Communications to the Editor

[Chem. Pharm. Bull.
32(9)3787—3788(1984)]

GUAVIN B, AN ELLAGITANNIN OF NOVEL TYPE

Takuo Okuda,* Tsutomu Hatano and Kazufumi Yazaki
Faculty of Pharmaceutical Sciences, Okayama University,
Tsushima, Okayama 700, Japan

Guavin B (1), an ellagitannin of novel type, has been isolated from Psidium guajava, and its structure showing hydroxybenzophenone moiety has been elucidated.

KEYWORDS —— Psidium guajava; Myrtaceae; tannin; ellagitannin; O-glucosidic tannin; benzophenone glucoside; FD mass spectrum; CD spectrum; $^{1}H/^{13}C$-NMR spectra; guavin B

Various parts of Psidium guajava L. (Myrtaceae) have been used widely in Southeast Asia for the treatment of diarrhea, stomachache, ulcer and several other diseases.1) In addition to the nine tannins of the leaf,2) we have isolated a tannin named guavin B, with a structure of a novel type, which forms a light brown amorphous powder, along with procyanidin-B1, B2 and B3, by column chromatography on Sephadex LH-20 of the ethyl acetate extract from the total extract of leaf.

Guavin B (1), $C_{33}H_{26}O_{17}\cdot 4H_2O$, $[\alpha]_D$ -71° (c=0.5, MeOH), UV λ^{max}_{MeOH} nm 208 (log ε 4.66), 221 (4.56) and 283 (4.27), gave orange → bluish gray color upon the spot test after being sprayed with sodium nitrite and acetic acid. This coloration is characteristic of ellagitannins having hexahydroxydiphenoyl (HHDP) group at O-4 and O-6 of the glucose moiety, such as tellimagrandin I,3) gemin D,4) 4,6-O-[(S)-hexahydroxydiphenoyl]-D-glucose5,6) and strictinin (2).3) The field desorption (FD) mass spectrum of 1 showed 695 (M+1) and 717 (M+Na) ions, and also peaks at m/z 415 and 393 assignable for (M-HHDP+2H+Na) and (M-HHDP+2H+1) ions which indicate the presence of a polyhydroxybenzophenone group. Upon electron impact (EI) mass spectral measurement, this tannin showed peaks at 392 (M-HHDP+2H), 374 (392-H_2O), 230, 229, 153, 126, 105 and 77 (Chart); octa-O-methyl derivative of 1, $C_{41}H_{42}O_{17}$, showed m/z 258, 257, 181, 105 and 77 peaks to indicate the presence of a polyhydroxybenzophenone, and an HHDP group (m/z 450, 436, 404 and 360) in 1. Methanolysis of the octa-O-methyl derivative gave dimethyl hexamethoxydiphenate.

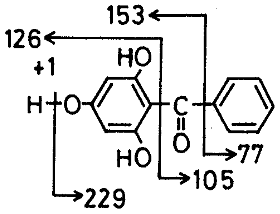
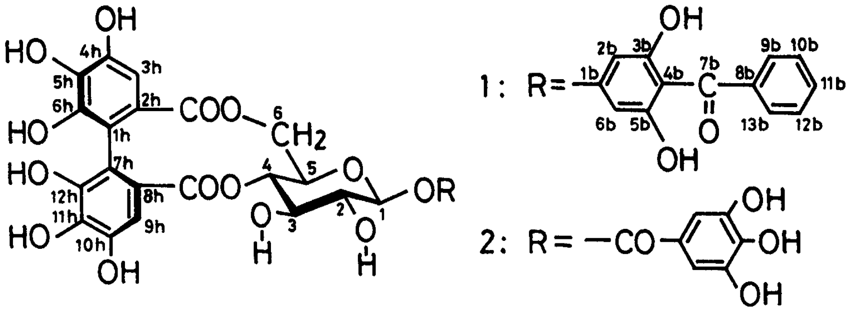


