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ISOFLAVONES OF *MOGHANIA MACROPHYLLA*

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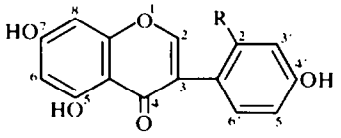
Key Word Index—*Moghania macrophylla*; Leguminosae; isoflavones; genistein; 5,7,2',4'-tetrahydroxyisoflavone; 5,7,4'-trihydroxy 6 (or 8)-C-(1,1-dimethylallyl)isoflavone.

Moghania macrophylla is one of the fifteen species of *Moghania* that occur in India and is an important host plant for the Indian lac insect. The dried pods of the plant are used for preparing the dye "Wars". Previous chemical work [1] on the leaves and flowers revealed the presence of novel chromenochalkones: flemingin D, E and F. From the wood sitosterol, α-amyrin, lupeol, procyanidin and a new isoflavone, identified as 5,7,2',4'-tetrahydroxyisoflavone (**1**, R = OH), were reported [2]. Isoflavones as a class occur quite characteristically in the Leguminosae [3] but there is no record of them in *Moghania* except for the above single instance. We wish to report here our analysis of the extracts of the wood of *M. macrophylla* and the isolation of another new isoflavone.

The combined acetone and ethanol extracts yielded three ferric positive compounds separated by column chromatography followed by prep. TLC. One of these was readily identified as genistein (**1**, R = H) based on UV, ^{1}H NMR and MS and direct comparison with an authentic sample: the second was identical with 5,7,2',4'-tetrahydroxyisoflavone (**1**, R = OH) [2]. The last compound is an isoflavone of molecular formula $C_{20}H_{18}O_5$, (MS and elemental analysis). Its UV and spectral shift data, IR bands at 1653 and 1333 cm^{-1} were consistent with the presence of a 5-hydroxyisoflavone chromophore. Assuming the other two oxygens to be present as hydroxyl groups, this leaves a C_5H_9 unit to be accommodated in the molecule. The structure **2** was deduced based on analysis of its ^{1}H NMR and MS.

Some of the ^{1}H NMR signals were readily assigned. A signal at δ 8.1 was due to the C-2 proton of the isoflavone. The protons at δ 7.40 and 6.84 were the two pairs of *ortho* coupled protons at 2',6' and 3',5' respectively. This fact required the placement of a hydroxyl at 4' position. No *meta* coupled proton signals were found; instead, a one proton singlet at δ 6.29 was observed. The high field of the signal indicated that it belonged to the phloroglucinol A ring of the isoflavone. Hence either 6 or 8 position of the isoflavone was substituted. The remaining signals for the aliphatic methyls and the olefinic protons confirmed the earlier inference of the presence of a C_5H_9 chain occupying either the 6 or 8 position. Since a six proton sharp singlet at δ 1.61 must be due to two methyls on a tertiary carbon, the presence of a 1,1-dimethylallyl was indicated and was then confirmed by the multiplets centred at δ 4.85 and 6.27 which together integrate for three protons and conform to an ABX system. A first order analysis of this system treated as AMX system has given the coupling constants, namely J_{AX} = 17.8 Hz, H_{BX} = 10 Hz and J_{AB} = 1.0 Hz, in close agreement with a vinyl group [4]. Catalytic hydrogenation of the compound gave a product whose ^{1}H NMR was devoid of the olefinic protons but showed the typical quartet and triplet of the ethyl group arising from the vinyl group. Consequently the original component could be formulated as either 6-C- or 8-C-(1,1-dimethylallyl)-5,7,4'-trihydroxyisoflavone. The MS was also in agreement with the proposed structures. It showed retro-Diels Alder fragmentation giving rise to diagnostic ions at *m/e* 118 (**3**, acetylenic ion) and 221 (**4**, ketenic + H ion).

The structure **2** is the most likely in view of the following observations. The compound responded readily to Gibbs test and brief methylation (CH_2N_2) gave a ferric positive product presumably the 7,4'-dimethyl ether. The methylated product on heating with formic acid formed a new product totally devoid of phenolic properties. This result required the location of the dimethylallyl group at



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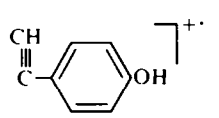

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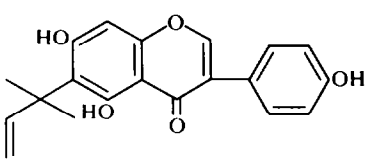

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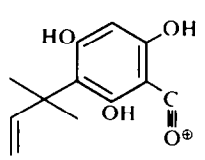

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C_6, which cyclises with the 5-OH of the isoflavone (TLC scale experiments).

2 is a new isoflavone and is the first natural flavonoid bearing a 1,1-dimethylallyl unit. The isomeric 3,3-dimethylallyl (isopentenyl) flavonoids are quite common [5].

