HETEROCYCLES, Vol. 10, 1978

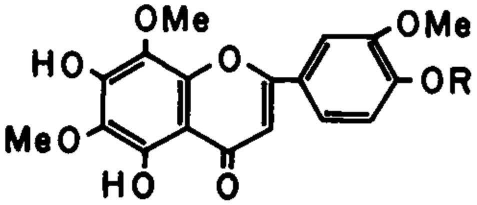
SUDACHIIN A, A NEW FLAVONE GLUCOSIDE FROM SUDACHI

Tokunaru Horie,* Mitsuru Nakayama,** Shûichi Hayashi,**
Masao Tsukayama,*** and Mitsuo Masumura***
Tokushima Technical College, Tokushima University, Minami-Josanjima, Tokushima 770, Japan
**Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730, Japan
***Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Minami-Josanjima, Tokushima 770, Japan

Sudachiin A was isolated from the green peels of *Citrus sudachi Hort. ex* SHIRAI. This structure was deduced to be sudachitin 4'-β-D-glucoside by spectra and degradation, and confirmed by synthesis.

In the previous papers, flavonoids occurring in green peels of *Citrus sudachi Hort. ex* SHIRAI were reported.[1,2] In this paper, we wish to report the isolation, structure determination, and synthesis of a new flavone glucoside, sudachiin A.

The fresh peels collected at Tokushima Prefecture in August were extracted with ethanol. The ethanol concentrate was washed with ether and then extracted with ethyl acetate. The extract dissolved in a small amount of methanol was allowed to stand in a refrigerator to give precipitates, which were removed by filtration. The resulting methanol solution was chromatographed over a polyamide-column with methanol to give a glycoside as yellow needles [mp 211-213°; $[\alpha]_D$ -37.4° (0.5% aq. NaOH, c=0.31); uv λ_{max}^{EtOH} nm (log ε) 282 (4.35), 335 (4.24), (AlCl$_3$) 298 (4.34), 354 (4.35), (AcONa) 283 (4.45), 309$_{inf.}$ (4.25), 383 (4.13)]. The glycoside, named sudachiin A, was hydrolyzed with 5% sulfuric acid to sudachitin (II)[1] and glucose. In the uv spectrum of the glucoside, the band I was shifted to 383 nm in the presence of sodium acetate and its intensity was markedly lower than that of band II.[3] Sudachiin A was exhaustively methylated with diazomethane, followed by hydrolysis to give sudachitin 5,7-dimethyl ether (mp 145-146°) which was identical with 4'-hydroxy-5,6,7,8,3'-pentamethoxyflavone synthesized by the method of Wagner et al..[4] From the above results, sudachiin A was found to be sudachitin 4'-glucoside (I).



I R = Glu.

II R = H

The nmr spectrum of the hexaacetate (mp 212-213°) of I showed the presence of two phenolic acetoxyl groups in the flavone nucleus and four acetoxyl groups in the sugar moiety (Fig. 1). The signals attributable to sugar moiety at δ 4.1-4.3 and 5.0-5.5 ppm were superimposable with those of cirsilineol 4'-β-D-tetraacetylglucoside.[5]

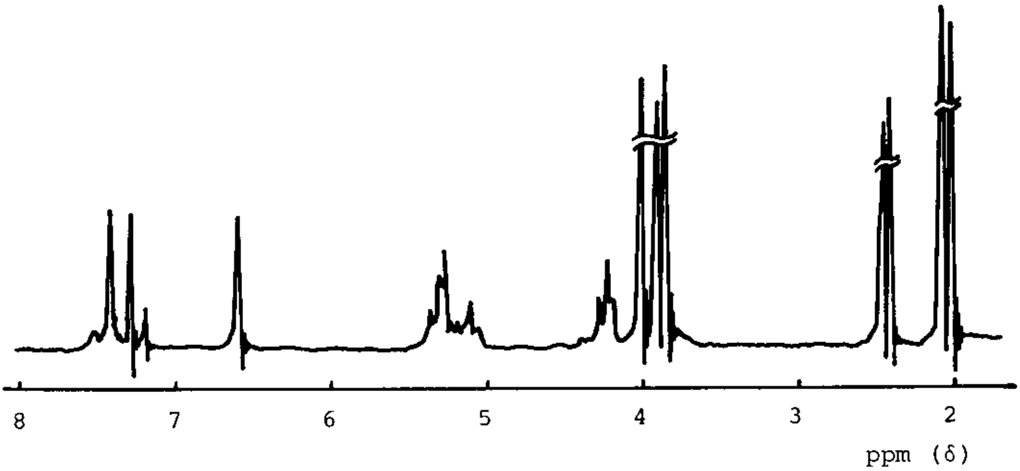


Fig. 1. Nmr spectrum of sudachiin A hexaacetate in $CDCl_3$.

Consequently, I was assumed to be sudachitin 4'-β-D-glucoside, and further the structure of I was confirmed by the following synthesis.

Sudachitin (II) was partially benzylated with benzyl chloride, potassium iodide and aqueous potassium hydroxide in acetone-DMF to give the 7-benzyl ether [mp 159-160°; uv λ_{max}^{EtOH} nm (log ε) 257 (4.21), 278 (4.27), 349 (4.36), (AcONa) 267 (4.32), 421 (4.53)], 4'-benzyl ether [mp 177-178°; uv λ_{max}^{EtOH} nm (log ε) 283 (4.31), 342 (4.36), (AcONa) 284 (4.44), 315 (4.24), 383 (4.16)], and 7,4'-dibenzyl ether (mp 126-127°) in yields of 40, 2, and 8%, respectively. The 7-benzyl ether was easily condensed with α-bromoacetoglucose to give the acetylglucoside (mp 156-157°), which was debenzylated to sudachitin 4'-acetylglucoside [mp 196-197°; $[\alpha]_D$ -22.5° ($CHCl_3$, c=0.196)] with palladium charcoal. The hydrolysis of the acetylglucoside gave the desired glucoside [mp 211-213°; $[\alpha]_D$ -39.2° (0.5% aq. NaOH, c=0.204)]. The synthetic glucoside was identical with natural sudachiin A on the basis of a mixed-melting point determination and by ir, uv, and nmr spectral comparisons.

Sudachitin 7-β-D-glucoside [mp 187-188°; $[\alpha]_D$ +58.9° (0.5% aq. NaOH, c=0.26)], one isomer of sudachiin A, was obtained from II and α-bromoacetoglucose *via* the corresponding acetylglucoside.

ACKNOWLEDGEMENT The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

REFERENCES

1 T. Horie, M. Masumura, and S. Okumura, Nippon Kagaku Zasshi, 1962, 83, 465, 468.

2 T. Horie, H. Shimoo, M. Masumura, and S. Okumura, Nippon Kagaku Zasshi, 1962, 83, 602.

3 T. J. Mabry, K. R. Markham, and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, Heidelberg, New York, 1970, p. 41; E. Rodriguez, G. V. Velde, T. J. Mabry, S. S. Subramanian, and A. G. R. Nair, Phytochemistry, 1972, 11, 2311.

4 H. Wagner, G. Maurer, L. Hörhammer, and L. Farkas, Chem. Ber., 1971, 101, 3357.

5 A. J. Kalra, M. Krishnamurti, and T. R. Seshadri, Indian J. Chem., 1974, 12, 1040: the nmr spectrum of cirsilineol 4'-β-D-tetraacetylglucoside was measured in this laboratory.

Received, 14th September, 1978