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# Geranylated flavanones from the secretion on the surface of the immature fruits of *Paulownia tomentosa*

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**Abstract**

Chemical investigation of the methanol extract of the viscous secretion on the surface of immature fruits of *Paulownia tomentosa* furnished nine geranylated flavanones, 6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (**1**), 6-geranyl-3′,5,7-trihydroxy-4′-methoxyflavanone (**2**), 6-geranyl-4′,5,7-trihydroxy-3′,5′-dimethoxyflavanone (**3**), 6-geranyl-4′,5,5′,7-tetrahydroxy-3′-methoxyflavanone (**4**), 6-geranyl-3,3′,5,7-tetrahydroxy-4′-methoxyflavanone (**5**), 4′,5,5′,7-tetrahydroxy-6-[6-hydroxy-3,7-dimethyl-2(*E*),7-octadienyl]-3′-methoxyflavanone (**6**), 3,3′,4′,5,7-pentahydroxy-6-[6-hydroxy-3,7-dimethyl-2(*E*),7-octadienyl]flavanone (**7**), 3,3′,4′,5,7-pentahydroxy-6-[7-hydroxy-3,7-dimethyl-2(*E*)-octenyl]flavanone (**8**), and 3,4′,5,5′,7-pentahydroxy-3′-methoxy-6-(3-methyl-2-butenyl)flavanone (**9**), along with six known geranylated flavanones. Among these, compounds **4**, **6**–**9** and the known 6-geranyl-3′,4′,5,7-tetraahydroxyflavanone (diplacone), 6-geranyl-3,3′,4′,5,7-pentahydroxyflavanone (diplacol) and 3′,4′,5,7-pentahydroxy-6-[7-hydroxy-3,7-dimethyl-2(*E*)-octenyl]flavanone showed potent radical scavenging effects towards DPPH radicals.


*Keywords:* *Paulownia tomentosa*; Scrophulariaceae; Flavanone; Flavanol; DPPH radical; Anti-oxidant activity

## 1. Introduction

*Paulownia tomentosa* Steud. (Scrophulariaceae) is an ornamental tree widely distributed throughout China, Korea and Japan. Its stem bark has been used in Chinese herbal medicine as a component of remedies for infectious diseases such as gonorrhea and erysipelas (Kang et al., 1999). Earlier studies of *P. tomentosa* led to the isolation of iridoids (Plouvier, 1971; Adriani et al., 1981; Damtoft and Jensen, 1993) and lignans (Ina et al., 1987; Takahashi and Nakagawa, 1966). Recently, diplacone, a geranylated favanone, has been reported from the flower (Du et al., 2004).

Plants often have unique small structures on their surface. However, in most cases, functions of these structures have remained unclear. Systematic chemical analysis of the constituents contained in the small structures would be helpful in understanding their possible ecological functions. The surface of immature fruits of *P. tomentosa* is coated with viscous materials, at least part of which are likely to be secreted from the glandular trichomes, a fine structure located on the surface of immature fruits. This paper describes the isolation and structure elucidation of nine new flavanones **1**–**9** from this secretion, together with six known flavanones **10**–**15**. Anti-oxidant activities of the isolated flavanones were tested using the diphenylpicrylhydrazyl (DPPH) assay.

## 2. Results and discussion

The viscous oily material on the surface of fresh immature fruits of *P. tomentosa* was dissolved in MeOH by

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briefly dipping the fruits in the solvent. The concentrated MeOH extract was separated on silica gel, Sephadex LH-20 and reversed-phase HPLC to give the new flavanones **1**–**9** (Fig. 1), together with the known flavanones **10**–**15**. These compounds were all found to bear a $C_{10}$ substituent (geranyl or its metabolite) at the C-6 position, except for compound **9** which has a prenyl group at C-6.

