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On the Active Components of the root of Citrus genus in Taiwan

III. The Components of the root of *Citrus nobilis* Lour. var. *sunki* Hort.

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Citrus nobilis Lour. var. *sunki* Hort. is cultivated in Taiwan. It is considered to be a stimulant to digestion, corrective and diuretic. The peel is used as a carminative and in alcoholism[1]. Its pericarps was first chemically investigated by Hsü et al[2]. who isolated flavanone glycoside——hesperidin. But the root part had never been reported. So that in the present paper the authors wish to research on the chemical constituents on the roots of this species.

The dried roots of *Citrus nobilis* var. *sunki* were crushed and percolated with ether. The ethereal extract was chromatograhed on silica gel column. The method is shown in Chart 1. Five crystalline compounds were isolated.

Compounds(II), (III)and (IV)gave a positive with Liebermann Burchard's reaction. According to the results from gas liquid chromatography and IR-spectrum analysis; Compound (II) is a mixture of campesterol and stigmasterol (3 : 7). (Fig. 1, 2). Compound(III) is a mixture of campesterol, stigmasterol and cholesterol. (Fig.3, 4). Compound (IV) is a mixture of stigmasterol and β-sitosterol(7 : 3). (Fig. 5, 6).

Compound(V) is a colorless prisms, $C_{14}H_{12}O_5$. In view of the melting point, composition and IR-spectrum of (V), to be (V) is xanthyletin. Comparison of the IR-spectrum and mixed melting point with the authentic sample showed that they were identical.

Chart 1

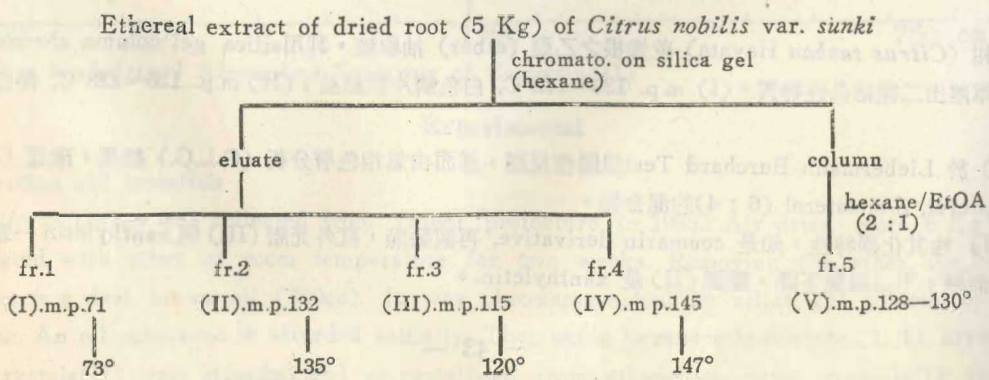

Table 1.

Relative Retention time of Steroid derivatives
Isolated from *Citrus nobilis* var. *sunki*

Compd.	Retention time (min) Column Temp.269°
Cholesterol	4.30
Campesterol	5.40 (5.50)
Stigmasterol	6.00 (5.80)
β-sitosterol	6.50

Shimazu GC-3AF

Column: 1.5% SE-30 on Chromosorb-W (60-80 mesh)
Glass column: 1.8m × 0.4cmϕ, Temp. 269°
Carrier gas: N_2, 0.8Kg/cm², 16sec/10ml
H_2, 0.65Kg/cm², 12sec/10ml
Air, 0.6Kg/cm², range3.2V

