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Note

Flavone and isoflavone derivative from the seeds of *Derris robusta* with pods

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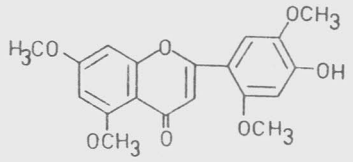
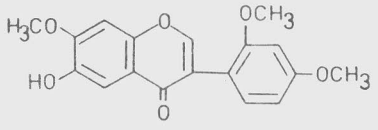
From the seeds of *Derris robusta* with pods, a new 4 the - hydroxy-5,7,3′,6′-tetramethoxyflavone and 6-hydroxy-7,2′,4′-trimethoxyisoflavone have been isolated and their structures elucidated.



(1)



(2)

Derris robusta[1,2] Benth. (Leguminosae) is a deciduous hardy tree, highly distributed in the Himalayas from Kumaon east ward, Assam and western parts of Indian peninsula. It is used for pest control[3] in horticuture, agriculture and in poultry. Earlier, the presence of robustic acid[4], rotenone[5], robustigenin[6], robone[7] and derrone[8] have been reported from the different parts of this plant. This paper describes the isolation of new flavone and isoflavone derivative from the seeds of *D. robusta* with pods.

The elemental analysis and molecular ion peak at m/z 358 in the mass spectrum of compound **1** led to the molecular formula $C_{19}H_{18}O_7$. Its colour reactions[9-13] indicated it to be a flavone. Its UV absorption bands[14] at λ_{max} 352 and 274 nm was in good agreement with flavonoid nature. The compound on acetylation gave mono acetate indicating the presence of only one hydroxyl group[15,16]. The solubility of the compound in aqueous sodium carbonate indicated the presence of phenolic hydroxyl group at position C-4′[17]. Its ^{1}H NMR spectrum exhibited the signal at δ 12.60 (s, 1H, OH) for one hydroxyl group and signals for four methoxyl groups at δ 3.03 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3) and 3.54 (s, 3H, OCH_3) each corresponding to three protons respectively. It showed the two aromatic protons at δ 6.28 (d, *J*=2.5 cps, 1H) and 6.44 (d, *J*=2.5 cps, 1H) for H-6 and H-8 positions. *J* values clearly indicated that both the protons were metacoupled[18]. Whereas the signals appeared as singlets at δ 6.91 (s, 1H) and 7.40 (s, 1H) for H-2′ and H-5′ positions respectively, this conclusion was further confirmed by its mass spectrum which exhibited a prominent peak at m/z 180 establishing the structure of ring A while fragment peak at m/z 178 supported the structure of ring B. Both these fragments confirmed that ring A had two methoxyl groups where as ring B had one hydroxyl and two methoxyl groups. Compound **1** was thus established to be 4′-hydroxy-5,7,3′,6′-tetramethoxyflavone. This structure was further supported by ^{13}C NMR data.

Compound **2**, m.p. 204°, gave the positive colour reactions of isoflavones[9,13,19,20] and was analysed for $C_{18}H_{16}O_6$ (M^+ 328). Its UV absorption bands at λ_{max} 255 and 290 nm[21] was in good agreement with isoflavone. Its ^{1}H NMR spectrum revealed the presence of one hydroxyl and three methoxyl groups. The presence of one hydroxyl and one methoxyl groups in ring A and the two methoxyl groups in ring B was evident from the mass spectrum of the compound. Its mass spectrum gave the prominent peak at m/z, 166 due to ring A fragment ion and at m/z 162 due to the ring B fragment ion. The ^{1}H NMR spectrum of the compound showed the position of hydroxyl group signal at δ 12.90 (s, 1H, OH) for single proton only which can be assigned to H-6 position. On acetylation, compound gave mono acetate which showed the signal at δ 2.28 (s, 3H,

