

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

I. The Components of the root of

Citrus medica L. var. *sarcodactylis* Swingle

By

Kun Ying Yen

Dept. of Pharmaceutical Phytochemistry, Taipei Medical College

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Citrus medica L. var. *sarcodactylis* Swingle is cultivated in Vietnam, Indonesia and Malaysia. The plant is an evergreen shrub, also wildy grown everywhere in South China. In Taiwan, it is cultivated in garden as an ornament, shade and pharmaceutical purpose. The pericarp is naturally cleavaged as palmate parted fingers, so called "Fo-shou"¹⁾. The endocarp almost vanishes and the mesocarp is well developed.

The pericarp consists of flavanone glycosides—hesperidin and naringin²⁾. That is the character on *Citrus* genus. Besides the above flavanones, Matsuno³⁾ has isolated a coumarin derivative—limettin. But the roots had never been researched before, so that the author started to study on the roots of *Citrus* genus in Taiwan.

At first study was made on the compounds of the roots of *Citrus medica* var. *sarcodactylis*. Four crystalline compounds were isolated.

Crystal (I): $C_{14}H_{12}O_3$, m.p. 132–133°, colorless prisms. Under UV-lamp irradiation, it emits a fresh blue fluorescence. It gives a negative ferric chloride reaction, decolorizes bromine and potassium permanganate and on adding concentration sulfuric acid, it changes into red orange color. The IR-spectrum (KBr) is identical and exhibits a characteristic peak at 1730 cm^{-1} which signs δ -lactone. The UV-spectrum of the compound shows a maximum at $350\text{ m}\mu$ and a minimum at $225\text{ m}\mu$. The foregoing mentions presume (I) as xanthyletin and the melting point was not depressed on admixture with an authentic sample. Xanthyletin is first isolated from the rinds of *Xanthoxylum americanum* by Bell et al.⁴⁾. Recently in Japan, Morita et al. it was also isolated from the root bark of *Fagara fauriei*⁴⁾, *F. ailanthoides* var. *yakumontano*⁶⁾. But it is initially isolated from the root of *Citrus* genus in Taiwan.

Crystal(II): colorless scales, m.p. 136–137°, isolated from ethereal portion was submitted to gas liquid chromatography(GLC) analysis (Table I, Fig. 1). It is identical and exhibits a mixture of four kinds of steroids. Those are campesterol, stigmasterol, β -sitosterol and cholesterol. The former three kinds occur in vast amount in the plant Kingdom and the later is a zoosteroid. Cholesterol is one of the most common zoosteroid. Recently however, it has been isolated from some plants.

Just a remarkable isolated from *Citrus* genus is not only a rare occurrence but also very interesting for research.

Crystal (III): $C_{19}H_{20}O_4$, m.p. 182–183°, pale yellow prisms. It gave a green color with ferric chloride. The IR-spectrum (Nujol) exhibits a characteristic peak, at 3350 cm^{-1} which signifies phenolic hydroxy group. The UV-spectrum of the compound, a maximum at $335\text{m}\mu$ is similar to that of nordentatin and the melting point was not depressed on admixture with an authentic sample. Nordentatin is isolated from the root bark of *Clausena dentata* by Govindachari et al.⁽⁹⁾ grown in South Indian. However, it is very interesting that nordentatin was initially isolated from the root of *Citrus* genus.

Crystal (IV): m.p. 242–244°, yellow crystalline needles. It is so small in quantity that the author was unable to detect.