Chart. Mass Fragmentation of Benzophenone Moiety of 1

The ^{1}H-NMR spectrum of 1 (200 MHz, in acetone-d_6) showed seven aromatic protons (δ7.70-7.38, 5H, m; 6.22, 2H, s) corresponding to a benzophenone moiety, and the protons of an HHDP group (δ6.72, 1H, s; 6.61, 1H, s). The glucose protons [δ5.16 (d, J=8 Hz, H-1), 3.67 (dd, J=8, 9 Hz, H-2), 3.82 (t, J=9 Hz, H-3), 4.92 (t, J=9 Hz, H-4), 4.23 (dd, J=6, 9 Hz, H-5), 5.24 (dd, J=6, 13 Hz, H-6) and 3.87 (d, J=13 Hz, H-6')] indicate location of the HHDP group identical to that in **2**,3) a ß-glucosidic linkage (by the chemical shift of H-1 and the coupling constant between H-1 and H-2), and the C1 conformation of glucose.

The ^{13}C-NMR spectrum (50.1 MHz, in acetone-d_6) clearly indicate the presence of a benzophenone moiety [δ164.3 (1b), 96.6 (2b and 6b), 162.8 (3b and 5b), 107.3 (4b), 199.6 (7b), 142.0 (8b), 128.5 (9b and 13b), 129.2 (10b and 12b) and 132.2 (11b)], and an HHDP group [δ116.1, 115.7 (1h and 7h), 126.9, 126.6 (2h and 8h), 108.3, 108.0 (3h and 9h), 145.2, 144.5, 144.4 (4h, 6h, 10h and 12h), 136.5, 136.2 (5h and 11h), 168.1 and 168.4 (two ester carbonyls)] and a ß-glucose [δ101.5, 75.6, 75.3, 72.8, 72.7 and 63.8].

The absolute configuration of the HHDP group was determined as S by the CD spectrum of **1** ($[\theta]_{233}$ +7.9 x 10^4 and $[\theta]_{260}$ -3.3 x 10^4, in MeOH).7)



These data indicate structure **1** for guavin B, which is the first example of ellagitannin having a polyhydroxybenzophenone, and also of that forming an O-glucoside linkage which is not an ester.

ACKNOWLEDGEMENT We thank Prof. T. Fujita, Assoc. Prof. Y. Takeda and Dr. K. Kida, Faculty of Pharmaceutical Sciences, Tokushima University, for 200 MHz ^{1}H-NMR and 50.1 MHz ^{13}C-NMR spectra; Prof. T. Koga and Miss N. Toh, Daiichi College of Pharmaceutical Sciences, for CD spectrum; and Dr. K. Fukushima, Research Institute for Chemobiodynamics, Chiba University, for FD mass spectrum.

REFERENCES

1) L. M. Perry, "Medicinal Plants of East and Southeast Asia," MIT Press, Cambridge, Massachusetts, 1980, p.284.
2) T. Okuda, T. Yoshida, T. Hatano, K. Yazaki and M. Ashida, Phytochemistry, **21**, 2871 (1982).
3) T. Okuda, T. Yoshida, M. Ashida and K. Yazaki, J. Chem. Soc., Perkin Trans. 1, **1983**, 1765.
4) T. Yoshida, Y. Maruyama, T. Okuda, M. U. Memon and T. Shingu, Chem. Pharm. Bull., **30**, 4245 (1982).
5) O. T. Schmidt, R. Schanz, R. Wurmb and W. Groebke, Ann. Chem., **706**, 154 (1967).
6) T. Okuda, T. Hatano and T. Yasui, Heterocycles, **16**, 1321 (1981).
7) T. Okuda, T. Yoshida, T. Hatano, T. Koga, N. Toh and K. Kuriyama, Tetrahedron Letters, **23**, 3931 (1982).

(Received July 28, 1984)