Sudachitin, a New Flavone Pigment of Sudachi

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(Received August 14, 1961)

A new flavone pigment was isolated in a 0.005% yield from the ether extract of the green fruit of *Citrus sudachi Hort ex Shirai*, one of the species of the family Rutaceae, which is produced only in Tokushima prefecture, Shikoku. The name, sudachitin is suggested for this new flavone. A better yield was obtained from the alcohol extract (0.014%) accompanying a second new flavone of m. p. 271~273°C from the mother liquor of sudachitin purifications in 0.004% yield.

Sudachitin crystallized as yellow needles from a mixture of ethyl acetate and methanol (1 : 1), 239.5~240.5°C, and its analytical values agreed with the formula $C_{18}H_{16}O_8$. When treated with metallic magnesium and hydrochloric acid, it gave typical reddish-orange color reaction for flavone pigments. It gave a greenish brown color with ferric chloride, indicating the presence of free hydroxyl groups.

The conversion of sudachitin (I) into a triacetate (II), $C_{24}H_{22}O_{11}$, m. p. 167.5~168.5°C, with acetic anhydride, and into a trimethyl ether (III), $C_{21}H_{22}O_8$, m. p. 135.5~136.5°C, with dimethyl sulfate, or into a triethyl ether (IV) $C_{24}H_{28}O_8$, m. p. 143~144°C, with diethyl sulfate, revealed the presence of three hydroxyl groups. These three derivatives gave the positive flavone color test with metallic magnesium and hydrochloric acid, but did not show a ferric chloride test. Diazomethane converted sudachitin into a dimethyl ether (V), $C_{20}H_{20}O_8$, m. p. 143~144°C, suggesting the existence of a free hydroxyl group at the 5-position of the flavone ring, at this stage, the similarity of the above two derivatives of sudachition to the nobiletin previously isolated by Robinson and coworkers[1], the structure of which has been confirmed as 3′, 4′, 5, 6, 7, 8-hexamethoxy flavone[2,3] (III), was noticed. The ultraviolet spectra of sudachitin trimethyl ether (III) and nobiletin*, and of sudachitin dimethyl ether (V) and 5-hydroxy-3′, 4′, 6, 7, 8-pentamethoxy flavone* were shown to be identical. The mixed melting point of the above two pairs also did not show any depression. From the above evidence, it is clear that the position of six substituents in sudachitin should be at 3′, 4′, 5, 6, 7 and 8

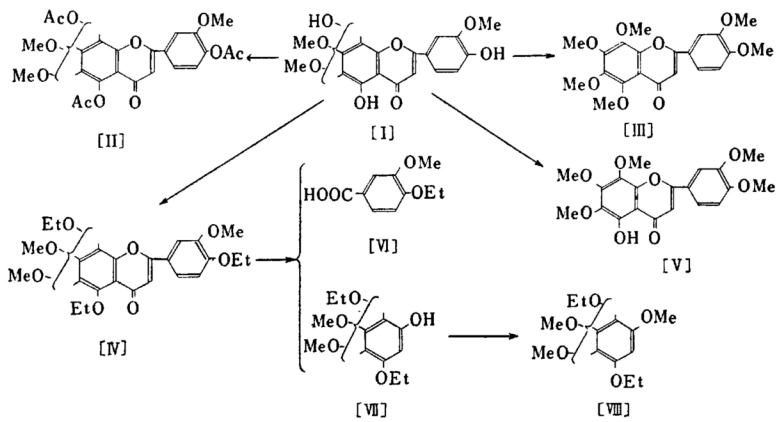

Fig. 1

1) Kwong-Fong Tseng, *J. Chem. Soc.*, **1938**, 1003; R. Robinson, Kwong-Fong Tseng, ibid., **1938**, 1004.
2) Z. Horii, *J. Pharm. Chem. Japan* (*Yukagaku Zasshi*), **60**, 614 (1940).
3) A. Tsukamoto and T. Ohtaki, ibid., **67**, 9 (1947).
* Samples of nobiletin and 5-hydroxy-3′, 4′, 6, 7, 8-pentamethoxy flavone were kindly provided by Dr. Z. Horii, University of Osaka.

positions, and one of the three free hydroxyl groups should be at the 5-position in the flavone ring.

In order to obtain furthur evidence regarding the position of the remaining two free hydroxyl groups, sudachitin triethyl ether (IV) was refluxed for 6 hr. in 10% potassium hydroxide solution. Acidificatin of the mother liquor from the ether extract of the hydrolysis mixture, gave a white precipitate in an 84% yield, which recrystallized from benzene, gave colorless needles, m. p. 193~194°C[4], (Found: C, 60.95; H, 6.23. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16%). The mixed melting point with 4-ethoxy-3-methoxybenzoic acid[4] (VI) synthesized from vanillin was not depressed. From this fact, the position of the second free hydroxyl group was proved to be the 4'-position in the flavone ring. From the ether extract of the above mentioned hydrolysis mixture which had been saturated with carbon dioxide before ether extraction, there was obtained an oily product VII which gave a positive phenol test with ferric chloride. This was converted with dimethyl sulfate into a methyl ether, a diethoxy-trimethoxy benzene (VIII), whose analytical values agreed with the formula $C_{13}H_{20}O_5$ (Found: C, 61.04; H, 7.95. Calcd. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%).

In the light of these findings, it was concluded that sudachitin most probably is the trihydroxy-trimethoxy flavone shown as structure I in Fig. 1.

An attempt to establish the relative positions of the hydroxyl- and methoxyl-groups on the benzene ring of VIII by direct comparison with three isomeric diethoxy-trimethoxybenzenes failed, because the amount of diethoxy-trimethoxybenzene from sudachitin was too small to purify.

The synthesis of three isomeric triethoxy-trimethoxy flavone which is only remaining way to confirm the final structure of sudachitin, is now in progress.

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4) F. Tiemann, *Ber.*, **8**, 1130 (1875).