Isolation and Identification of Two New Flavanones and a Chalcone from *Citrus kinokuni*[1)]

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Two new flavanones and one chalcone were isolated from the peel of *Citrus kinokuni* HORT. *ex* TANAKA and identified as (2*S*)-5,6,7,8,4′-pentamethoxyflavanone (1), (2*S*)-5,6,7,3′,4′-pentamethoxyflavanone (2) and 2′-hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (3). The structures of new compounds were elucidated by spectroscopic analysis.

Key words flavanone; chalcone; *Citrus kinokuni*; Rutaceae

Recently, we carried out primary screening of extracts of *Citrus* fruit to search for useful compounds for cancer chemoprevention.[2)] As a part of our studies on the constituents of these extracts, two new flavanones and one chalcone were isolated and identified as (2*S*)-5,6,7,8,4′-pentamethoxyflavanone (**1**), (2*S*)-5,6,7,3′,4′-pentamethoxyflavanone (**2**) and 2′-hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (**3**) from the peel of *Citrus kinokuni* HORT. *ex* TANAKA, along with 21 known compounds.

(2*S*)-5,6,7,8,4′-Pentamethoxyflavanone (**1**) was obtained as a yellow oil. The molecular formula $C_{20}H_{22}O_7$ was defined by a molecular ion peak at *m/z* 374.1366 in the high resolution (HR)-MS. The ^{1}H-NMR spectrum showed three characteristic signals for H-2, H-3$_{ax}$ and H-3$_{eq}$ at δ 5.38 (1H, dd, J=12.8, 3.1 Hz), 3.03 (1H, dd, J=16.5, 12.8 Hz) and 2.84 (1H, dd, J=16.5, 3.1 Hz), respectively, indicating that **1** had a flavanone skeleton. Five methoxy signals were observed at δ 4.05—3.83. In the aromatic proton region, A_2B_2 signals at δ 7.39 (2H, d, J=8.5 Hz) and 6.94 (2H, d, J=8.5 Hz) indicated substitution at 4′ on the B-ring. This was confirmed by the nuclear Overhauser effect (NOE) experiment, in which irradiation of the signal at δ 3.83 (4′-OMe) caused 5% enhancement of the signal at δ 6.94. Thus, the B-ring is 4′-methoxylated and the A_2B_2 signals at δ 7.39 and 6.94 were assigned to H-2′/H-6′ and H-3′/H-5′ on the B-ring, respectively. In the ^{13}C-NMR spectrum, four methoxy signals were observed at lower magnetic field (δ 61.7—61.4). This suggests the presence of substituents at both *ortho* positions of the four methoxy groups,[3)] which were assigned to methoxyls on C-5, C-6, C-7 and C-8 of the A-ring. The circular dichroism (CD) spectrum showed a positive Cotton effect at 352 nm and a negative one at 315 nm, consistent with the *S*-configuration at C-2.[4)] On the basis of the above evidence, **1** was determined to be (2*S*)-5,6,7,8,4′-pentamethoxyflavanone.

(2*S*)-5,6,7,3′,4′-Pentamethoxyflavanone (**2**) was obtained as a yellow oil. The molecular formula $C_{20}H_{22}O_7$ was defined by a molecular ion peak at *m/z* 374.1365 in the HR-MS. In the ^{1}H-NMR spectrum, characteristic flavanone proton signals for H-2 [δ 5.34 (1H, dd, J=13.3, 2.6 Hz)], H-3$_{ax}$ [δ 3.03 (1H, dd, J=16.7, 13.3 Hz)] and H-3$_{eq}$ [δ 2.77 (1H, dd, J=16.7, 2.6 Hz)] were recorded. Three ABC type aromatic proton signals at δ 7.00 (1H, dd, J=1.7, 8.5 Hz), 6.99 (1H, d, J=1.7 Hz) and 6.90 (1H, d, J=8.5 Hz) were characteristic of H-6′, H-2′ and H-5′, respectively, which means the B-ring is 3′,4′-methoxylated. The NOE experiment verified the B-ring substitution. Irradiation of the signal at δ 3.92 (3′-OMe) caused 11% enhancement of the signal at δ 6.99 (H-2′) and irradiation of the signal at δ 3.90 (4′-OMe) caused 12% enhancement of the signal at δ 6.90 (H-5′). Among five methoxy signals observed at δ 3.95—3.83, it remained to assign the position of the three methoxy groups on the A-ring. In the NOE experiment, irradiation of the signal at δ 3.88 (7-OMe) caused 15% enhancement of the signal at δ 6.35 and irradiation of the signals at δ 3.95 and 3.83 showed no enhancement of any aromatic proton signals. The ^{13}C-NMR spectrum showed that the signals of two methoxy carbons were observed at lower magnetic field (δ 61.6, 61.3), and suggested that these two methoxy groups had substituents at both *ortho* positions, respectively.[3)] The H-5 and H-8 signals of flavonoids resonate at δ 7.5—7.6 and δ 6.5—6.9,[5,6)] respectively. Thus, the A-ring aromatic proton signal at δ 6.35 (1H, s) was assigned to H-8. Though **2** had no optical activity in a polarimeter at 589 nm,[7)] the CD spectrum showed a positive Cotton effect at 345 nm and a negative one at 313 nm, consistent with the *S*-configuration at C-2.[4)] The structure of **2** was deduced as (2*S*)-5,6,7,3′,4′-pentamethoxyflavanone.