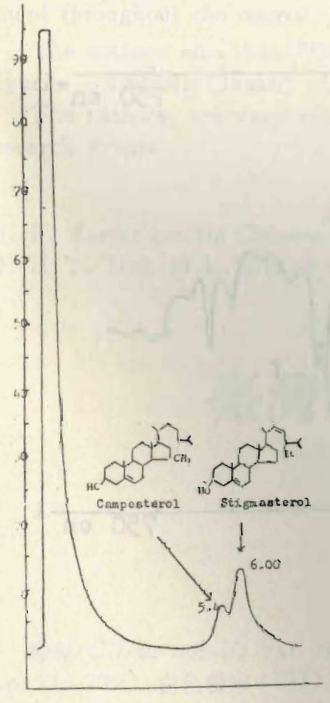

Fig. 1. GLC of Compound (II) Isolated from *Citrus nobilis* var. *sunki*

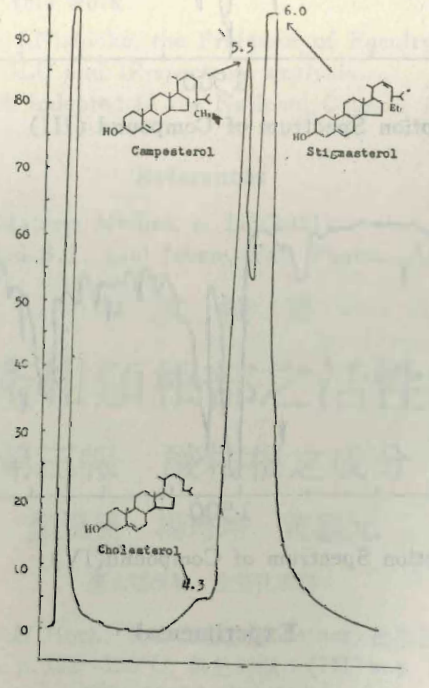

Fig. 3. GLC of Compound (III) Isolated from *Citrus nobilis* var. *sunki*

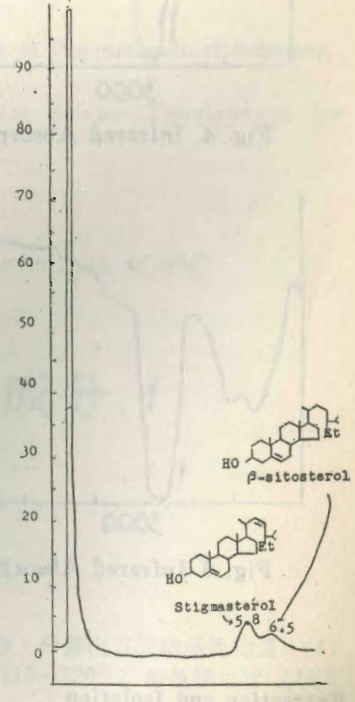

Fig. 5. GLC of Compound (IV) Isolated from *Citrus nobilis* var. *sunki*

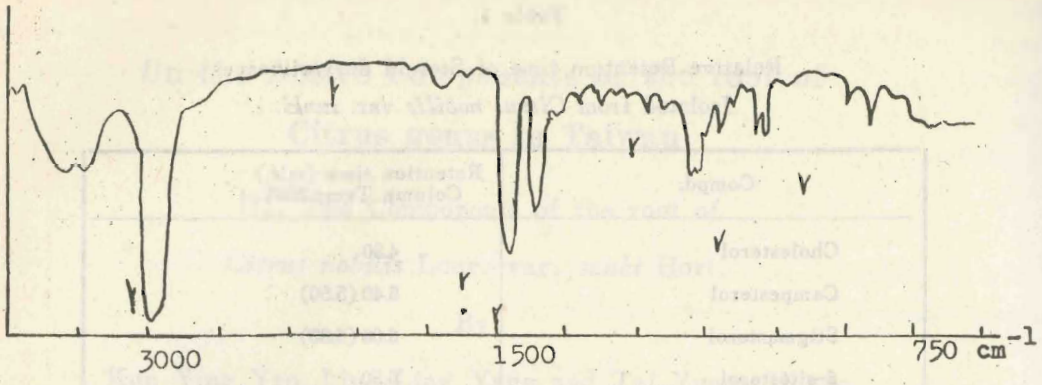

Fig. 2. Infrared Absorption Spectrum of Compound (II)

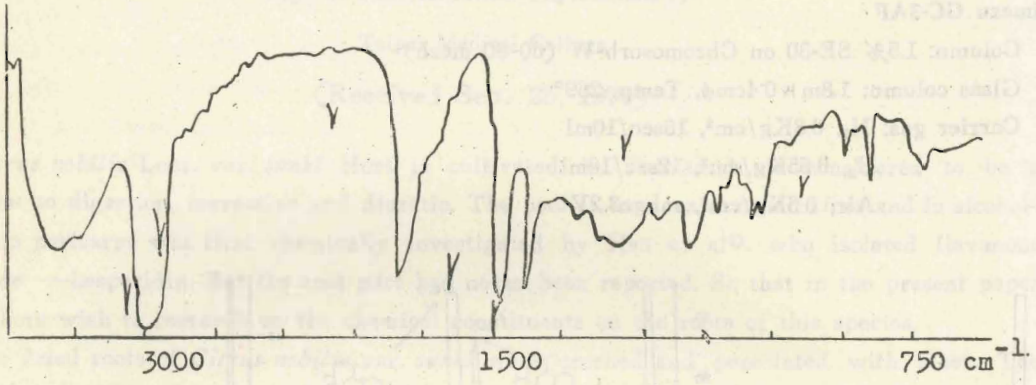

Fig. 4. Infrared Absorption Spectrum of Compound (III)

