Phytochemistry, Vol 22, No 1, pp 308-309, 1983
Printed in Great Britain

0031-9422/83/010308-02$03 00/0

ISOPONGACHROMENE, A CHROMENOFLAVONE FROM *PONGAMIA GLABRA* SEEDS

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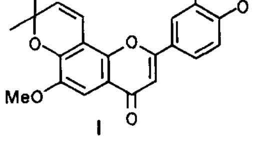
(*Received* 20 *May* 1982)

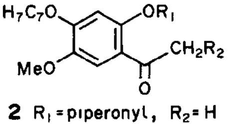
Key Word Index—*Pongamia glabra*, Leguminosae, seeds, chromenoflavone, isopongachromene, karanjin, pongamol, pongapin, kanjone, pongaglabrone, synthesis

Abstract—Isopongachromene, a new chromenoflavone together with karanjin, pongamol, pongapin, kanjone and pongaglabrone were isolated from the ethanolic extract of the seed oil of *Pongamia glabra* The structure of isopongachromene has been established as 6-methoxy-6″,6″-dimethyl-3′,4′-methylenedioxychromeno (7,8,2″,3″)flavone on the basis of spectral evidence and confirmed by synthesis

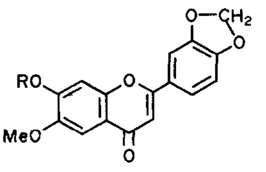
Earlier papers on the immature seeds of *Pongamia glabra* reported the presence of karanjin, pongamol, lanceolatin B, pongapin, kanjone, isopongaflavone and pongol [1, 2] While investigating the seed oil of *P glabra*, we isolated a new chromenoflavone, isopongachromene, isomeric to pongachromene [3] besides karanjin, pongamol, pongapin, kanjone [4] and pongaglabrone [5] Isopongachromene, $C_{22}H_{18}O_5$, a light yellow crystalline solid, has been assigned structure 1 on the basis of spectral and synthetic evidence On TLC plates, it exhibited a deep blue fluorescence in UV light It gave no ferric reaction indicating the absence of any phenolic groups The compound gave a green colour with sulphuric and gallic acids showing the presence of a methylenedioxy group, which was supported by IR (920 cm^{-1}) and ^{1}H NMR spectra (δ6 02) UV and IR spectra resembled closely those of pongachromene [3]



1



2 R_1 = piperonyl, R_2 = H
3 R_1 = H, R_2 = piperonyl



4 R = C_7H_7
5 R = H

The ^{1}H NMR spectrum (90 MHz, $CDCl_3$) exhibited a sharp singlet at δ1 56 for six protons, characteristic of a gem-dimethyl group adjacent to oxygen functions The two doublets at δ5 73 and 6 85, each for one proton, can be assigned to *cis* olefinic protons of the dimethylchromeno system H-5 was indicated downfield at δ7 42 due to a paramagnetic shift caused by a flavone carbonyl group Signals of H-2′ and H-6′ protons appeared at δ7 20–7 35 as a multiplet while H-5′ at δ6 87 appeared as a doublet The methoxyl group and methylenedioxy groups appeared at δ3 93 and 6 02, respectively The structure **1** was confirmed by its synthesis from **2** [6] via the route **2** → **3** → **4** → **5** → **1** (see Experimental)

EXPERIMENTAL

Mps uncorr, IR KBr, UV 95% EtOH, ^{1}H NMR, δ-values in ppm downfield from TMS, Si gel used for chromatography, spots visualized on exposure to I_2

Extraction Mature seeds (10 kg) of *P glabra* were collected from north Delhi in June 1979 The seeds were crushed and extracted with petrol (in a Soxhlet) for 80 hr The petrol extract on evaporation gave an oil (2 5 l), which was subjected to liquid–liquid extraction with EtOH for 80 hr The EtOH extract was concd and kept in a refrigerator for 7 days, when karanjin (3 5 g), mp 156–157° was deposited It was filtered and the residue chromatographed over Si gel

Elution with petrol gave karanjin (1 5 g), petrol–C_6H_6 (9 1) gave pongamol (800 mg), mp 128° and pongapin (200 mg), mp 190–191°, petrol–C_6H_6 (8 2) gave kanjone (30 mg), mp 191° and pongaglabrone (30 mg), mp 233°, and petrol–C_6H_6 (3 2) gave isopongachromene

