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FLAVONES FROM *CITRUS SUDACHI*

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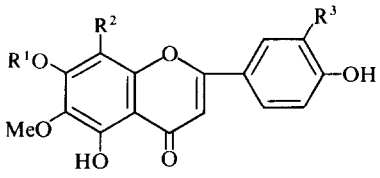
Key Word Index—*Citrus sudachi*; Rutaceae; green peels; 7-methylsudachitin; dinatin; xanthomicrol; 5,7,4′-trihydroxy-6,3′-dimethoxyflavone; structural determination.

Previously we reported the isolation of three flavonoids, sudachitin (**1**) [1,2], demethoxysudachitin (**2**) [3] and sudachiin A (**3**) [4] from green peel of *Citrus sudachi*. We now wish to report the isolation of four further flavones from the ether extract of the green peel. Three of the flavones not previously reported from *C. sudachi* are dinatin (**4**) [5,6], xanthomicrol (**5**) [7] and 5,7,4′-trihydroxy-6,3′-dimethoxyflavone (**6**) [8,9]. The fourth, a new flavone namely 7-methylsudachitin, has been assigned the structure 5,4′-dihydroxy-6,7,8,3′-tetramethoxyflavone (**7**) based on the following spectral evidence.



1 $R^1 = H$, $R^2 = R^3 = OMe$
2 $R^1 = R^3 = H$, $R^2 = OMe$
3 $R^1 = Glu$, $R^2 = R^3 = OMe$
4 $R^1 = R^2 = R^3 = H$
5 $R^1 = Me$, $R^2 = OMe$, $R^3 = H$
6 $R^1 = R^2 = H$, $R^3 = OMe$
7 $R^1 = Me$, $R^2 = R^3 = OMe$

7-Methylsudachitin (**7**) formed yellow needles from EtOH, mp 160–61°, $C_{19}H_{18}O_8$ (M^+, 374). Spectral data of **7** revealed the presence of a flavone skeleton with 2 OH and 4 OMe groups. Its ^1H NMR spectrum indicated that the 3-, 2′-, 5′- and 6′-positions in the flavone skeleton are unsubstituted. In the UV spectrum of **7**, the band I (349 nm) in EtOH undergoes a bathochromic shift upon the addition of $AlCl_3$ or NaOAc. It shows that one hydroxyl group is located at the 5-position and the remaining hydroxyl group at the 7- or 4′-position. The presence of a 4′-hydroxyl group is indicated by a large bathochromic shift (420 nm) of band I and its intensity markedly greater than that of band II in the presence of NaOAc [10]. Therefore, **7** has a 5,4′-dihydroxyflavone skeleton with four OMe groups. The confirmation of the structure of **7** was made by a direct comparison with an authentic sample of 5,4′-dihydroxy-6,7,8,3′-tetramethoxyflavone [11, 12].

This is the first isolation from a natural source of **7**. The two flavones, **7** and **5**, are the 7-methyl ethers of sudachitin (**1**) and demethoxysudachitin (**2**), respectively.

EXPERIMENTAL

^1H NMR spectrum was taken at 90 MHz in $CDCl_3$ and chemical shifts are given in δ (ppm) scale relative to TMS; UV spectra were obtained in EtOH.

Isolation. The fresh green peels (5 kg) of *C. sudachi* Hort. ex Shirai collected in Tokushima prefecture were extracted with EtOH. The EtOH concentrate was washed with hexane and then extracted with Et_2O. The extract dissolved in a small amount of MeOH, was allowed to stand in refrigerator to give a ppt., which was separated by filtration. The ppt. contained sudachitin (**1**) and demethoxysudachitin (**2**), by recrystallization. From the mother liquor, compound A (5 mg) was isolated by HPLC with the column packed with Hitachi gel No. 3011 using aq. MeOH. The MeOH filtrate was subjected to column chromatography over a polyamide using MeOH as the eluent to give three fractions. Fraction 1 was rechromatographed with Si gel ($CHCl_3$–EtOAc, 20:3) to give compounds B (20 mg) and C (20 mg). Fraction 3 was extracted with aq. Na_2CO_3 soln and then the extract was acidified with dilute HCl. The separated ppts were rechromatographed with a Si gel ($CHCl_3$–EtMeCO, 10:1) to give compound D (16 mg).

Identification. Compound B crystallized from EtOH as yellow needles, mp 160–161°: MS: M^+ 374 ($C_{19}H_{18}O_8$). It gave positive $FeCl_3$ and Mg–HCl tests. UV $\lambda_{max}^{E.OH}$ nm (log ε): 256 (4.17); 280 (4.23), 349 (4.36); + $AlCl_3$ 261 (4.12), 288 (4.21), 302sh (4.19), 363 (4.39); + NaOAc 267 (4.26), 420 (4.47). ^1H NMR ($CDCl_3$): δ 3.94 (3 H, *s*, OMe), 3.97 (6 H, *s*, OMe), 4.10 (3 H, *s*, OMe), 6.57 (1 H, *s*, H_3), 7.02 (1 H, *d*, $J = 9$ Hz, Ar–$H_{5'}$), 7.40 (1 H, *d*, $J = 3$ Hz, Ar–$H_{2'}$), 7.54 (1 H, *q*, $J = 9$, 3 Hz, Ar–$H_{6'}$). It was identified as 5,4′-dihydroxy-6,7,8,3′-tetramethoxyflavone (**7**) by mp, UV, IR and direct comparison with an authentic sample. Compounds A, C and D were identified as dinatin (**4**) (mp 297–299°), xanthomicrol (**5**) (mp 225–226°) and 5,7,4′-trihydroxy-6,3′-dimethoxyflavone (**6**) (mp 226–227°) by direct comparison with authentic samples.

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