Four New Flavonoids Isolated from *Alnus sieboldiana*[1]

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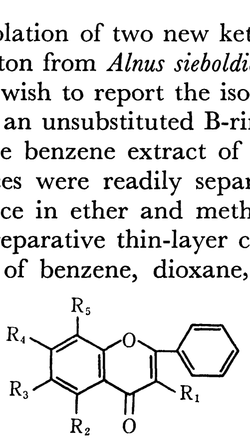
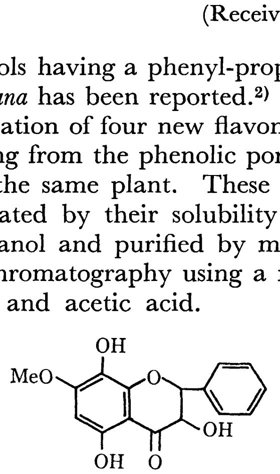
Isolation of two new ketols having a phenyl-propane skeleton from *Alnus sieboldiana* has been reported.[2] We now wish to report the isolation of four new flavonoids with an unsubstituted B-ring from the phenolic portion of the benzene extract of the same plant. These substances were readily separated by their solubility difference in ether and methanol and purified by means of preparative thin-layer chromatography using a mixture of benzene, dioxane, and acetic acid.





$R_1=R_2=R_4=OH$ $R_3=OMe$ $R_5=H$ (I) (IV)
$R_1=R_3=R_4=OMe$ $R_2=OH$ $R_5=H$ (II)
$R_1=H$ $R_2=OH$ $R_3=R_4=R_5=OMe$ (III)

3,5,7-Trihydroxy-6-methoxyflavone (I). Compound I (a main flavonoid of the plant), $C_{16}H_{12}O_6$, M^+ 300, mp 239.0—241.0°C, exhibited positive coloration with $FeCl_3$ and Mg-HCl tests and the spectral properties as follows: *m/e* 285 (M-15), 282 (M-H_2O), 257 (M-43, base), 105, 77, 69; λ_{max}^{EtOH} mμ (log ε) 270 (4.25), 325 (4.26), 362_{sh} (4.20), $\lambda_{max}^{EtOH+AcONa}$ 271 (4.39), 328 (4.15), 368 (4.20), $\lambda_{max}^{EtOH+AlCl_3}$ 278 (4.38), 350 (4.25), 415 (4.26); ν_{max}^{Nujol} 3350, 3300 (OH), 1640 (C=O), 762, 680 cm^{-1} (monosubst. benzene ring); $\delta_{ppm}^{CD_3COCD_3}$ (60 MHz) 3.89 (s, 3H, OMe), 6.68 (s, 1H, C_8-H), 7.60, 8.20 (m, 5H, B-ring), 9.25 (s, 1H, OH), 12.23 (s, 1H, C_5-OH). No bathochromic shifts in the UV spectrum on addition of H_3BO_3 and AcONa indicated the absence of *o*-dihydroxy group.[3] The results suggested that the structure of I is 3,5,7-trihydroxy-6-methoxy- or 3,5,7-trihydroxy-8-methoxyflavone. The strong fragment peak at *m/e* 285 (M-15) indicated the presence of the OMe group at C-6 position.[4] Methylation of I gave 3,5,6,7-tetramethoxyflavone[5] (mp 112.0—112.5°C), which was converted into benzoic acid and 2-hydroxy-ω,4,5,6-tetramethoxyacetophenone with alkali. Thus, compound I was determined to be 3,5,7-trihydroxy-6-methoxyflavone.

5-Hydroxy-3,6,7-trimethoxyflavone (II). Compound II possessed the following physical properties: mp 175.0—176.0°C; λ_{max}^{EtOH} 271 (4.30), 317 (4.09), $\lambda_{max}^{EtOH+AlCl_3}$ 286 (4.29), 337 (4.08), 392 (4.01); ν_{max}^{Nujol} 1660 (C=O), 765, 695 cm^{-1} (monosubst. benzene ring); $\delta_{ppm}^{CDCl_3}$ 3.89, 3.94, 3.97 (s, 9H, 3 OMe), 6.54 (s, 1H, C_8-H), 7.56, 8.10 (m, 5H, B-ring), 12.58 (s, 1H, C_5-OH). Methylation gave 3,5,6,7-tetramethoxyflavone. The results indicated the structure of II to be 5-hydroxy-3,6,7-trimethoxyflavone.

5-Hydroxy-6,7,8-trimethoxyflavone (III). Compound III, mp 100.0—101.0°C, showed the NMR signals at $\delta_{ppm}^{CDCl_3}$ 3.95, 3.97, 4.10, (s, 9H, 3 OMe), 6.69 (s, 1H, C_3-H), 7.56, 7.95 (m, 5H, B-ring), 12.45 (s, 1H, C_5-OH). Methylation gave 5,6,7,8-tetramethoxyflavone[6]: mp 112.0—113.0; λ_{max}^{EtOH} 270 (4.34), 305 (4.08); $\delta_{ppm}^{CDCl_3}$ 3.98 (s, 6H, 2 OMe), 4.04 (s, 3H, OMe), 4.10 (s, 3H, OMe), 6.70 (s, 1H, C_3-H), 7.57, 7.95 (m, 5H, B-ring). Thus, the structure of III was established to be 5-hydroxy-6,7,8-trimethoxyflavone.

3,5,8-Trihydroxy-7-methoxyflavone (IV). Compound IV, $C_{16}H_{14}O_6$, M^+ 302, mp 175.0—177.0°C, showed positive coloration with $FeCl_3$, Mg-HCl, Zn-HCl, and Pachcós tests and the following spectral properties: *m/e* 273, 91 (M-CHO and 120-CHO, characteristic for flavanonol), 195, 183 (base), 167, 156, 120, 91, 77; λ_{max}^{EtOH} 215 (4.58), 226_{sh} (4.48), 290 (3.87), $\lambda_{max}^{EtOH+AlCl_3}$ 313 (4.74), $\lambda_{max}^{EtOH+AcONa}$ and $\lambda_{max}^{EtOH+AcONa+H_3BO_3}$ no bathochromic shifts[2]; ν_{max}^{Nujol} 3480, 3460, 3340 (OH), 1635—1654 cm^{-1} (C=O); $\delta_{ppm}^{CDCl_3}$ 3.86 (s, 3H, OMe), 4.40, 4.97 (d, J= 12 Hz, C_3-H and C_2-H), 5.99 (s, 1H, C_6-H), 7.33 (s, 5H, B-ring), 11.34 (s, 1H, C_5-OH). The small fragment peak at *m/e* 301 (M-1) indicated the absence of OH and OMe groups at C_6 position.[4] The spectral data as well as the specific color reaction thus indicated that IV is 3,5,8-trihydroxy-7-methoxyflavone.

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[1] The plant name "*Alnus firma* Sieb. et Zucc." has been given in our previous papers.[2a–c] We wish to correct it to "*Alnus sieboldiana.*"

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[5] A. C. Jain, T. R. Seshadri, and K. R. Sreenivasan, *J. Chem. Soc.*, **1955**, 3908.

[6] H. H. Lee and C. H. Tan, *ibid.*, **1965**, 2743.