Communications to the Editor

Chem. Pharm. Bull.
30(6)2255—2257(1982)

A DIMERIC HYDROLYZABLE TANNIN, SANGUIIN H-6 FROM *SANGUISORBA OFFICINALIS* L.

Gen-ichiro Nonaka, Takashi Tanaka, Meiko Nita, and Itsuo Nishioka*
Faculty of Pharmaceutical Sciences, Kyushu University, 3-1-1, Maidashi, Higashi-ku
Fukuoka 812, Japan

A new hydrolyzable tannin, sanguiin H-6, has been isolated from the underground parts of *Sanguisorba officinalis* L. (Rosaceae), and on the basis of spectroscopic data and partial hydrolysis study has been shown to have a novel dimeric structure containing sanguiin H-2 and pedunculagin moieties.

KEYWORDS——*Sanguisorba officinalis*; Rosaceae; sanguiin H-6; dimeric ellagitannin; ^{1}H NMR; ^{13}C NMR; partial hydrolysis; *Rubus chingii*

We have recently reported the structure of sanguiin H-3 (1), a novel dimeric ellagitannin containing two glucose residues, isolated from the underground parts of *Sanguisorba officinalis* L. (Rosaceae).[1] Further chemical examination of the tannins of this plant has resulted in the isolation of an additional ellagitannin dimer, sanguiin H-6 (2), and we report herein the structure elucidation of this new tannin.

The more polar fraction,[1] after removal of sanguiin H-3, was subsequently chromatographed over cellulose (2% AcOH) and Sephadex LH-20 dextran gel (EtOH-H_2O-Me_2CO)[2] to yield the tannin (2) as a brown amorphous powder, $[\alpha]_D$ +72.0° (Me_2CO). The occurrence of two carbohydrate moieties in 2 was easily deduced from the ^{13}C NMR spectrum which exhibited signals due to twelve aliphatic carbons bearing oxygen functions, including two anomeric carbon signals (δ 90.8 and 92.6). This was further supported by ^{1}H NMR resonances for two anomeric protons at δ 6.17 (d, J=8 Hz) and δ 6.52 (d, J=3 Hz) analogous to sanguiin H-3.

2 gave a red color characteristic of ellagitannins with Na_2SO_3-Na_2CO_3 reagent.[3] Acid hydrolysis afforded gallic acid, ellagic acid, sanguisorbic acid dilactone,[1] and glucose. The appearance of seven aromatic singlets (δ 6.26, 6.33, 6.39, 6.48, 6.53, 6.76, and 6.78) and two *meta*-coupled doublets (δ 7.11 and 7.26, J=2 Hz) in the ^{1}H NMR spectrum suggests the presence of three hexahydroxydiphenoyl groups and one sanguisorboyl group. In addition, a two-proton singlet at δ 7.16 corresponds to a galloyl group. These characteristics closely resemble those of sanguiin H-3 except that sanguiin H-6 contains an extra hexahydroxydiphenoyl group. The molecular weight of 2 was confirmed by the FD-MS (M^+ at m/z 2276) of the corresponding methyl ether prepared by methylation with $(CH_3)_2SO_4$ and K_2CO_3 in dry Me_2CO. Since the ^{13}C NMR spectrum shows signals due to ten ester carbons [δ 165.0, 165.2, 165.4, 165.7, 167.8 (2C), 168.1 (2C), 168.4, and 169.3], all hydroxy-groups in two glucose residues are presumably acylated. Substitution patterns of these phenolic carboxylic acid groups on glucose residues were inferred by careful ^{13}C NMR examination. Namely, of the twelve sugar carbon signals, six (δ 63.1, 69.2, 71.3, 73.9, 75.5, and 90.8) are in close agreement with those of sanguiin H-2 (3) whose structure has been characterized as 1-O-galloyl-2,4-(hexahydroxydiphenoyl)-3,6-(sanguisorboyl)-

