

GERANIIN, A NEW ELLAGITANNIN FROM GERANIUM THUNBERGII

Takuo Okuda*, Takashi Yoshida and Hidekazu Nayeshiro

Faculty of Pharmaceutical Sciences, Okayama University, Tsushima, Okayama 700, Japan

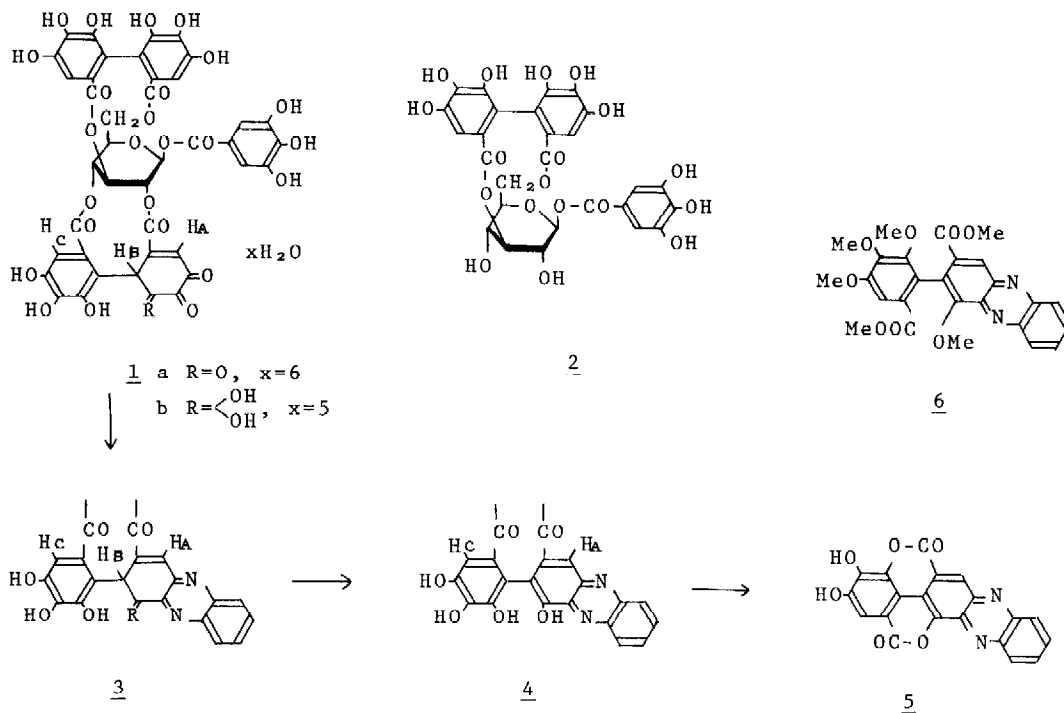
(Received in Japan 3 August 1976; received in UK for publication 31 August 1976)

The tannin-rich herb of *Geranium thunbergii* Sieb. et Zucc. (Geraniaceae) is an official antidiarrhoics, and is one of the most frequently used folkmedicines in Japan. We have isolated geraniin (1), a new ellagitannin which is regarded as the main tannin of this plant.

The herb was homogenized in aqueous acetone, and concentrated solution was extracted with EtOAc. Droplet countercurrent chromatography of the EtOAc extract, which yielded the crude ellagitannin, temporarily named "Tannin 1"¹, was followed by recrystallization from MeOH-H₂O at room temperature to afford 1 as yellow crystals which show almost no astringency on the tongue. This tannin, C₄₁H₂₈O₂₇·5H₂O, $[\alpha]_D^{15} -141^\circ$ (c=0.5, MeOH), was hydrolyzed in boiling water to give gallic acid, hexahydroxydiphenic acid, ellagic acid and corilagin (2) in a few hours, which were identified after methylation with CH₂N₂ followed by fractionation by prep. TLC. The PMR spectrum of 1 (90 MHz, CD₃COCD₃) shows, in addition to the protons of 2², a proton at δ 5.16, and two protons in the region of aromatic and vinyl protons. Downfield shifts of H-2 and H-4 on the glucopyranose ring to δ 5.4-5.6 from those of 2 (δ 4.06 and 4.42)² are also shown. Geraniin, therefore, should be a corilagin derivative esterified at O-2 and O-4 of D-glucopyranose.

