

Studies on the Morphology and the Chemotaxonomy of *Citrus* Plants Native to Je Ju Island and on its Application (II)

On the Chemical Components of *Citrus platymamma* Hort. ex Tanaka

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제주도 재래감귤의 식물학적 특성과 이용에 관한 연구 (II)

병귤(瓶橘)의 성분연구

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濟州島 재래감귤인 병귤 *Citrus platymamma* HORT. ex TANAKA의 葉, 果皮, 樹皮의 클로로포름 可溶部에서 無色針狀晶, $C_{10}H_{10}O_4$, mp 139~140°을 單離하고 理化學的 性狀 및 UV, IR, NMR, Mass spectra를 이용하여 그 化學構造를 究明한바 1,4-benzenedicarboxylic acid dimethyl ester이었다. 또 果皮의 水溶部에서 單離한 2개의 flavonoid 配糖體는 그 理化學的인 性狀 및 IR-spectrum으로 보아 naringin과 hesperidin이었다.

Introduction

Byungkyoul or Binkitsu cultivated in Je Ju Island is *Citrus platymamma* HORT. ex TANAKA which is classified into the Section Acrumen of Subgenus Metacitrus by TANAKA systematics¹⁾. This plant is a small evergreen shrub with stiff and short thorns at the base; leaves elliptical lanceolate, 6~8.5cm in length and 2.5~3.5cm in width, whose petiole is 0.9~1.5cm with narrowed wings; flowers solitary or in clusters. The fruit is oval or oval-ovlong, 6.5~8cm in height and 5.6~6.5cm in width, and contain sweet pulp. Apical part of the fruit is prominent, 1~1.6cm in height and 2.5~3.5cm in width; ovary about 10-loculus, seeds about 6,

and fruit 80~120g in weight²⁾.

On the other hand, flavanone glycosides found in *Citrus* are classified into three groups; 1) the 7-O-rutinosides, 2) the 7-O-neohesperidosides, and 3) miscellaneous compounds⁴⁾. The results of ALBACH and REDMAN⁵⁾ and NISHIURA and coworkers⁶⁾ indicate that the flavanone glycoside patterns are useful in the characterization and identification of specific *Citrus* fruits.

Although isonaringin was isolated from the fruit peels of *C. platymamma* HORT. ex TANAKA in 1971⁶⁾, the data obtained were not sufficient to discuss its flavonoid patterns. From above reason the authors investigated the flavanone glycosides and other chemical components in this plants.

This paper describes two flavanone glycosides, namely naringin and hesperidin isolated from the water-soluble fraction of its fruit peels, and 1,4-benzenedicarboxylic acid dimethyl ester from the chloroform-soluble fraction of its leaves, peels and barks.

Experimental

Materials. The leaves, barks and immature fruit peels were obtained from labeled trees in Je Ju City in July of 1978.

Isolation procedure of chemical components. Finely chopped fresh materials (150g) were refluxed three times with 500ml of 80% methanol for five hours and filtered. After concentration of the combined filtrates in vacuo to a small quantity, the resulting aqueous solution was extracted with 30ml of chloroform five times and then saturated with ether by shaking and allowed to stand in an ice box.

The above combined chloroform extracts was evaporated to dryness in vacuo and the residue was dissolved in a small quantity of hot absolute ethanol. On standing overnight in an ice box it afforded almost colorless needles (substance I). I was repeatedly recrystallized from absolute ethanol as colorless needles which melted at 139~140°C.

After one month pale yellow needles which had been separated from the above aqueous solution were filtered and washed with a small quantity of water. Absolute ethanol was added to the residue, and the insoluble part (substance II). II was recrystallized from formamide-water (1:1) as colorless needles which melted at 260~262°C.

The above filtrate was evaporated to dryness in vacuo and the residue was dissolved in a small quantity of water. After standing overnight colorless needles separated were repeatedly

recrystallized as colorless needles (substance III) which melted at 170~171°C.

Identification of substance I (1,4-benzenedicarboxylic acid dimethyl ester; terephthalic acid dimethyl ester). I was isolated from the leaves, fruit peels and barks of this plant. mp. 139~140°C. Anal. Calcd. for $C_{10}H_{10}O_4$: C, 62.8; H, 5.51. Found: C, 61.85; H, 5.19. Ms mle: 194(M⁺). IR(KBr) $\nu_{max}(cm^{-1})$: 1720(C=O), 1285, 1270, 1125, 1115 (Ar-CO-O-), 1950, 1920, 1680, 1200, 1012, 825 (p-substituted phenyl) (Fig.1). UV. $\nu_{MeOH}(nm)$ 285, 240. NMR (CDCl₃) δ : 3.9(6H, S, CH₃OCO-), 8.1(4H, S, ϕ -H). (Fig. 2).

Identification of substance II (hesperidin). Anal. Calcd. for $C_{28}H_{34}O_{15}$: C, 53.6; H, 5.16. Found: C, 55.08; H, 5.61. IR(KBr) $\nu_{max}(cm^{-1})$: 3500(-OH), 1645, 1605 (2,3-dihydro- γ -pyrane). mp 260~262°C, either alone or as an admixture with an authentic sample of naringin.

Identification of substance III (naringin). Anal. calcd. for $C_{27}H_{32}O_{14}$: C, 55.92; H, 5.66. Found: C, 55.86; H, 5.56. IR(KBr) $\nu_{max}(cm^{-1})$: 3500(-OH), 1640, 1620 (2,3-dihydro- γ -pyrane). mp 170~171°C, either alone or as an admixture with an authentic sample of naringin.

Results and Discussion

As a part of a continuing search for the morphology and the chemotaxonomy of *Citrus* plants native to Je Ju Island and on its application⁷⁾, *C.platymamma* Hort. ex Tanaka was investigated for its chemical components. The colorless needles isolated from chloroform soluble fraction of the leaves, fruit peels and barks of this plant were identified as 1,4-benzenedicarboxylic acid dimethyl ester by its physical and chemical evidence, and its IR, UV, NMR and Mass spectral data.

Two flavanone glycosides isolated from water-soluble fraction of its fruit peels were identified as hesperidin and naringin by its IR spectrum and as compared with an authentic samples.

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