CH_3COO) in its ^1H NMR spectrum. The compound showed a low field singlet at δ 7.89 (s, 1H) characteristic of the C-2 proton of the isoflavone nucleus[22]. Further, it exhibited two sharp singlets at δ 6.87 (s, 1H) and 6.65 (s, 1H) for C-5 and C-8 positions. The doublet at δ 7.42 (d, 1H) and double doublet at δ 6.46 (dd, 2H) were assignable to C-6′, C-3′ and C-5′ positions respectively. The remaining positions were inferred by three singlets at δ 3.70 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3) and 3.88 (s, 3H, OCH_3) each integrating for three protons confirming the presence of three methoxyl groups at C-7, C-2′ and C-4′ positions. The structure of the compound was further confirmed by ^{13}C NMR spectrum. Thus, the structure of the compound **2** was identified as 6-hydroxy-7,2′,4′-trimethoxyisoflavone.

Experimental Section

The seeds of *D. robusta* with pods were collected from Dehradun, India. All m.ps are uncorrected and were determined on an electrically heated melting point apparatus. TLC was carried out on silica gel G (Merck 7731) with (i) DCM (ii) DCM-EtOH AC (9:1). Column chromatography was done on silica gel 60 (Merck 7734). UV spectra were recorded in (i) EtOH and (ii) MeOH solution on a Beckmann-DK2 spectrophotometer. ^1H NMR spectra were measured at 90 MHz in (benzene) D_6 and DMSO solution on a Varian EM-360 spectrometer using TMS as internal standard. ^{13}C NMR spectra were also recorded at 90 MHz in $CDCl_3$ and DMSO soln. Mass spectra were recorded on a Jeol-JMS-D 300 instru-ment.

Air dried and finely crushed seeds of *D. robusta* with pods (5 kg) were extracted with boiling hexane. The concd. extract was loaded over a flash column and then eluted with different organic solvents of increasing polarity. Elution with C_6H_6-DCM (4:6) fraction yielded a creamish white compound (I). Then the defatted seeds were finally extracted with ethanol. The concd. extract was loaded over a flash cc. using different organic solvents in increasing order of their polarity. Elution with DCM-EtOAc (9:1) fraction yielded a greenish yellow coloured compound with fluorescence in UV light (2).

Compound **1**: Yield 400 mg, m.p. 156°, homogenous on TLC, Rf 0.60 (solvent i) 0.63 (solvent ii). Found: C, 63.5%, H, 5.03%. Calculated for $C_{19}H_{18}O_7$: C, 63.3%. H, 5.028%. UV λ_{max}^{MeOH} nm, 274, 352. ^1H NMR [$(C_6H_6)D_6$, 90 MHz]: δ 3,03 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 6.22 (d, J=2.5 cps, 1H, H-6), 6.35 (s, 1H, H-3), 6.44 (d, J=2.5 cps, 1H, H-8), 6.91 (s, 1H, H-2′), 12.60 (s, 1H, OH), ^{13}C NMR: δ 121.8 (s, C-1′), 115.5 (d, C-2′), 144.8 (s, C-6′), 144.8 (s, C-4′), 117.1 (d, C-5′), 119.2 (s, C-6′), 164.9 (s, C-2), 107.2 (d, C-3), 181.0 (s, C-4), 155.0 (s, C-5), 98.3 (d, C-6), 164.1 (s, C-7), 92.8 (d, C-8), 116.8 (s, C-9), 100.2 (s, C-10), 55.2 (q), 56.3 (q), 56.5 (q), 57.1 (q), MS: 358 $(M)^+$, m/z 357, 343, 327, 315, 180, 178, 149.