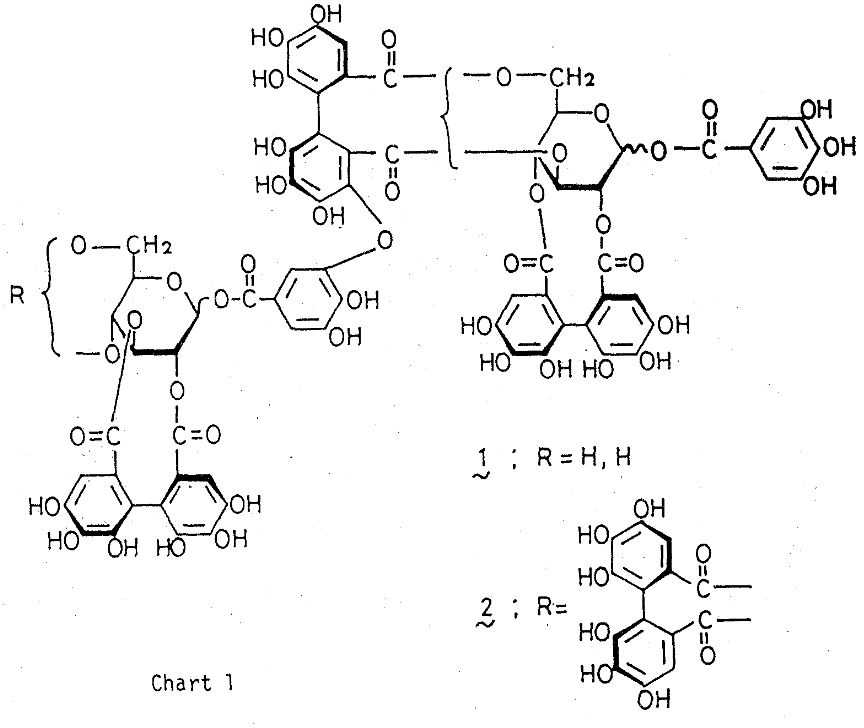


Chart 1

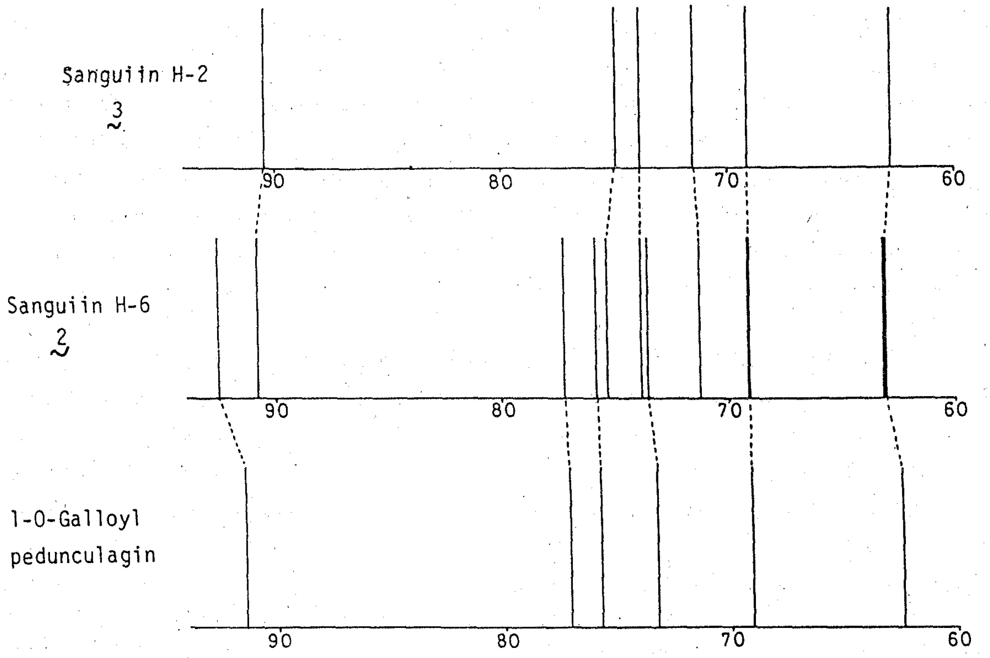
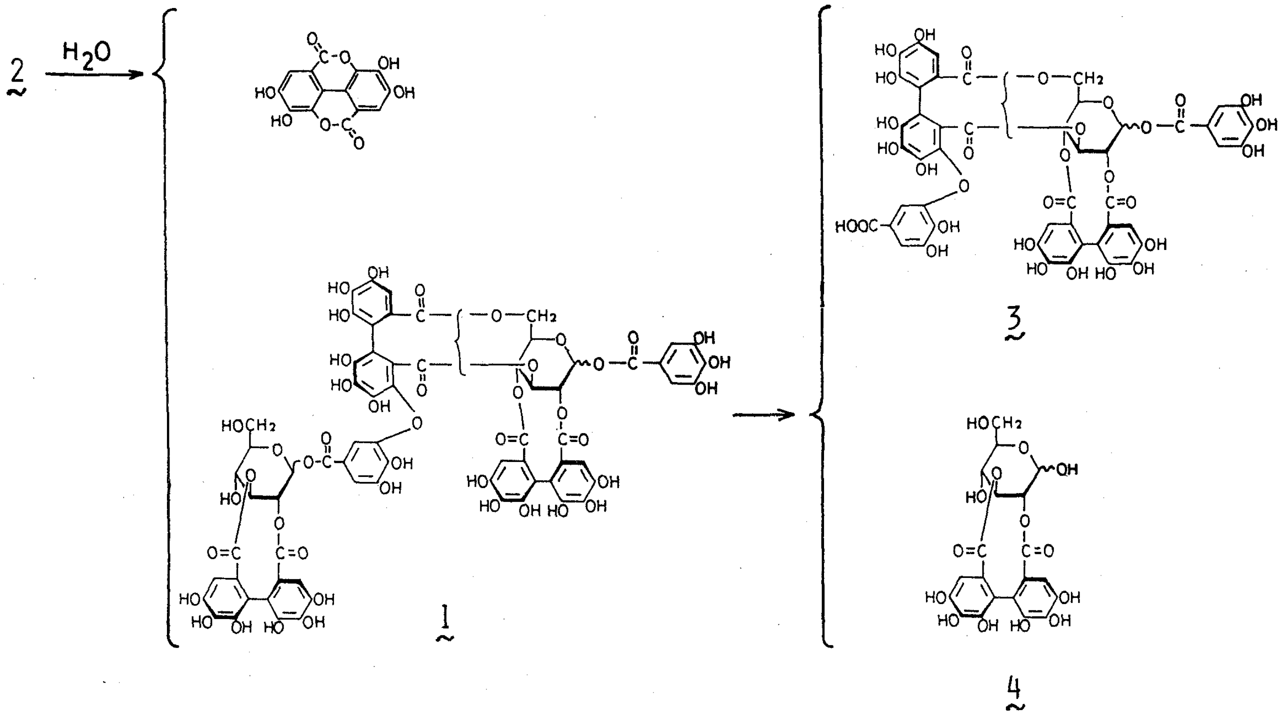


