

羅氏鹽膚木虫癭之研究

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中文摘要

五倍子為某些植物蚜蟲螫刺鹽膚木（漆樹科）而形成者，含有豐富之鞣質。羅氏鹽膚木為鹽膚木之類緣植物。其百分之六十之水性丙酮萃取物，藉由各種管柱層析之純化，共得到十七個化合物，其結構經光譜之解析，分別確認為：shikimic acid, protocatechuic acid, gallic acid, methylgallate, digallic acid, methyl digallate, 1-*O*-galloyl- β -D-glucose, 1,2,3,4,6-penta-*O*-galloyl- β -D-glucose, (+)-catechin, eriodictyol, luteoline, quercetine, (-)-rhusflavone, agathisflavone, amentoflavone, butein, *p*-hydroxyacetophenone。

關鍵詞：鞣質、羅氏鹽膚木、漆樹科

Abstract

Chinese galls are formed on *Rhus chinensis* Mill (Fam. Anacardiaceae) owing to the stings of certain plant lice, and they are rich in tannins. *Rhus semialata* Murr. var. *roxburghii* DC., an allied plant of *Rhus chinensis*, by means of various column chromatographies, seventeen compounds were obtained from the 60 % aqueous acetone extract of the galls. The structure of

these compounds were elucidated respectively as shikimic acid, protocatechuic acid, gallic acid, methylgallate, digallic acid, methyl digallate, 1-*O*-galloyl- β -D-glucose, 1,2,3,4,6-penta-*O*-galloyl- β -D-glucose, (+)-catechin, eriodictyol, luteoline, quercetine, (-)-rhusflavone, agathisflavone, amentoflavone, butein, *p*-hydroxyacetophenone。

Keywords: Tannin, *Rhus semialata* Murr. var. *roxburghiana* DC., Anacardiaceae

Introduction

The tannins in Chinese galls resemble in many respects to the gallotannins of Turkish galls, although it is more heterogenous in composition [1]. Recently, it was reported that the activity of gallotannin samples is believed to derive from the variation in the number of despidically linked galloyl groups in the polygalloyl chain [2]. Thus, the chemical structure and activity relationship is worth to be studied. *Rhus semialata* Murr. var. *roxburghii* DC., an allied plant of *Rhus chinensis*, has been used in Taiwan as a folk medicine for the treatment of rheumatism and peptic ulcer [3]. Preliminary examination showed that the galls of this plant contain

abundant tannins, but given different chromatographic pattern from Chinese galls in TLC. In this work, we try to isolate and identify the tannins contained in the galls.

Results and Discussion

Several types of column packings were employed to separate these tannins from the aqueous acetone extract of the galls of *R. semialata* Murr. var. *roxburghii* DC., including polydextran gel, high-porous polystyrene-based and reverse-phase packing materials. These efforts led to the isolation of seventeen compounds (1-17) in total. The structure of these pure compounds were elucidated respectively as shikimic acid (1) [4], protocatechuic acid (2) [5], gallic acid (3) [6], methylgallate (4) [7], digallic acid (5) [8], methyl digallate (6) [8], 1-*O*-galloyl- β -D-glucose (7) [9], 1,2,3,4,6-penta-*O*-galloyl- β -D-glucose (8) [10], (+)-catechin (9) [11], eriodictyol (10) [12], luteoline (11) [12], quercetine (12) [12], (-)-rhusflavone (13) [13], agathisflavone (14) [13,14], amentoflavone (15) [13,15], butein (16) [16], *p*-hydroxyacetophenone (17) [17], by comparison of its ^1H NMR, ^{13}C NMR, MS spectral data with literature values. Base on the characteristic of chemical structures, these compounds may be divided as organic acid, small phenolics, gallotannins, flavan-3-ol, flavonoids, chalcone and other classes. The phenolics and its related derivatives are the major, flavonoids are the

second ones, flavan-3-ol and chalcone are the minor. (Table 1)

Experimental

General procedures

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 FT spectrometer in acetone- d_6 , acetone- d_6 -D₂O or DMSO- d_6 , using TMS as reference standard. 2D-NMR spectra were recorded using the Bruker standard pulse programs. Optical rotations were measured on a Jasco DIP-140 digital polarimeter.

Plant material

The galls of *R. semialata* Murr. var. *roxburghii* DC. were collected at Tsu-Yung Mountain, Kaohsiung, Taiwan in Sep. 1997. The plant was identified by Prof. Ih-Sheng Chen, School of Pharmacy, Kaohsiung Medical College, Kaohsiung, Taiwan. The fresh galls were crushed and extracted four times with 60 % aqueous acetone. The extracted solution was concentrated, and fractionated through a Diaion (100-200 mesh, Mitsubishi Chemical Industries) column using H₂O-MeOH as eluent. The obtained fractions were further subjected to repeated chromatography on Sephadex LH-20 and ODS Columns to yield compounds 1-17.

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Table 1. Polar Compounds from the Galls of *Rhus semialata* Murr. var. *roxburghii* DC

Compound	Weight* (mg)	Yield (%)
Organic acids:		
(-)-Shikimic acid (1)	134.5	1.12×10^{-2}
Phenolics:		
Protocatechuic acid (2)	112.4	9.36×10^{-3}
Gallic acid (3)	3504.6	2.92×10^{-1}
Methyl gallate (4)	2493.1	2.08×10^{-1}
Digallic acid (5)	1839.6	1.53×10^{-1}
Methyl digallate (6)	2580.8	2.15×10^{-1}
Galltannins:		
1- <i>O</i> -galloyl- β -D-glucose (7)	15.2	1.27×10^{-3}
1,2,3,4,6-penta- <i>O</i> -galloyl- β -D-glucose (8)	1180.8	9.84×10^{-2}
Flavan-3-ol:		
(+)-catechin (9)	28.7	2.39×10^{-3}
Flavonoids:		
Eriodictyol (10)	7.1	5.93×10^{-4}
Luteolin (11)	15.3	1.28×10^{-3}
Quercetin (12)	12.3	1.03×10^{-3}
(-)-Rhusflavone (13)	29.2	2.44×10^{-3}
Agathisflavone (14)	196.8	1.64×10^{-2}
Amentoflavone (15)	85.2	7.10×10^{-3}
Chalcone:		
Butein (16)	5.7	4.73×10^{-4}
Other:		
<i>p</i> -Hydroxyacetophenone (17)	8.0	6.65×10^{-4}

* from 1.2 Kg of Galls