POLYMETHOXYLATED FLAVONOIDS FROM THE PEEL OF UNSHIU MANDARIN FRUIT

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We have studied the polymethoxylated flavonoids of ripe mandarin fruit of the Unshiu variety, Citrus unshiu Marc., gathered in the Sukhumi experimental station of the All-Union Scientific-Research Institute of Plant Breeding. The peel of the fruit was separated and dried and extracted successively with hexane and benzene. On repeated chromatography of the evaporated benzene extract on silica gel columns (benzene–acetone and hexane–butanol mixtures), five compounds of flavonoid nature were isolated.

Compound (I) – yellow crystals with the composition $C_{20}H_{20}O_8$; M^+ 388; mp 147-149°C; $\lambda_{max}^{CH_3OH}$ 252, 283, 339; + $AlCl_3$ 261, 291, 364, + $AlCl_3$ + HCl 261, 296, 362 nm. PMR spectrum ($CDCl_3$, δ, ppm): 12.48 (s, 5-OH); 7.55 (d.d, $J_{H-6',5'}$ = 8.5 Hz, $J_{H-6',2'}$ = 2 Hz, H-6'); 7.42 (d, J = 2 Hz, H-2'); 6.93 (d, J = 8.5 Hz, H-5'); 6.55 (s, H-3); 4.05 (s, 3H, OCH_3); 3.92 (s, 9H, 3 × OCH_3); 3.89 (s, 3H, OCH_3). The facts given, in comparison with the literature [1, 2, 4], made it possible to identify compound (I) as 5-hydroxy-3',4',6,7,8-pentamethoxyflavone.

Compound (II) – colorless crystals with the composition $C_{22}H_{24}O_9$; M^+ 432; mp 133-134°C; $\lambda_{max}^{CH_3OH}$ 215, 272, 342 nm. PMR spectrum ($CDCl_3$, δ, ppm): 7.83 (m, 2H, H-2' and H-6'); 6.99 (d, J = 9 Hz, H-5'); 4.04 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3); 3.91 (s, 9H, 3 × OCH_3); 3.89 (s, 3H, OCH_3); 3.83 (s, 3H, OCH_3). The facts given, in comparison with the literature [1], permitted compound (II) to be identified as 3,3',4',5,6,7,8-heptamethoxyflavone.

Compound (III) – colorless crystal with the composition $C_{20}H_{20}O_7$; M^+ 372; mp 155-156°C; $\lambda_{max}^{CH_3OH}$ 270, 322 nm. PMR spectrum ($CDCl_3$, δ, ppm): 7.82 (d, J = 9 Hz, 2H, H-2' and H-6'); 6.97 (d, J = 9 Hz, 2H, H-3' and H-5'); 6.54 (s, H-3); 4.04 (s, 3H, OCH_3); 3.96 (s, 3H, OCH_3); 3.89 (s, 6H, 2 × OCH_3); 3.82 (s, 3H, OCH_3). The facts given, in comparison with the literature [1], made it possible to identify compound (III) as 4',5,6,7,8-pentamethoxyflavone (tangeretin).

Compound (IV) – colorless crystals with the composition $C_{21}H_{22}O_8$; M^+ 402; mp 136-137°C; $\lambda_{max}^{CH_3OH}$ 248, 269, 355 nm. PMR spectrum ($CDCl_3$, δ, ppm): 7.56 (d.d, $J_{H-6',5'}$ = 8.5 Hz, $J_{H-6',2'}$ = 2 Hz, H-6'), 7.36 (d, J = 2 Hz, H-2'); 6.97 (d, J = 8.5 Hz, H-5'); 6.57 (s, H-3); 4.04 (s, 3H, OCH_3); 3.96 (s, 3H, OCH_3), 3.89 (s, 12H, 4 × OCH_3). On the basis of the facts given, in comparison with the literature [1, 3, 4], compound (IV) was identified as 3',4',-5,6,7,8-hexamethoxyflavone (nobiletin).

Compound (V) – colorless crystals with the composition $C_{19}H_{19}O_7$; M^+ 372; mp 174-175°C; $\lambda_{max}^{CH_2OH}$ 240, 264, 328 nm. PMR spectrum ($CDCl_3$, δ, ppm): 7.50 (d.d, $J_{H-6',5'}$ = 8.5 Hz, $J_{H-6',2'}$ = 2 Hz, H-6'); 7.28 (d, J = 2 Hz, H-2'); 6.94 (d, J = 8.5 Hz, H-5'); 6.74 (s, H-8); 6.56 (s, H-3); 3.93 (s, 9H, 3 × OCH_3); 3.89 (s, 3H, OCH_3); 3.85 (s, 3H, OCH_3). The facts together with information in the literature [1, 4] permitted compound (V) to be identified as 3',4',5,6,7-pentamethoxyflavone (sinensetin).

This is the first time that compounds (I) and (II) have been isolated from Citrus unshiu Marc.

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