2′-Hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (**3**) was obtained as pale yellow needles, mp 134—136 °C. The molecular formula $C_{20}H_{22}O_7$ was defined by a molecular ion peak at *m/z* 374.1368 in the HR-MS. The UV absorption (373 nm), the ^{1}H-NMR signals [δ 7.74 (1H, d, J=15.6 Hz, H-β), 7.87 (1H, d, J=15.6 Hz, H-α)] and the ^{13}C-NMR signals [δ_C 144.2 (C-β), 126.6 (C-α)] strongly suggested the presence of a chalcone skeleton. The ^{1}H-NMR spectrum showed five methoxy signals (δ 4.03—3.70) and a hydrogen

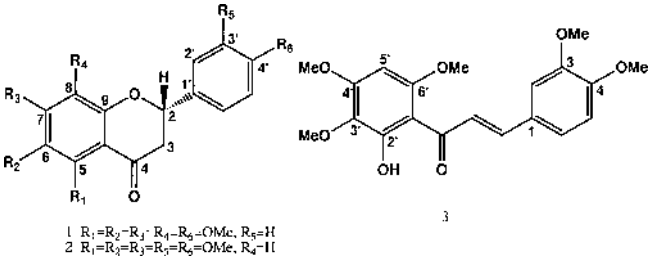

Fig. 1. Structures of **1**—**3**

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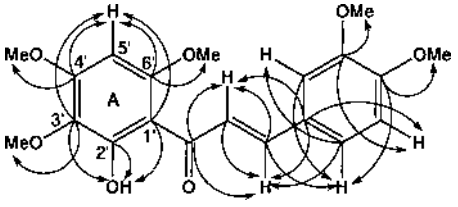

Fig. 2. C–H Long-Range Correlation in the HMBC Spectrum of 2′-Hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (**3**)

bonded 2′-OH resonating at δ 13.88. The ABC type protons at δ 7.29 (1H, dd, J=8.3, 1.8 Hz), 7.32 (1H, d, J=1.8 Hz) and 7.02 (1H, d, J=8.3 Hz) could be assigned to H-6, H-2 and H-5 of a 3,4-methoxylated B-ring. In the NOE experiment, irradiation of the signal at δ 3.90 (3-OMe) caused 11% enhancement of the signal at δ 7.32 (H-2) and irradiation of the signal at δ 3.87 (4-OMe) caused 14% enhancement of the signal at δ 7.02 (H-5). These results indicated the presence of a 3,4-dimethoxylated B-ring. In the NOE experiment, irradiation of the methoxy signals at δ 4.03 and 3.96 caused 12% and 16% enhancement of the signal at δ 6.32, respectively. Two possibilities (3′,4′,6′- or 3′,5′,6′-methoxylated) remained for the A-ring substitution. The positions of the three methoxy groups on the A-ring were elucidated through the use of the heteronuclear multiple bond correlation (HMBC) experiment (Fig. 2). The key correlation for assignment of A-ring substitution were observed for H-5′/C-1′, C-3′; 2′-OH/C-1′. Thus, the A-ring aromatic proton signal at δ 6.32 (1H, s) was assigned to H-5′, and **3** must therefore be 2′-hydroxy-3,4,3′,4′,6′-pentamethoxychalcone.