Upon the reaction of 1 with o-phenylenediamine in 15% AcOH, pale yellow powder was precipitated out. This precipitate, phenazine A (3), purified by reprecipitation from MeOH-CHCl₃, C₄₇H₃₀N₂O₂₄·6H₂O, $[\alpha]_D^{15} -163^\circ$ (c=0.5, MeOH), was slowly converted on standing in the reaction mixture, to a yellow powder, phenazine B, (4), C₄₇H₃₀N₂O₂₄·5H₂O, $[\alpha]_D^{15} -90^\circ$ (c=0.5, dioxane). Phenazine B was directly produced by condensation of 1 with o-phenylenediamine in 50% AcOH. In boiling water, phenazine A and B yielded along with 2 and gallic acid, a dark brown-red precipitate which was recrystallized from tetrahydrofuran to give needles of phenazine C (5), C₂₀H₈N₂O₆·H₂O, M⁺ m/e 372. Phenazine C gave dibenzoate, C₃₄H₁₆N₂O₈, M⁺ 580, diacetate, C₂₄H₁₂N₂O₈, M⁺ 456, and dimethyl ether, C₂₂H₁₂N₂O₆, M⁺ 400, and also upon hydrolysis of the dimethyl ether followed by methylation, dimethyl ester (6), C₂₆H₂₄N₂O₈, m.p. 130°, M⁺ 492, which was identified with a specimen synthesized by a route essentially analogous to Schmidt's method.³ The shifts in the PMR spectra (CD₃COCD₃ for 1, 3 and 4, and CF₃COOD for 5) of H_A (1, δ 6.53, s; 3, δ 7.07, d, J=2 Hz; 4, δ 8.27, s; 5, δ 9.61, s), H_B (1, δ 5.16, s; 3, δ 5.34, d, J=2 Hz; 4, none; 5, none), and H_C (1, δ 7.13, s; 3, δ 7.33, s; 4, δ 7.46, s; 5, δ 8.06, s) in the reaction sequences, 1 → 3 → 4 → 5, are attributable to the transformations illustrated in Scheme 1.

As for the ester linkages at O-2 and O-4 of the sugar in 1, the carboxytriketohexene moiety in 1a rather than the galloyl moiety is presumed to be linked to O-2, on the basis of the marked downfield shift of H-1 of glucose, from δ 6.62 to 6.16, upon conversion of phenazine A to phenazine B.



Scheme 1

Among the three ketones in 1a, the one adjacent to H_B-carrying methine carbon, is presumed to be hydrated to form a geminal diol group as in 1b, since the CMR spectrum of geraniin in THF-d₈ shows two peaks of conjugated ketone at δ 191.8 and 194.9, and a geminal diol carbon at δ 92.1.

The yield of geraniin (up to ca. 2% from dried herb) and the results of fractionation show that fairly large parts of the smaller phenolic compounds previously reported^{4,5} could be hydrolysis products of geraniin.

Acknowledgements. The authors wish to thank Dr. N. Nagakura of Kobe Women's College of Pharmacy for the CMR spectral measurements. This work was supported in part by a grant from the Ministry of Education, Japan, which is greatly acknowledged.

REFERENCES

- 1 T. Okuda, T. Yoshida and K. Mori, *Yakugaku Zasshi*, 95, 1462 (1975).
- 2 M. K. Seikel and W. E. Hillis, *Phytochemistry*, 9, 1115 (1970).
- 3 O. T. Schmidt and G. Wiedner, *Liebigs Ann. Chem.*, 706, 198 (1967).
- 4 T. Okuda, T. Yoshida and K. Mori, *Phytochemistry*, 14, 1877 (1975).
- 5 Y. Asahina and K. Tominaga, *Yakugaku Zasshi*, 19, 213 (1899).