TLC on Si gel PF_{254} developed either with $CHCl_3$–MeOH (49.1) or hexane–EtOAc (1 1). Nectriafurone was finally obtained by reversed-phase HPLC by using a column (250 × 9 mm) of Lichrosorb 10 RP 18 developed with MeOH–H_2O (19 1)

In a typical expt with 300 Petri dishes, corresponding to 8 l. of medium, after 12 days of growth of the mutant strain 58, the yields (mg) were. fusarubin 350, anhydrofusarubin 90, anhydrofusarubin lactone 7, javanicin 40, norjavanicin 10, nectriafurone 8 5 All the known substances were identified by direct comparison of the physical properties (R_f, mps) and spectra (UV, IR, MS, NMR) with those of authentic standards and with data in the lit.

Anhydrofusarubine lactone (**1**) Amorphous dark purple powder; UV $\lambda_{\max}^{\text{EtOH}}$ nm 240, 285, 355, 500, IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} 3250–2500, 2840, 1735, 1605, 1585, 1400, MS *m/z* (rel int) 302 $[M]^+$ (100); ^1H NMR, (250 MHz, $CDCl_3$, TMS as int standard) see formula **1**.

Nectriafurone (**2**) Obtained directly as crystals, mp 230° UV $\lambda_{\max}^{\text{EtOH}}$ nm 255, 320, 443, 465, IR $\nu_{\max}$ cm^{-1}. 3350, 3250–2500, 2880, 2820, 1600, 1545, 1450, MS *m/z* (rel. int) 304 $[M]^+$ (100), 286 (86), ^1H NMR. see formula **2**

Triacetate of **2**. Obtained in pyridine–Ac_2O (1 1) amorphous, purified by HPLC (conditions given above) MS *m/z* (rel int)· 430 $[M]^+$ (1), 388 $[M - CH_2CO]^+$ (32), 346 $[388 - CH_2CO]^+$ (12), 286 $[346 - HOAc]^+$ (100), ^1H NMR δ 1 60 (*d*, 3H, $\mathrm{Me\underset{|}{C}HO}$–), 2.44 (3H, *s*, MeCOO–), 2 07 (3H, *s*, MeCOO–), 2.45 (3H, *s*, MeCOO–), 3 91 (3H, *s*, MeO–), 6.44 (*q*, 1H, $\mathrm{Me\underset{|}{C}HO}$–), 6 90 (1H, *s*), 7 98 (1H, *s*)

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GLABRACHALCONE, A CHROMENOCHALCONE FROM *PONGAMIA GLABRA* SEEDS

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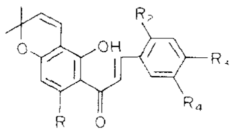
Key Word Index—*Pongamia glabra*, Leguminosae, seeds, chromenochalcone, glabrachalcone, synthesis

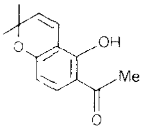
Abstract—Glabrachalcone, a new chromenochalcone has been isolated along with a known chromenochalcone from an ethanolic extract of the seed oil of *Pongamia glabra* The structure of glabrachalcone has been established as 2′-hydroxy-2,4,5-trimethoxy-6″,6″-dimethylchromeno(4′,3′:2″,3″)chalcone on the basis of spectral evidence and was confirmed by synthesis.

In an earlier paper [1] we reported the isolation of a new chromenoflavone, isopongachromene In continuation of this work, we now wish to report the isolation of two chromenochalcones **1** and **2**. Compound **1** is a new compound while **2** has been reported earlier [2] from the heartwood of *Pongamia glabra* and confirmed syntheti-

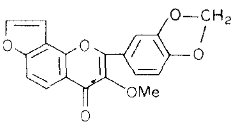


1 R = H, R_2 = R_3 = R_4 = OMe

2 R_1 = OMe, R_2 = R_3 = R_4 = H



3



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cally [3] Compound **1** has been named glabrachalcone

Glabrachalcone, mp 163°, $C_{23}H_{24}O_6$, an orange coloured solid gave a positive ferric chloride reaction It exhibited a characteristic orange colour on TLC when heated with sulphuric acid (10%) Its UV spectrum was characteristic of a chalcone and a bathochromic shift of the 395 nm band on addition of aluminium chloride indicated the presence of a chelated hydroxyl group