The known compounds were fully characterized as scoparone (**4**), scopoletin (**5**), nobiletin (**6**),[8] sinensetin (**7**),[8] tangeretin (**8**),[8] 5-hydroxy-6,7,8,4′-tetramethoxyflavone (**9**),[9] 5-hydroxy-6,7,3′,4′-tetramethoxyflavone (**10**),[10,11] 5-demethylnobiletin (**11**),[9,12] 6-demethoxynobiletin (**12**),[8] 6-demethoxytangeretin (**13**),[8] 5,6,7,4′-tetramethoxyflavone (**14**),[13,14] 3,5,6,7,3′,4′-hexamethoxyflavone (**15**),[15,16] 3′-hydroxy-5,6,7,8,4′-pentamethoxyflavone (**16**),[17] 3,5,6,7,8,3′,4′-heptamethoxyflavone (**17**),[8] 7-hydroxy-5,6,3′,4′-tetramethoxyflavone (**18**),[17] 7-hydroxy-5,6,8,3′,4′-pentamethoxyflavone (**19**),[18] 5,7,8,3′,4′-pentamethoxyflavanone (**20**),[19] 5-*O*-demethylcitromitin (**21**),[20] 3,4,3′,4′,5′,6′-hexamethoxy-2′-hydroxychalcone (**22**),[21] 2′-hydroxy-4,4′,5′,6′-tetramethoxychalcone (**23**)[22,23] and β-sitosterol (**24**) by direct comparison with authentic samples and/or spectral data reported in the literature.

Experimental

All melting points were measured on a micro melting point apparatus (Yanaco). ^{1}H-, ^{13}C-NMR, NOE and HMBC spectra were recorded on A-500 or A-600 (JEOL) spectrometers in $CDCl_3$ or acetone-d_6. Chemical shifts are shown in δ-values (ppm) with tetramethylsilane (TMS) as an internal reference. Electron impact (EI)-MS and HR-MS were taken with an JMS DX-303 (JEOL) spectrometer having a direct inlet system. UV spectra were recorded on a Shimadzu UV-160 A in EtOH, IR spectra on a Shimadzu IR-435 in $CHCl_3$, optical rotation on a DIP-370 (Jasco) in MeOH and CD spectra on a J-600 (Jasco) in MeOH.

Extraction and Isolation *Citrus kinokuni* HORT. *ex* TANAKA was cultivated and collected at the National Institute of Fruit Tree Science, Okitsu, Shizuoka. The dried peels (2.3 kg) of *C. kinokuni* HORT. *ex* TANAKA were extracted with acetone (5450 ml) at room temperature (3 d, 4 d) and under reflux for 7.5 h. The acetone extract (219.75 g) dissolved in 1 l of water was first extracted with AcOEt (1 l×3) and then extracted with *n*-butanol (750 ml×3). The AcOEt extract (13.47 g) was chromatographed over silica gel with toluene, CH_2Cl_2, AcOEt, acetone, and MeOH, successively. Each eluate was further subjected to preparative TLC repeatedly and furnished the known compounds, scoparone (**4**) (2.8 mg), scopoletin (**5**) (4.5 mg), nobiletin (**6**) (2.563 g), sinensetin (**7**) (15.5 mg), tangeretin (**8**) (649.3 mg), 5-hydroxy-6,7,8,4′-tetramethoxyflavone (**9**) (2.5 mg), 5-hydroxy-6,7,3′,4′-tetramethoxyflavone (**10**) (12.8 mg), 5-demethylnobiletin (**11**) (185.3 mg), 6-demethoxynobiletin (**12**) (1.3 mg), 6-demethoxytangeretin (**13**) (149.2 mg), 5,6,7,4′-tetramethoxyflavone (**14**) (3.3 mg), 3,5,6,7,3′,4′-hexamethoxyflavone (**15**) (3.4 mg), 3′-hydroxy-5,6,7,8,4′-pentamethoxyflavone (**16**) (22.9 mg), 3,5,6,7,8,3′,4′-heptamethoxyflavone (**17**) (7.6 mg), 7-hydroxy-5,6,3′,4′-tetramethoxyflavone (**18**) (3.7 mg), 7-hydroxy-5,6,8,3′,4′-pentamethoxyflavone (**19**) (5.3 mg), 5,7,8,3′,4′-pentamethoxyflavanone (**20**) (1.3 mg), 5-*O*-demethylcitromitin (**21**) (3.6 mg), 3,4,3′,4′,5′,6′-hexamethoxy-2′-hydroxychalcone (**22**) (37.5 mg), 2′-hydroxy-4,4′,5′,6′-tetramethoxychalcone (**23**) (4.8 mg) and β-sitosterol (**24**) (42.8 mg), in addition to the new compounds, (2*S*)-5,6,7,8,4′-pentamethoxyflavanone (**1**) (4.8 mg), (2*S*)-5,6,7,3′,4′-pentamethoxyflavanone (**2**) (25.7 mg) and 2′-hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (**3**) (3.3 mg). The new compounds were obtained from the AcOEt eluate by repeated PTLC [solvent system: acetone–$CHCl_3$ (1 : 9, 1 : 19 or 1 : 29), acetone–benzene (2 : 8), acetone–hexane (3 : 7), AcOEt–benzene (1 : 1), AcOEt–hexane (1 : 1)].