Compound **2**: Yield 325 mg, m.p. 204°, homogenous on TLC, Rf 0.50 (solvent ii), Found: C 65.9%, H-4.95%. Calculated for $C_{18}H_{16}O_6$: C, 65.95%, H-4.87%. UV λ_{max}^{MeOH} nm 255, 290. ^1H NMR [DMSO, 90 MHz]: δ 3.70 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.46 (dd, 2H, H-3′ and H-5′), 6.65 (s, 1H, H-8), 6.87 (s, 1H, H-5), 7.42 (d, 1H, H-6′), 7.89 (s, 1H, H-2), 12.90 (s, 1H, OH), 2.28 (s, 3H, CH_3COO), ^{13}C NMR [DMSO, 90 MHz]: δ 120.30 (s, C-1′), 151.91 (s, C-2′), 109.33 (d, C-3′), 147.20 (s, C-4′), 106.00 (d, C-5′), 114.91 (d, C-6′), 154.72 (d, C-2), 140.74 (s, C-3), 180.60 (s, C-4), 97.81 (d, C-5), 162.20 (s, C-6). 165.11 (s, C-7), 92.00 (d, C-8), 157.60 (s, C-9), 100.31 (s, C-10), 55.50 (q), 56.12 (q), 56.51 (q), MS: 328 $[M]^+$, m/z 327, 313, 285, 166, 164, 162.

Monoacetate of compound **2**: Compound **2** (20 mg) was acetylated with Ac_2O (5 mL) and pyridine (1 mL) at room temperature for 48 hr. Crystallization from EtOAc gave a solid. Found: $COCH_3$ 10.31%. Calculated for $C_{18}H_{15}O_6$: $(COCH_3)$-$COCH_3$ 10.39%.

References

1 Kirtikaran K R & Basu B D, *Indian medicinal plants* (L M Basu, India), **1933**.
2 Chopra R N, Nayar S L & Chopra I C, *Glossary of Indian medicinal plants* (CSIR, New Delhi), **1956**.
3 Molyneux F, *Aust Chem Process*, 25, **1972**, 9.
4 Mercier & Christiane, C R *Acad Sci Ser*, 270, **1970**, 1422.
5 Delfel & Norman E, *J Ass off Anal Chem*, 56, **1973**, 1343. *Chem Abstr*, reference.
6 Chibber S S & Sharma R P, *Phytochemistry*, 18, **1979**, 1082.
7 Chibber S S, Sharma R P & Dutt S K, *Phytochemistry*, 18, **1979**, 2056.
8 Chibber S S & Sharma R P, *Phytochemistry*, 19, **1980**, 1857.
9 Shinoda J, *J Chem Pharm Soc Japan*, 48, **1928**, 214.

10 Geissman T A, *Modern methods of plant analysis,* Vol. III, edited by K Peach & M V Tracey (Julius Springer, Berlin), **1955,** p. 450.
11 Horhammer L & Wagner H, Deut, Apetheber K, 759, **1962**, 102.
12 Horowitz r M, *J Org Chem*, 22, **1957**, 1733.
13 Brigg L H & Locker R H, *J Chem Soc*, **1951**, 3136.
14 Geissman T A, *Modern methods of plant analysis*, Vol. III, edited by K Peach & M V Tracey (Julius Springer, Berlin), **1955,** p. 485.
15 Wisenberger E, *Mikrochemie*, 33, **1947,** 51.
16 Belcher R & Godbert A I, *Semi micro quantitatie organic analysis* (Longman, Green and Company, New York), **1954,** p. 164.
17 Thomson R H, *Naturally occurring quinones* (Academic Press, London), **1971,** p. 40.
18 Harborne J B, Mabry T J & Mabry Helga, *The flavonoids* (Chapman & Hall, London), 1975, p. 63.
19 Asahina Y & Inubuse M, *Ber dt Chem Gres*, 61, **1928,** 1646.
20 Geissman T A, in *The Chemistry of flavonoid compounds* (INC, New York), **1962,** p. 72.
21 Mabry T J, Markham K R & Thomas M B, *The systematic identification of flavonoids* (Springer Verlag, New York), **1970,** p. 166.
22 Mabry T J, Markham K R & Thomas M B, *The systematic identification of flavonoids* (Springer Verlag, New York), **1970,** 267.