EXPERIMENTAL

Isolation of the isoflavones. The finely cut air dried wood (1 kg) was extracted successively with petrol, C_6H_6, Me_2CO and EtOH. The Me_2CO extracts and the ether soluble portion of the alcoholic extracts were combined, evapd and the residue was subjected to chromatography over Si gel. The vol. of each fraction was about 100 ml. Fractionation was monitored by TLC using alcoholic $FeCl_3$ as spray reagent. Elution of the column with C_6H_6–EtOAc (9:1) yielded a mixture containing two ferric positive compounds. They were separated by prep. TLC on Si gel 0.5 mm C_6H_6–EtOAc, 9:1 (the new isoflavone and genistein). Elution of the column with C_6H_6–EtOAc (17:3), yielded a mixture of phenolic compounds containing one major compound. This mixture was subjected to prep. TLC ($CHCl_3$–MeOH, 94:6) and the chief phenolic was isolated. Further elution of the column gave a complex mixture giving a very faint ferric positive reaction.

5,7,4′-Trihydroxy-6-C(1,1-dimethylallyl) isoflavone. Crystallized from $CHCl_3$–MeOH as prisms, mp 123–24° (20 mg). It gave a purple colour with Gibbs reagent. (Found: C, 70.9; H, 5.2. $C_{21}H_{18}O_5$ requires C, 70.9; H, 5.3%). λ_{max}^{MeOH}: 266, 315 (sh) nm; +NaOH: 268, 315 (sh) nm; +$AlCl_3$: 278, 322 nm; +NaOAc H_3BO_3: 266, 315 (sh) nm. ν_{max}^{KBr}: 3333, 1653, 1585, 1515, 1399, 1333, 1253, 1235, 1205, 1170, 1064, 1010, 901, 889 and 835 cm^{-1}. ^1H NMR (100 MHz, CD_3COCD_3): 1.61 (6H, $-C(Me)(Me)$), 4.90 (1H, *d*, J_{AX} = 17.8, $=CH_X(H_A)(H_B)$), 4.80 (1H, *d*, J_{BX} = 10.00 Hz, $=CH_X(H_A)(H_B)$), 6.25 (1H, *dd*, $J_{AX} + J_{BX}$ = 28, $-CH_X=C(H_A)(H_B)$), 6.29 (1H, *s*, C_8-H), 6.84 (2H, *d*, *J* = 8 Hz, $C_{3',5'}$-H), 7.40 (2H, *d*, *J* = 8 Hz, $C_{2',6'}$-H) and 8.10 (1H, *s*, C_2-H). MS (*m/e*, % abundance): 338 (M^+, 13.9), 323 (14.0), 294 (10.8), 283 (16.8), 221 (11.4), 203 (18.1), 190 (26.7), 153 (7.4), 152 (4.5), 141 (28.4), 121 (21.6) and 118 (15.5).

Genistein. Crystallized from $CHCl_3$–MeOH (20 mg), mp 292–3° (Found: C, 66.4; H, 3.1. $C_{15}H_{10}O_5$ requires C, 66.6; H, 3.7%). λ_{max}^{MeOH}: 261, 315 (sh) nm, +NaOAc: 270 nm, +$AlCl_3$: 273, 332 nm, +NaOAc–H_3BO_3: 262 nm, λ_{max}^{KBr}: 3340, 1655 cm^{-1}. ^1H NMR (100 MHz, CD_3COCD_3): 6.20 (1H, *d*, *J* = 2 Hz, C_6-H), 6.31 (1H, *d*, *J* = 2 Hz, C_8-H), 6.84 (2H, *d*, *J* = 9 Hz, $C_{3',5'}$-H), 7.38 (2H, *d*, *J* = 9 Hz, $C_{2',6'}$) and 8.10 (1H, *s*, C_2-H). MS (*m/e*, % abundance): 270 (M^+, 10.2%), 269 (2.6), 165 (5.4), 153 (76.1), 152 (50.5), 135 (13.6), 124 (54.3) and 118 (100). Mmp with an authentic sample of genistein was undepressed. The IR spectrum of the compound was superimposable with that of genistein.

5,7,2′,4′-Tetrahydroxyisoflavone. It was crystallized from $CHCl_3$–MeOH (30 mg), mp 270–73°. (Found: C, 62.7; H, 3.5. $C_{15}H_{10}O_6$ requires C, 62.9; H, 3.5%). λ_{max}^{MeOH}: 258, 315 (sh) nm, +$AlCl_3$: 268, 315 (sh) nm, +NaOAc: 270, 320 (sh) nm, +NaOAc–H_3BO_3: 258, 315 (sh) nm. ν_{max}^{KBr}: 3300, 1655, 1615. Mmp with a sample of 5,7,2′,4′-tetrahydroxyisoflavone was undepressed.

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