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ROBUSTIGENIN, A NEW ISOFLAVONE FROM *DERRIS ROBUSTA* SEED SHELLS

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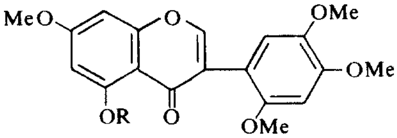
Key Word Index—*Derris robusta*; Leguminosae; robustigenin; 5-hydroxy-7,2′,4′,5′-tetramethoxyisoflavone.

Though *Derris robusta* [1–3] has yielded many compounds with coumarin and isoflavone skeletons, no work has been reported on its seed shells. We now report the isolation of a new isoflavone robustigenin from the benzene extract of the pods (from which seeds had been removed) of *D. robusta*.

It analysed for $C_{19}H_{18}O_7$ (M^+, 358). That robustigenin is an isoflavone containing a chelated hydroxyl was shown by absorptions at 3450 and 1661 cm^{-1} in IR, λ_{max}^{MeOH} 260 nm in UV and δ 13.30 (chelated hydroxyl) and 7.87 (H-2 of the isoflavones) in NMR. The location of a chelated hydroxyl at the 5-position is shown by a bathochromic shift of 10 nm with $AlCl_3$ in UV. Absence of a shift [4] with NaOAc in the UV spectrum indicated the absence of a free hydroxyl at the 7-position. NMR showed three singlets at δ 3.91, 3.85 and 3.76 corresponding to 3, 6 and 3 protons, respectively, due to four methoxyls. The compound gave a positive Gibb's test and a two-proton singlet at δ 6.37 corresponding to H-6 and H-8, thus placing one methoxyl at the 7-position and the remaining three methoxyls in the B-ring. This was confirmed by peaks at *m/e* 167 and 191 arising from retro-Diels–Alder fission of the heterocyclic ring. The presence of M-31 peak [5, 6] in high abundance in the MS indicates a 2′-methoxyl in robustigenin. Sharp singlets at δ 6.88 and 6.60, integrating for one proton each, were attributed to 6′,3′-protons, respectively. Thus robustigenin has 2′,4′,5′-substitution pattern in the side phenyl ring, which was confirmed by its oxidation with alkaline permanganate solution when 2,4,5-trimethoxybenzoic acid was obtained. The identity of the latter was confirmed by comparison with a synthetic sample [7]. The presence of only one hydroxyl is supported by the NMR of its monoacetate and monomethyl ether. Hence robustigenin is 5-hydroxy-7,2′,4′,5′-tetramethoxyisoflavone (**1**).



1 R = H
2 R = Me
3 R = Ac

EXPERIMENTAL

^1H NMR spectra were taken at 60 MHz (unless otherwise stated) in $CDCl_3$ and chemical shifts are given in δ (ppm) scale relative to TMS; UV spectra were obtained in MeOH and IR spectra as KBr discs.

Isolation. Air-dried and coarsely powdered seed shells (750 g) of *D. robusta* were defatted with hot petrol (bp 60–80°) and then extracted with hot C_6H_6 (4 × 500 ml). The C_6H_6 extract was concd and treated with Et_2O when a green solid separated out, which on column chromatography over Si gel using C_6H_6–EtOAc (49:1) as eluent, gave a crystalline compound (200 mg), robustigenin (**1**). TLC: R_f 0.50 (C_6H_6–EtOAc, 9:1); mp 174–5°; λ_{max}^{MeOH} nm: 260, 295 sh; + NaOAc 260, 295 sh; + $AlCl_3$ 270, 300; + NaOMe: 268, 295, 335. γ_{max}^{KBr} cm^{-1}: 3450, 1661, 1610, 1042 and 830. ^1H NMR (90 MHz, $CDCl_3$): δ 3.76 (*s*, 3H, $OC\underline{H}_3$), 3.85 (*s*, 6H, 2 × $OC\underline{H}_3$), 3.91 (*s*, 3H, $OC\underline{H}_3$), 6.37 (*s*, 2H, $Ar\underline{H}_6$ and $Ar\underline{H}_8$), 6.60 (*s*, 1H, $Ar\underline{H}_{3'}$), 6.88 (*s*, 1H, $Ar\underline{H}_{6'}$), 7.87 (*s*, 1H, $\underline{H}_2$) and 13.30 (*s*, 1H, chelated hydroxyl). MS (*m/e*, %): 358 (M^+, 100), 343 (M − Me, 20), 327 (M − OMe, 20), 191 (7) and 167 (17) (RDA fragments).

Robustigenin acetate. Acetylation of robustigenin (Ac_2O/Py) gave the monoacetate (**3**) as needles, mp 168°; γ_{max}^{KBr} cm^{-1}: 1767, 1645, 1621, 1042, 841 and 823. ^1H NMR ($CDCl_3$): δ 2.38 (*s*, 3H, $-OCOC\underline{H}_3$), 3.73 (*s*, 3H, $OC\underline{H}_3$), 3.83 (*s*, 3H, $OC\underline{H}_3$), 3.88 (*s*, 6H, 2 × $OC\underline{H}_3$), 6.56 (*d*, *J* = 2.5 Hz, 1H, Ar-$\underline{H}_6$), 6.75 (*d*, *J* = 2.5 Hz, 1H, Ar-$\underline{H}_8$), 6.59 (*s*, 1H, Ar-$\underline{H}_{3'}$), 6.83 (*s*, 1H, Ar-$\underline{H}_{6'}$) and 7.78 (*s*, 1H, $\underline{H}_2$).

Robustigenin methyl ether. Methylation of robustigenin with Me_2CO–K_2CO_3–Me_2SO_4 gave the monomethyl ether (**2**) as needles, mp 192–3°; γ_{max}^{KBr} cm^{-1}: 1653, 1605, 1040, 857 and 820. ^1H NMR ($CDCl_3$): δ 3.70 (*s*, 3H, $OC\underline{H}_3$), 3.81 (*s*, 3H, $OC\underline{H}_3$), 3.85 (*s*, 3H, $OC\underline{H}_3$), 3.89 (*s*, 6H, 2 × $OC\underline{H}_3$), 6.32 (*d*, *J* = 2.5 Hz, 1H, Ar-$\underline{H}_6$), 6.42 (*d*, *J* = 2.5 Hz, 1H, Ar-$\underline{H}_8$), 6.57 (*s*, 1H, Ar-$\underline{H}_{3'}$), 6.93 (*s*, 1H, Ar-$\underline{H}_{6'}$) and 7.75 (*s*, 1H, $\underline{H}_2$).

Oxidation of robustigenin. Oxidation of robustigenin (80 mg) with alkaline $KMnO_4$ at 50–60° and subsequent work-up gave a compound (10 mg), mp 144° (lit. [7] mp 144–145.5°); γ_{max}^{KBr} cm−1: 1709, 1563, 1040, 1015 and 876; identified as 2,4,5-trimethoxybenzoic acid by direct comparison (mmp, co-TLC and co-IR) with a synthetic sample.

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