Isopongachromene (**1**) crystallized from $CHCl_3$–Me_2CO as light yellow crystals (45 mg), mp 272–273° Found C, 69 82, H, 4 78% $C_{22}H_{18}O_6$ requires C, 69.84, H, 4 76% Pink colour with Mg-HCl, UV λ_{max}^{EtOH} nm (log ε) 235 (4 45), 280 (3 00), 328 (4 09) and 340 (4 13), IR ν_{max}^{KBr} cm^{-1} 1640 (C = O), 1380 (gem-diMe), 1245, 1120, 920 (OCH_2O) and 720 (*cis* C = C), ^1H NMR (90 MHz, $CDCl_3$) δ7 42 (*s*, H-5), 7 20–7 35 (*m*, H-2′, H-6′), 6 87 (*d*, *J* = 9Hz, H-5′), 6 85 (*d*, *J* = 10 Hz, H-α), 6 58 (*s*, H-3), 6 02 (*s*, OCH_2O), 5 73 (*d*, *J* = 10 Hz, H-β), 3 93 (*s*, OMe) and 1 56 (*s*, gem-diMe)

Synthesis of isopongachromene (**1**) *and 7-benzyloxy-6-methoxy-3′,4′-methylenedioxyflavone* (**4**) 4-Benzyloxy-5-methoxy-2-(3′,4′-methylenedioxybenzoyloxy)acetophenone (**2**) (100 mg) [6] was dissolved in dry pyridine (2 ml) and powdered KOH (450 mg) was added The mixture was heated at 50–60° for 90 min with occasional shaking It was poured into ice and acidified with HCl, pptated diketone (**3**) was filtered, dried and crystallized from $CHCl_3$–MeOH as yellow plates (70 mg), mp 188–189° It gave a greenish blue ferric reaction

The above diketone (**3**) (70 mg) was dissolved in HOAc (3 ml) and conc HCl (0 2 ml) was added The mixture was refluxed for 3 hr, cooled and poured into ice-cold H_2O The pptated solid (**4**) was filtered and crystallized from MeOH as silky needles (55 mg), mp 199–200° (lit [6] mp 195°), ^1H NMR (90 MHz, $CDCl_3$) δ7 48 (*s*, H-5), 7 17–7 45 (*m*, H-2′, H-6′ and $OCH_2C_6H_5$), 6 91 (*s*, H-8), 6 83 (*d*, *J* = 9 Hz, H-5′), 6 53 (*s*, H-3), 5 98 (*s*, OCH_2O), 5 20 (*s*, $OCH_2C_6H_5$) and 3 95 (*s*, OMe)

Isopongachromene (**1**) A soln of **4** (55 mg) in EtOAc (20 ml) was stirred for 3 hr in the presence of 10% Pd–C in a H_2 atmosphere at *ca* 1 atm pres The crude product obtained after removal of EtOAc was chromatographed over Si gel The $CHCl_3$–MeOH eluate on concn afforded a solid (**5**) which crystallized from EtOH as pale-yellow needles (25 mg), mp 278–280°

5 (25 mg) was dissolved in dioxane (5 ml) and refluxed with 2-chloro-2-methylbut-3-yne (0 2 ml), K_2CO_3 (50 mg) and KI (50 mg) for 16 hr The reaction mixture was diluted with H_2O, extracted with EtOAc and dried After evaporation of the solvent, the residue on purification with prep TLC gave a solid, which crystallized from $CHCl_3$–Me_2CO as light yellow crystals (15 mg), identical with **1** in all respects

Acknowledgement—We thank the C S I R (New Delhi) for financial assistance to one of us (V P P)

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Phytochemistry, Vol 22, No 1, pp 309–311, 1983
Printed in Great Britain

0031-9422/83/010309-03$03 00/0

C-GLYCOSYLXANTHONES IN THE FERN GENERA *DAVALLIA*, *HUMATA* AND *NEPHROLEPIS*

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(*Received* 7 *April* 1982)

Key Word Index—*Davallia*, *Humata*, *Nephrolepis*, Davalliaceae, xanthones, *C*-glycosylation, mangiferin, isomangiferin, biochemical systematics

Abstract—*C*-Glycosylxanthones have been detected in several species of *Davallia*, *Humata* and *Nephrolepis*, while other species lack these compounds This increases the number of fern taxa known to contain *C*-glycosylxanthones from 20 to 33 and the number of xanthone-containing genera from 9 to 11 The taxonomic value of these compounds is still uncertain

C-Glycosylxanthones have previously been reported from the following fern genera *Asplenium* (one species and its hybrids), *Athyrium* (1), *Cardiomanes* (1), *Ctenitis* (1), *Davallia* (1), *Elaphoglossum* (5), *Hymenophyllum* (5), *Marsilia* (3) and *Trichomanes* (2) [1, 2] This paper reports the occurrence of *C*-glycosylxanthones in several additional *Davallia* species as well as in several species of the closely related genera *Humata* and *Nephrolepis*, all members of the Davalliaceae *sensu* Crabbe *et al* [3]

The results of the present survey of 27 fern species for *C*-glycosylxanthones are presented in Table 1 Mangiferin and isomangiferin were found in five of nine species of *Davallia*, one of three species of *Humata* and five of eleven species of *Nephrolepis* Mangiferin alone