(2*S*)-5,6,7,8,4′-Pentamethoxyflavanone (**1**): Yellow oil, $[\alpha]_D$ +8° (c= 0.074, MeOH); HR-MS *m/z*: 374.1366 ($[M]^+$, Found), 374.1364 (Calcd for $C_{20}H_{22}O_7$); EI-MS *m/z*: 374 $[M]^+$, 344, 240 (base peak), 225, 210, 197, 195, 167; UV λ_{max} (EtOH, nm) : 226, 277, 331; IR ν_{max} ($CHCl_3$, cm^{-1}): 1680, 1600, 1580, 1510; ^{1}H-NMR ($CDCl_3$, δ): 7.39 (2H, d, J=8.5 Hz, H-2′ and H-6′), 6.94 (2H, d, J=8.5 Hz, H-3′, H-5′), 5.38 (1H, dd, J=12.8, 3.1 Hz, H-2), 4.05, 3.90, 3.85 (each 3H, s, OMe), 3.83 (6H, s, 2×OMe), 3.03 (1H, dd, J=16.5, 12.8 Hz, H-3$_{ax}$), 2.84 (1H, dd, J=16.5, 3.1 Hz, H-3$_{eq}$); Differential NOE: irradiation of 4′-OMe (δ 3.83) gave 5% NOE at H-3′ and H-5′ (δ 6.94); ^{13}C-NMR ($CDCl_3$, δ): 189.9 (s, C-4), 159.9 (s, C-4′), 153.4 (s, C-7), 152.6 (s, C-5), 150.2 (s, C-9), 141.1 (s, C-6), 137.9 (s, C-8), 130.9 (s, C-1′), 127.6 (d, C-2′, C-6′), 114.2 (d, C-3′, C-5′), 111.6 (s, C-10), 79.1 (d, C-2), 61.7, 61.6, 61.5, 61.4 (each q, OMe), 55.4 (q, 4′-OMe), 45.8 (t, C-3); CD (c 7.91×10^{-5} mol/l, MeOH): $[\theta]_{218}$ +14600 (max), $[\theta]_{238}$ +6800, $[\theta]_{273}$ 0, $[\theta]_{286}$ −3400, $[\theta]_{315}$ −7500 (max), $[\theta]_{333}$ 0, $[\theta]_{352}$ +9200 (max).

