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COUMARINS FROM *FRAXINUS FLORIBUNDA* LEAVES

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Key Word Index—*Fraxinus floribunda*; Oleaceae; coumarins; 8-acetyl-7-hydroxy-6-methoxycoumarin; 8-methoxycoumarin; fraxetin; aesculetin; 2,5-dihydroxy-6-methoxyacetophenone.

Fraxinus floribunda Wall, a large tree, grows in India in the eastern Himalayas and Khasi Hills. In an earlier communication [1], the chemistry of some of its bark constituents was discussed. We have now isolated 8-acetyl-7-hydroxy-6-methoxycoumarin (**1**), 8-methoxycoumarin (**2**), 2,5-dihydroxy-6-methoxyacetophenone (**3**), fraxetin and aesculetin from an alcoholic extract of the leaves.

Compound **1**

$C_{12}H_{10}O_5$, mp 178–179°, M^+ 234, gave a reddish brown ferric colour and had UV and IR spectra characteristic of a coumarin. Its NMR spectrum ($CDCl_3$) showed signals for an acetyl, a methoxyl and a chelated hydroxyl group, an aromatic proton and the two olefinic protons of the pyrone ring. Its UV maxima shifted bathochromically in the presence of $AlCl_3$, further supporting the chelation of a hydroxyl with an acetyl group. In the NMR spectrum, the benzene-induced upfield shift of the methoxyl signal was *ca* 0.3 ppm which excluded its presence at the C-5 and C-7 positions [2]. The presence of M − 15 peak in the MS supported this conclusion [3]. On the basis of the above spectral data and also its mp, **1** was considered to be 8-acetyl-7-hydroxy-6-methoxycoumarin, known synthetically [4]. Complete identity of **1** in all respects with a synthetic sample confirmed the above structure.

Compound **2**

$C_{10}H_8O_3$, mp 89–90°, M^+ 176, had IR absorption frequency at 1715 and 1610 cm^{-1} attributable to a coumarin system. Its NMR spectrum showed that the compound is a monomethoxycoumarin. The benzene-induced upfield shift of the methoxyl signal by 0.30 ppm, the presence of M − 15 peak in the MS [3] and the hypsochromic shift of the UV maxima of **2** with respect to the parent coumarin by 24 and 20 nm [5] suggested that **2** is 8-methoxycoumarin. Comparison with a synthetic sample confirmed the identity [6].

Compound **3**

$C_9H_{10}O_4$, mp 89–90°, gave a green ferric colour. Its NMR spectrum showed it to be a tetra-substituted benzene derivative having an acetyl, a methoxy and two hydroxyl groups, one of which is chelated. The two aromatic protons appeared as *ortho*-coupled doublets (J = 9 Hz) at δ 6.62 and 7.06. Absence of a shift with NaOAc–H_3BO_3 in the UV spectrum indicated that the two hydroxyl groups are not *ortho* to each other. From the above data, **3** has been identified as 2,5-dihydroxy-6-methoxyacetophenone. Its identity has been confirmed by comparison with a synthetic sample [7].

To our knowledge, this is the first reported isolation of

1–3 from a natural source.

EXPERIMENTAL

All mps are uncorr. ^{1}H NMR spectra were recorded at 60 MHz in $CDCl_3$ soln with TMS as internal standard and IR spectra were taken in KBr. For comparison studies, synthetic samples were prepared as described in the literature. The plant material was collected from eastern Himalayas (ht ≈ 5000′), India.

Air-dried leaves (1.5 kg) were extracted in hot petrol and alcohol in succession. The concentrate of the alcoholic extract was treated with petrol and then with MeOH when a solid (4 g) was left behind which was identified as mannitol. The MeOH solubles were chromatographed on a Si gel column. Subsequent prep. TLC of the earlier $CHCl_3$ fractions yielded **1** (40 mg), **2** (50 mg) and **3** (30 mg) (Si gel G, C_6H_6–petrol–EtOAc, 4:4:1; R_f: 0.57, 0.71 and 0.65, respectively). The $CHCl_3$–MeOH (98:2, 95:5) fractions yielded fraxetin (50 mg) and aesculetin (60 mg) and their identities were established by comparison with authentic samples.

1 crystallized as pale yellow needles from EtOH, mp 178–179°; λ_{max}^{MeOH} nm (log ε); 260 (3.87); 355 (3.865); +$AlCl_3$: 298, 350, 400 nm; +NaOH: 310, 385 nm. ν_{max}^{KBr} cm^{-1}: 3420 (br), 1728, 1628, 1560, 1465, 1415, 1370, 1330, 1290, 1270, 1095, 1050, 982, 870, 820. ^{1}H NMR ($CDCl_3$): δ 2.92 (3 H, *s*, –COMe), 3.9 (3 H, *s*, –OMe), 6.22 (1 H, *d*, *J* = 10 Hz, C-3 proton), 6.95 (1 H, *s*, C-5 proton), 7.55 (1 H, *d*, *J* = 10 Hz, C-4 proton), 14.3 (1 H, *s*, –OH, exchanged with D_2O). MS (*m/e*, rel. int.): 234 (M^+, 63), 219 (M − Me, 43) 206 (M − CO, 6), 191 (M − COMe, 13), 43 (–COMe, 100). (Found: C, 61.8; H, 4.4. $C_{12}H_{10}O_5$ requires: C, 61.53; H, 4.27%). **2** separated as pale yellow needles from EtOH, mp 89–90°. λ_{max}^{MeOH} nm (log ε): 250 (3.94), 290 (4.21); ν_{max}^{KBr} cm^{-1}: 1715, 1610, 1575, 1475, 1410, 1282, 1170, 1085, 825, 750; ^{1}H NMR ($CDCl_3$): δ 3.92 (3 H, *s*, –OMe), 6.42 (1 H, *d*, *J* = 10 Hz, C-3 proton), 7.15 (3 H, *m*, C-5, C-6, C-7 protons), 7.63 (1 H, *d*, *J* = 10 Hz, C-4 proton): MS (*m/e*, rel. int.): 176 (M^+, 100), 161 (M − Me, 8), 148 (M − CO, 15), 133 (15), 105 (19), 77 (16). (Found: C, 68.3; H, 4.8; $C_{10}H_8O_3$ requires: C, 68.18; H, 4.54%). **3** crystallized as yellow plates, mp 89–90°; λ_{max}^{MeOH} nm: 263, 365; +$AlCl_3$: 285, 360, 440 nm: +NaOAc + H_3BO_3: 265, 365 nm; + NaOH: 280, 310, 385 nm; ν_{max}^{KBr} cm^{-1}: 3350, 1640, 1600, 1575, 1475, 1360, 1280, 1055, 940, 915, 830. ^{1}H NMR ($CDCl_3$): δ 2.72 (3 H, *s*, –COMe), 3.85 (3 H, *s*, –OMe), 5.5 (1 H, *s*, C-5 OH, exchanged with D_2O), 6.62 (1 H, *d*, *J* = 9 Hz, C-3 proton), 7.06 (1 H, *d*, *J* = 9 Hz, C-4 proton), 12.2 (1 H, *s*, C-2OH, exchanged with D_2O). (Found: C, 59.1; H, 5.7. $C_9H_{10}O_4$ requires: C, 59.34; H, 5.49%).

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