Chart 1

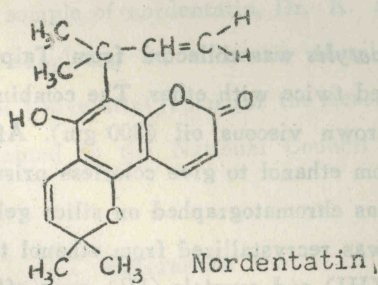
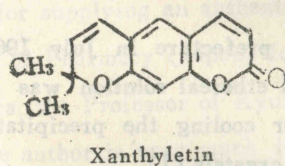
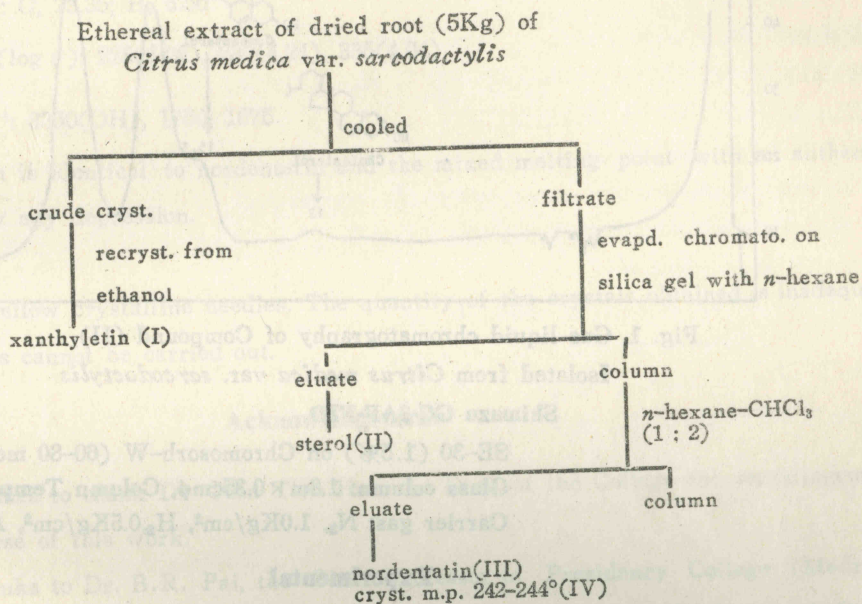


Table 1

Relative Retention time of Steroid derivatives Isolation from *Citrus medica* var. *sarcodactylis*

Compd.	Retention time (min), Column Temp. 245°
Cholesterol	12.0
Campesterol	15.3
Stigmasterol	16.5
β -sitosterol	18.7

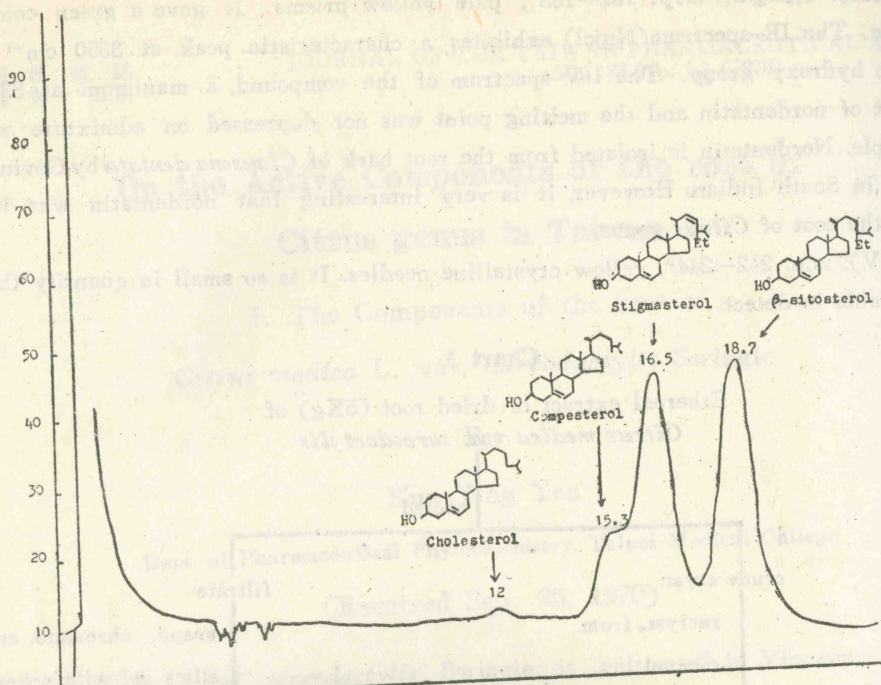


Fig. 1. Gas liquid chromatography of Compound (II),
Isolated from *Citrus medica* var. *sarcodactylis*

Shimazu GC-3AF-FID

SE-30 (1.5%) on Chromosorb-W (60-80 mesh)

Glass column: 1.8m $\times$ 0.35cm ϕ , Column Temp. 245 $^{\circ}$

Carrier gas: N₂, 1.0Kg/cm², H₂, 0.5Kg/cm², Air, 0.6Kg/cm²

Experimental

Extraction and Isolation

Citrus medica var. *sarcodactylis* was collected from Taipei prefecture in July 1968. Air dried roots (5Kg) were extracted twice with ether. The combined ethereal solution was concentrated to dryness to yield a brown viscous oil (300 gm). After cooling the precipitate was collected and recrystallized from ethanol to give colorless prism crystals (I).