(2*S*)-5,6,7,3′,4′-Pentamethoxyflavanone (**2**): Yellow oil, $[\alpha]_D$ ±0° (c= 0.1325, MeOH); HR-MS *m/z*: 374.1365 ($[M]^+$, Found), 374.1364 (Calcd for $C_{20}H_{22}O_7$); EI-MS *m/z*: 374 $[M]^+$ (base peak), 210, 195, 164, 151; UV λ_{max} (EtOH, nm): 233, 278, 323; IR ν_{max} ($CHCl_3$, cm^{-1}) : 1680, 1600, 1520; ^{1}H-NMR ($CDCl_3$, δ): 7.00 (1H, dd, J=8.5, 1.7 Hz, H-6′), 6.99 (1H, d, J=1.7 Hz, H-2′), 6.90 (1H, d, J=8.5 Hz, H-5′), 6.35 (1H, s, H-8), 5.34 (1H, dd, J=13.3, 2.6 Hz, H-2), 3.95 (3H, s, 6 or 5-OMe), 3.92 (3H, s, 3′-OMe), 3.90 (3H, s, 4′-OMe), 3.88 (3H, s, 7-OMe), 3.83 (3H, s, 5 or 6-OMe), 3.03 (1H, dd, J=16.7, 13.3 Hz, H-3$_{ax}$), 2.77 (1H, dd, J=16.7, 2.6 Hz, H-3$_{eq}$); Differential NOE: irradiation of 3′-OMe (δ 3.92) gave 11% NOE at H-2′ (δ 6.99); irradiation of 4′-OMe (δ 3.90) gave 12% NOE at H-5′ (δ 6.90); irradiation of 7-OMe (δ 3.88) gave 15% NOE at H-8 (δ 6.35); ^{13}C-NMR ($CDCl_3$, δ): 189.4 (s, C-4), 159.8 (s, C-9 or C-7), 159.5 (s, C-7 or C-9), 154.3 (s, C-5), 149.6 (s, C-4′ or C-3′), 149.4 (s, C-3′ or C-4′), 137.7 (s, C-6), 131.2 (s, C-1′), 118.9 (d, C-6′), 111.4 (d, C-5′), 109.6 (d, C-2′), 109.3 (s, C-10), 96.5 (d, C-8), 79.5 (d, C-2), 61.6, 61.3 (each q, 5 or 6-OMe), 56.14, 56.05, 56.04 (q, 7, 3′ or 4′-OMe), 45.6 (t, C-3); CD (c 7.11×10^{-5} mol/l, MeOH): $[\theta]_{215}$ +10100 (max), $[\theta]_{223}$ +4400 (valley), $[\theta]_{236}$ +13900 (max), $[\theta]_{256}$ +5300, $[\theta]_{271}$ +6000, $[\theta]_{281}$ 0, $[\theta]_{290}$ −7900, $[\theta]_{313}$ −20700 (max), $[\theta]_{330}$ 0, $[\theta]_{345}$ +17300 (max).

2′-Hydroxy-3,4,3′,4′,6′-pentamethoxychalcone (**3**): Pale yellow needles, mp 134—136 °C; HR-MS *m/z*: 374.1368 ($[M]^+$, Found), 374.1366 (Calcd for $C_{20}H_{22}O_7$); EI-MS *m/z*: 374 $[M]^+$, 210 (base peak), 195, 181, 167; UV λ_{max} (EtOH, nm): 373; IR ν_{max} ($CHCl_3$, cm^{-1}): 1620, 1560, 1510; ^{1}H-NMR (acetone-d_6, δ): 13.88 (1H, s, 2′-OH), 7.87 (1H, d, J=15.6 Hz, H-α), 7.74 (1H, d, J=15.6 Hz, H-β), 7.32 (1H, d, J=1.8 Hz, H-2), 7.29 (1H, dd, J=8.3, 1.8 Hz, H-6), 7.02 (1H, d, J=8.3 Hz, H-5), 6.32 (1H, s, H-5′), 4.03, 3.96 (each 3H, s, 4′ or 6′-OMe), 3.90 (3H, s, 3-OMe), 3.87 (3H, s, 4-OMe), 3.70 (3H, s, 3′-OMe); Differential NOE: irradiation of 4′ or 6′-OMe (δ 3.96) gave 15% NOE at H-5′ (δ 6.32); irradiation of 6′ or 4′-OMe (δ 4.03) gave 12% NOE at H-5′ (δ 6.32); irradiation of 3-OMe (δ 3.90) gave 11% NOE at H-2 (δ 7.32); irradiation of 4-OMe (δ 3.87) gave 14% NOE at H-5 (δ 7.02); ^{13}C-NMR (acetone-d_6, δ): 194.4 (s, C=O), 160.5 (s, C-2′), 160.2, 160.0 (each s, C-4′ or 6′), 153.2 (s, C-4), 151.1 (s, C-3), 144.2 (d, C-β), 132.1 (s, C-3′), 129.7 (s, C-1), 126.6 (d, C-α), 124.3 (d, C-6), 113.1 (d, C-5), 112.2 (d, C-2), 107.9 (s, C-1′), 89.2 (d, C-5′), 60.8, 57.1, 56.9, 56.65, 56.58 (each q, 5×OMe).

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