alpha} = 15.7$ Hz, H-β) and 13.87 (1H, *s*, exchangeable with D_2O, chelated OH on C-2').

4',6-Dimethoxyfurano(8,7-4'',5'')flavone or 6-methoxyisopongaglabol methyl ether (**4**). The chalcone **18** (18 mg) was converted to **4** following the method used for the conversion of **17** to **3**. **4** crystallized from $CHCl_3$–MeOH as colourless needles (13 mg), mp 225–226°, identical in all respects with the methyl ether of natural 6-methoxyisopongaglabol.

Synthesis of 6-methoxyisopongaglabol (**2**). *p*-Benzyloxybenzaldehyde. *p*-Hydroxybenzaldehyde (1 g) was refluxed in Me_2CO with benzyl bromide (1 ml) in the presence of dry K_2CO_3 (3.5 g) for 1 hr in a N_2 atmosphere. The residue obtained after removal of K_2CO_3 and Me_2CO was crystallized from aq. EtOH to furnish *p*-benzyloxybenzaldehyde as colourless needles (1.5 g), mp 80°, ν_{max}^{KBr} cm^{-1}: 2800, 2720, 1700, 1610, 1585, 1255, 1165, 1020, 827 and 735.

4 - Benzyloxy - 2' - hydroxy - 5' - methoxyfurano(3',4'–4'',5'') chalcone (**19**). 5-Acetyl-4-hydroxy-7-methoxy-coumarone (**15**) (25 mg) was converted to 4 - benzyloxy - 2'-hydroxy-5'-methoxyfurano(3',4'–4'',5'')chalcone (**19**) following the procedure used to the conversion of **14** to **17** using *p*-benzyloxybenzaldehyde instead of *p*-anisaldehyde. **19** crystallized from $CHCl_3$–petrol as deep-red needles (35 mg), mp 151°; λ_{max}^{EtOH} nm (log ϵ): 229.5 (4.36), 234.5 (4.37), 245 (sh, 4.33) and 358.5 (4.44); ν_{max}^{KBr} cm^{-1}: 1635 (w), 1598, 1533, 1465, 1357, 1292, 1238, 1157, 1093, 992, 808, 760 and 700; ^1H NMR (80 MHz,$CDCl_3$): δ 4.05 (3H, *s*, OCH_3 on C-5'), 5.14 (2H, *s*, $OCH_2C_6H_5$ on C-4), 7.04 (2H, pattern resembled a pair of triplets [2], $J_{3,2} = J_{5,6} = 8.9$ Hz and $J_{3,5} = 2.0$ or 3.1 Hz, H-3 and H-5), 7.06 (1H, *d*, $J_{3',2'} = 2.1$ Hz, H-3''), 7.22 (1H, *s*, H-6'), 7.42 (5H, *br s*, $-OCH_2C_6H_5$ on C-4), 7.47 (1H, *d*, $J_{\alpha,\beta} = 15.8$ Hz, H-α), 7.62 (1H, *d*, $J_{2'',3''} = 2.1$ Hz, H-2''), 7.65 (2H, pattern resembled a pair of triplets [2], $J_{2,3} = J_{6,5} = 8.9$ Hz and $J_{2,6} = 3.1$ or 2.0 Hz, H-2 and H-6), 7.95 (1H, *d*, $J_{\beta,\alpha} = 15.8$ Hz, H-β) and 13.88 (1H, *s*, exchangeable with D_2O, chelated OH on C-2').

4'-Benzyloxy-6-methoxyfurano(8,7–4'',5'')flavone (**7**). The chalcone **19** (25 mg) was converted to **7** following the method used to convert **17** to **3**. **7** crystallized from EtOAc–petrol as pale yellow needles (20 mg), mp 167°; λ_{max}^{EtOH} nm (log ϵ): 221 (4.66), 259 (4.2), 277.5 (4.31) and 322 (4.52); ν_{max}^{KBr} cm^{-1}: 1625, 1585, 1503, 1477, 1368, 1238, 1173, 1145, 1068, 1000, 922, 822, 745, 752 and 690; ^1H NMR (80 MHz, $CDCl_3$): δ 4.10 (3H, *s*, OCH_3 on C-6), 5.17 (2H, *s*, $OCH_2C_6H_5$ on C-4'), 6.79 (1H, *s*, H-3), 7.12 (2H, pattern resembled a pair of triplets [2], $J_{3',2'} = J_{5',6'} = 9$ Hz and $J_{3',5'} = 2.1$ or 3.1 Hz, H-3' and H-5'), 7.20 (1H, *d*, $J_{3'',2''} = 2.2$ Hz, H-3''), 7.43 (5H, *br s* $OCH_2C_6H_5$ on C-4'), 7.54 (1H, *s*, H-5), 7.79 (1H, *d*, $J_{2'',3''} = 2.2$ Hz, H-2'') and 7.91 (2H, pattern resembled a pair of triplets [2], $J_{2',3'} = J_{6',5'} = 9$ Hz and $J_{2',6'} = 3.1$ or 2.1 Hz, H-2' and H-6').

Hydrogenolysis of 4'-benzyloxy-6-methoxyfurano(8,7-4'',5'')flavone (**7**). A soln of **7** (15 mg) in EtOAc (25 ml) was stirred for 15 min in the presence of 10% Pd–C in a H_2 atm. at *ca* 1 atmosphere pressure. The crude product obtained after removal of EtOAc was chromatographed over Si gel. $CHCl_3$–MeOH (47:3) eluate on concn afforded a solid (R_f comparable to that of PG-R) which crystallized from EtOH as pale-yellow needles (8 mg), mp 320–325°. The ^1H NMR and mass spectra of the crystalline solid indicated it to be a mixture of 6-methoxyisopongaglabol (**2**) and its 2'',3''-dihydro derivative in the ratio of *ca* 3:1. By ^1H NMR two sets of signals were obtained for the two components of the mixture. The appearance of one triplet at δ 4.75 (J = 8.5 Hz) and the possible existence of the other in the region δ 3.2–3.5 (region for the signal of H_2O present in DMSO-d_6) indicated the presence of the 2'',3''-dihydro compound. In the MS also two sets of peaks appeared, the important pairs of peaks are *m/z* 310, 308 (M^+;s) 192, 190; 177 175 and 164, 162.

Acknowledgements—We are grateful to Professor I. Ninomiya, Kobe Women's College of Pharmacy, Japan, Professor F. Bohlmann, Technische Universität, Berlin, West Germany, and Mr. D. F. Dance, Stirling University, U.K. for ^1H NMR and MS measurements. The financial assistance of the University Grants Commission, New Delhi, is acknowledged.

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