^{1}H NMR (90 MHz, $CDCl_3$) exhibited a sharp singlet at δ 1 56 for six protons, characteristic of a *gem*-dimethyl group adjacent to an oxygen function The two doublets at δ 5 47 and 6 65, each integrating for one proton, were assigned to the *cis* olefinic protons of the dimethylchromeno system H-5′ and H-6′ appeared as two *ortho*-coupled doublets at δ 6 25 and 7 50, respectively The two singlets at δ 6 41 and 6 99 can be assigned to H-3 and H-6 H-α and H-β appeared at δ 7 21 and 7 55 as doublets A singlet at δ 14 13 was assigned to a chelated hydroxyl group Based on these data glabrachalcone has been assigned the structure 2′-hydroxy-2,4,5-trimethoxy-6″,6″-dimethylchromeno(4′,3′ 2″,3″)chalcone and this was confirmed by synthesis starting from 6-acetyl-5-hydroxy-2,2-dimethylchromene (**3**)

The physical and spectral data of **2** agreed with the reported data for 2′-hydroxy-6′-methoxy-6″,6″-dimethylchromeno(4′,3′ 2″,3″)chalcone [2]

EXPERIMENTAL

Mps are uncorr, IR Nujol, UV 95% MeOH, ^{1}H NMR δ values in ppm downfield from TMS Si gel was used for chromatography and TLC spots were visualized by exposure to I_2 and heating after spraying with 10% H_2SO_4

Extraction Mature seeds of *P glabra* (10 kg) were collected from north Delhi in June 1979 and extracted with petrol (Soxhlet) for 80 hr and worked-up as described in ref [1] Further elution of the column with C_6H_6–petrol (9 1) gave a fraction which showed three spots on TLC (C_6H_6) Two spots were characteristic of chalcones and the third was yellow These were separated by prep TLC Chalcones were characterized as **1** and **2** while the yellow spot was identified as pongapin (**4**)

Glabrachalcone (**1**) crystallized from EtOH as orange crystals (12 mg), mp 163° Found C, 69 68, H, 6 12, $C_{23}H_{24}O_6$ requires C, 69 68, H, 6 06. UV λ_{max}^{MeOH} nm 228, 272, 332 (sh), 395 IR ν_{max}^{Nujol} cm^{-1} 3380 (chelated OH), 1625 (>C=O), 1370, 1341 (*gem*-diMe), 1020 970 (C=C), 890 and 841 ^{1}H NMR 1 44 (*s*, *gem*-diMe), 3 87 (*s*, OMe), 3 84 (*s*, 2 OMe), 5 47 (*d*, *J* = 10 Hz, H-5″), 6 25 (*d*, *J* = 9 Hz, H-5′) 6 41 (*s*, H-3) 6 65 (*d* *J* = 10 Hz, H-4″), 6 99 (*s*, H-6), 7 21 (*d*, *J* = 17 Hz, H-α), 7 50 (*d*, *J* = 9 Hz, H-6′), 7 55 (*d*, *J* = 17 Hz, H-β) and 14 13 (*s*, chelated O<u>H</u>)

Compound **2** crystallized from EtOH as yellowish-orange needles (15 mg), mp 109 (lit [3] mp 108 109) ^{1}H NMR δ 1 44 (*s*, *gem*-diMe), 3 88 (*s*, OMe) 5 41 (*d* *J* = 10 Hz, H-5″), 5 87 (*s*, H-5′), 6 65 (*d*, *J* = 10 Hz, H-4″), 7 20 7 61 (*m* 5H of ring **B**) 7 75 (*s*, H-α and H-β) and 14 58 (*s*, O<u>H</u>)

Synthesis of glabrachalcone 6-Acetyl-5-hydroxy-2,2-dimethylchromene [4] (resacetophenone) (50 mg) was dissolved in dry dioxane (2 ml) and refluxed with 2-methyl-2-chlorobut-3-yne (0 2 ml), K_2CO_3 (50 mg) and KI (50 mg) for 17 hr The reaction mixture was diluted with H_2O, extracted with Et_2O (2 × 30 ml) and dried (Na_2SO_4) After evaporation of solvent the residue was purified by prep TLC It gave a solid, which crystallized from MeOH as shiny crystals (30 mg), mp 103 ^{1}H NMR ($CDCl_3$) 1 44 (*s*, *gem*-diMe), 2 5 (*s* CO<u>Me</u>), 5 59 (*d*, *J* = 10 Hz, H-3), 6 26 (*d*, *J* = 9 Hz, H-8), 6 65 (*d*, *J* = 10 Hz, H-4), 7 43 (*d*, *J* = 9 Hz, H-7) and 13 30 (*s* OH)

Glabrachalcone (**1**) Compound **3** (30 mg) and 2,4,5-trimethoxybenzaldehyde (35 mg) were dissolved in EtOH (10 ml) and aq NaOH (100 mg in 0 5 ml H_2O) was added The mixture was refluxed for 10 min and cooled The reaction mixture was then diluted with H_2O (10 ml) and extracted with Et_2O (2 × 10 ml) and dried After evaporation of solvent the residue obtained was triturated with petrol, when an orange solid was obtained This was filtered and crystallized from EtOH, giving **1** (20 mg), identical in all respects with the natural sample

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