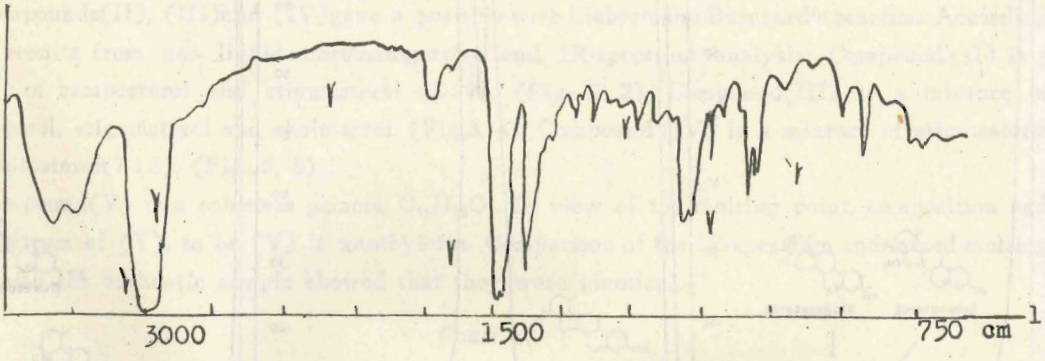

Fig. 6. Infrared Absorption Spectrum of Compound(IV)

Experimental

Extraction and Isolation

Citrus nobilis var. *sunki* was collected from Taipei prefecture in 1968. Air dried roots(5 Kg) were extracted with ether for two weeks. Removal of ether from the bulk of ether extract, a dark brown oily substance (300 cc) was obtained. It was chromatographed on silica gel column with eluting solvents: hexane, hexane-ethylacetate (2 : 1) in order.

Compound(I): The fraction-1 of hexane eluting portion. First removed the solvent, and a wax-like substance was obtained. Recrystallized with ethanol. m.p. 71–73°. But it is inadequate so that it has not yet been determined in detail.

Compound(II): The fraction-2 of hexane eluting portion. Removed the solvent, crude crystals filtrated and recrystallized with ethanol. m.p.132–135°, colorless needles. It gave a positive result with Liebermann Burchard's reaction. Determined the retention time of GLC analysis, (II) is confirmed to consist of a mixture of campesterol and stigmasterol. (Fig. 1 and 2).

Compound(III): The fraction-3 of hexane eluting portion. Removed solvent to get crude crystals. Later recrystallized with ethanol. m.p. 115–120°, colorless scales. It gave a positive result with Liebermann Burchard's reaction. According to the results of GLC analysis, (III) is confirmed to consist of a mixture of cholesterol, campesterol and stigmasterol. (Fig. 3 and 4).

Compound(IV): The fraction-4 of hexane eluting portion. Removed the solvent to get crude crystals. Recrystallized with ethanol to give m.p. 145–147°, colorless scales. It was a positive with Liebermann Burchard's reaction. According to GLC analysis, (IV) is confirmed to contain a mixture of stigmasterol and β-sitosterol(7 : 3). (Fig.5, 6).

Compound(V): The fraction-5 of hexane-ethylacetate (2 : 1) eluting portion. Removed the solvent to get yellowish crude crystals. Then decolorized with activated carbon and recrystallized with ethanol to give colorless prisms of m.p. 128–130°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 73.67; H, 5.30

Found: C, 72.90; H, 5.38

In view of the above results, (V) is presumed as xanthyletin. The IR-spectrum were essentially identical to xanthyletin and the mixed melting point with the authentic sample did not show any depression.

Acknowledgement

The authors wish to depress his deep to Dr. C.T.Hsü, the Dean of the College for encouragement throughout the course of this work.

The authors also thank Dr. I.Nishioka, the Professor of Faculty of Pharmaceutical Sciences, Kyushu University(Japan) of GLC and IR-spectrum analysis.

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2). H.Y. Hsü, M.L. Chang and S.J. Liu: Journ. Tai. Pharm. Associ. ,16, 6(1964)

中 文 摘 要

臺灣產柑類根部之活性成分

第三報　酸桔根之成分

顏焜熒　楊玲玲　黃泰元

臺北醫學院　生藥化學科

酸桔(*Citrus nobilis* var. *sunki* Hort.) 乾燥根之乙醚 (ether) 抽取液，分離出五種結晶性物質。(I) m.p. 71～73°C, 白色粉末；(II) m.p. 132～135°C, 無色針狀；(III) m.p. 115～120°C, 無色鱗片狀; (IV) m.p. 145～147°C, 無色鱗片狀；(V) m.p.128～130°C, 無色板狀。

(II), (III), (IV)於Liebermann Burchard Test呈陽性反應，且依據氣相色層分析(G.L.C.)結果如下：

(II): Campesterol, stigmasterol (3 : 7)

(III): Cholesterol, campesterol, stigmasterol

(IV): Stigmasterol, β-sitosterol (7 : 3)

(V) 由其融點，組成及紅外光譜，(IR), 均與 xanthyletin一致。經與標品混融，不呈融點下降，確認(V)爲xanthyletin。

柑類之根，共同含有 coumarin derivative的xanthyletin, 同時亦共存有各種不同混合型的植物固醇類(phyto-sterol), 此在化學分類之檢討上，爲一有趣之事。