Fig. 1. ^{13}C NMR Chemical Shifts of Sugar Carbons in Sanguiins H-2 (3) and H-6 (2) and 1-O-Galloyl Pedunculagin (at 25.05 MHz, in Me_2CO-d_6)



glucose,[1,4] while the remaining six signals (δ 63.1, 69.2, 73.5, 73.8, 77.3, and 92.6) show close similarities to those of 1-O-galloyl pedunculagin [1-O-galloyl-2,3;4,6-bis(hexahydroxydiphenoyl)-β-D-glucose],[5] thus suggesting that the phenolic acid residues are located in patterns similar to those of these compounds.

Selective cleavage of the linkage between the two units by refluxing **2** in aqueous solution[1] was unsuccessful. However, from this reaction mixture three partial hydrolysates could be obtained, and these were characterized as sanguiin H-3 (**1**) and H-2 (**3**), and 2,3-hexahydroxydiphenoyl glucose (**4**) by direct comparisons of physical and spectral data with authentic samples.[1] Consequently, sanguiin H-6 was assigned the formula (**2**), a dimeric structure containing sanguiin H-2 and pedunculagin moieties. Sanguiin H-6 has also been isolated from the unripe fruits of *Rubus chingii* Hu,[6] and this suggests the possibility of the wide distribution of this tannin in the Rosaceous plants.

ACKNOWLEDGEMENT We thank Mr. Y. Tanaka, Miss K. Soeda, and Mr. I. Maetani for recording the ^{1}H and ^{13}C NMR spectra and FD-MS. This work was supported in part by a grant from the Ministry of Education, Science and Culture, Japan, which is gratefully acknowledged.

REFERENCES AND NOTES

1) G. Nonaka, T. Tanaka, and I. Nishioka, J. Chem. Soc. Perkin Trans. I, 1982, 1067.
2) M. Nishizawa, T. Yamagishi, G. Nonaka, and I. Nishioka, Chem. Pharm. Bull., 28, 2850 (1980).
3) W. E. Hillis and Y. Yazaki, Phytochemistry, 12, 2969 (1973).
4) The configuration at the anomeric center remains to be solved.
5) 1-O-Galloyl pedunculagin has been isolated from *Quercus stenophylla* Makino, and the structure was presented at the 28th Annual Meeting of Japanese Society of Pharmacognosy, held in Tokyo, October, 1981. Abstract Papers, p. 27.
6) Unpublished data.

(Received April 14, 1982)