Compound **1** was assigned the molecular formula $C_{27}H_{32}O_6$ on the basis of HREIMS data. The $^1$H NMR spectrum of compound **1** showed three protons at $\delta$ 2.80 (*dd*, $J = 17.3$, 2.9 Hz), 3.10 (*dd*, $J = 17.3$, 13.1 Hz) and 5.34 (*dd*, $J = 13.1$, 2.9 Hz), typically assignable to $H_2$-3 and H-2 of a flavanone skeleton. In addition, signals for three protons at $\delta$ 6.99 (*d*, $J = 1.9$ Hz), 6.96 (*dd*, 8.2, 1.9 Hz), 6.89 (*d*, $J = 8.2$ Hz) assignable to the aromatic protons of a 3,4-disubstituted B-ring, resonances for protons of a geranyl group, a downfield proton at $\delta$ 12.41 assignable to C-5-OH chelated to C-4 carbonyl, and an additional aromatic proton at $\delta$ 6.01 (*s*) were observed (Table 1). Furthermore, two methoxy signals appeared at $\delta$ 3.92 and 3.90. These spectroscopic data suggested that compound **1** was a 5-hydroxyflavanone substituted with a geranyl group, two methoxy groups and an additional hydroxy group. The substitution pattern was unambiguously established by HMBC correlations (Fig. 2) which gave evidence for the 3′,4′-dimethoxy B-ring and the 6-geranyl-5,7-dihydroxy A-ring structures. This substitution pattern was also consistent with the EIMS data, which exhibited ions at *m*/*z* 288 and 164 from a retro-Diels-Alder fragmentation. Hence, the structure of **1** was determined to be 6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone. Complete assignments of $^1$H and $^{13}$C signals of **1**, obtained by 2D NMR studies (H-H COSY, HMQC, HMBC) are listed in Tables 1 and 2. The absolute stereochemistry at C-2 of **1** was elucidated as *S* on the basis of the CD data (a positive absorption at 328 nm and a negative absorption at 288 nm) (Gaffield, 1970). The C-2 configurations of the other flavavones **2**, **3**, **4** and **6** were studied in the same manner and established to be *S*.

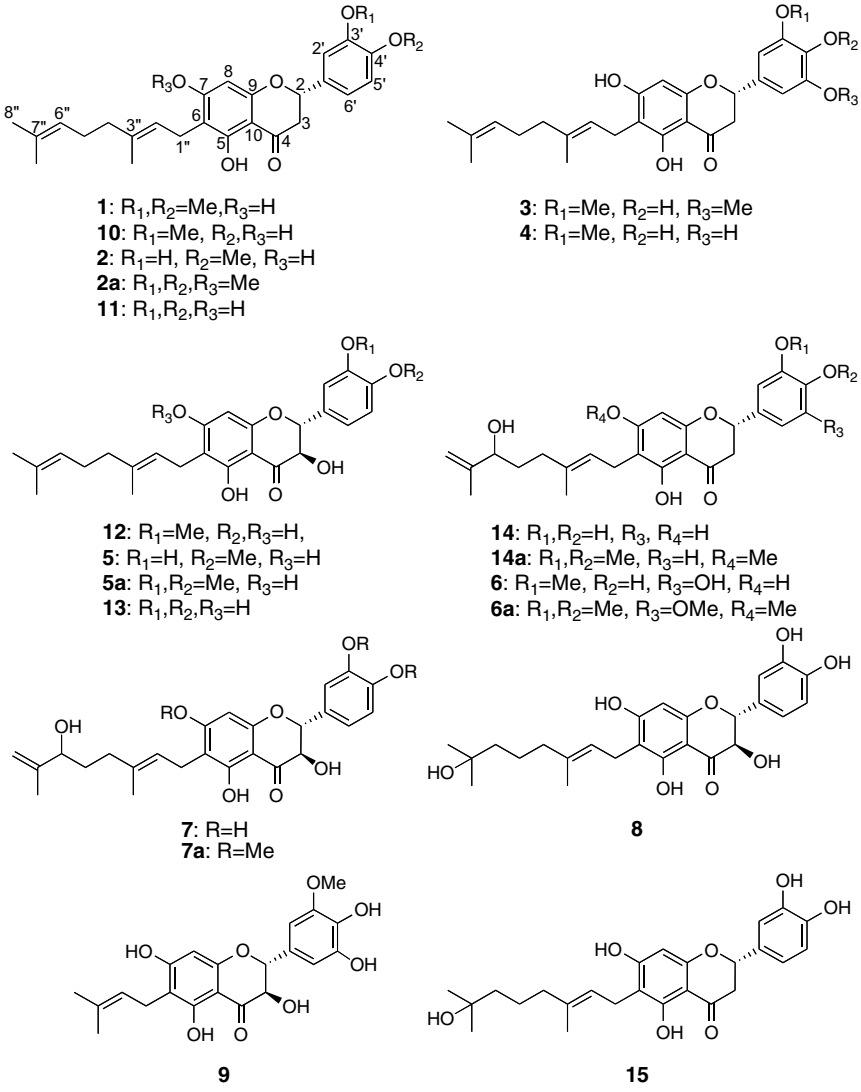


Fig. 1. Chemical structures of flavonoids **1**–**15**.