The ether mother liquor was chromatographed on silica gel column by using hexane, crystals (II) afforded initially, which was recrystallized from ethanol to pure colorless scales. Then using hexane-CHCl₃ (1:2), crystals (III) and crystals (IV) were afforded, which were recrystallized from ethanol to pure crystals (III) pale yellow prisms, and crystals (IV) yellow needles.

Xanthyletin (I):

m. p. 132-133 $^{\circ}$, colorless prisms

Anal. Calcd. for C₁₄H₁₂O₃: C, 73.67; H, 5.30

Found: C, 73.41; H, 5.21

UV λ $\frac{EtOH}{max}$ $m\mu$ (log ϵ): 225(4.35), 267(4.30), 350(4.07)

IR ν $\frac{KBr}{max}$ cm⁻¹: 1730(δ -lactone)

The IR-spectrum is identical to xanthyletin and the mixed melting point with an authentic sample did not show any depression.

Mixed sterols (II):

m.p. 136–137°, colorless scales, which gave a positive Liebermann Burchard's reaction. By carrying out gas liquid chromatography analysis, the retention values indicate there were four kinds of mixed compounds. They are cholesterol, campesterol, stigmasterol and β -sitosterol. (As shown in Fig. 1 and Table 1.)

Nordentatin (III):

m.p. 182–183.5°, pale yellow prisms

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 73.07; H, 6.40

Found: C, 73.35; H, 6.50

UV $\lambda_{\text{max}}^{\text{EtOH}}$ $m\mu$ ($\log \epsilon$): 225(4.22), 280(4.24), 335(4.04)

IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3350(OH), 1750, 1675

The IR-spectrum is identical to nordentatin and the mixed melting point with an authentic sample did not show any depression.

Crystal (IV):

m.p. 242–244°, yellow crystalline needles. The quantity of the crystals obtained is inadequate that further analysis cannot be carried out.

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References

- 1). W.S. Gan: Manual of Medicinal Plants in Taiwan II, 367 (1960)
- 2). T. Matsuno: Yakugaku Zasshi(Tokyo), 74, 363(1954), 79, 540(1959)
- 3). J.C. Bell, A. Robertson: Soc. 1936, 1828
- 4). N. Morita, M. Arisawa, T. Takezaki: Yakugaku Zasshi(Tokyo), 88, 1214(1968)
- 5). N. Morita, M. Arisawa: Yakugaku Zasshi(Tokyo), 87, 1017(1967)
- 6). T.R. Govindachari, B.R. Pai, P.S. Subramaniam: Tetrahedron, 24, 753(1968)

臺灣產柑類根部之活性成分

第一報 佛手柑根之成分

顏 焜 熒

臺北醫學院 生藥化學科

著者由佛手柑 (*Citrus medica* L. var. *sarcodactylis* Swingle) 乾燥根之乙醚 (ether) 抽取液部分，分離出四種結晶性物質。(I) m.p. 132~133°C，無色板狀結晶；(II) m.p. 136~137°C，無色鱗片狀結晶；(III) m.p. 182~183.5°C，淡黃色板狀結晶；(IV) m.p. 242~244°C，黃色針狀結晶。

(II) 於 Liebermann Burchard Test 呈陽性反應，同時依 Gas Liquid Chromatography 分析，確認為 cholesterol, β -sitosterol, stigmasterol 及 campesterol 的混合物。又由諸化學特性知 (I) 及 (III) 為 coumarin derivatives，觀其融點，紅外光譜 (IR)，紫外光譜 (UV) 之性質分析分別，確認為 xanthyletin 及 nor-dentatin。