

Two New Gallotannins from *Pistacia weinmannifolia*

Ai Jun HOU¹, Li Yan PENG¹, Yan Ze LIU², Zhong Wen LIN¹, Han Dong SUN^{1,*}

¹Laboratory of Phytochemistry, Kunming Institute of Botany,
Chinese Academy of Sciences, Kunming 650204

²Department of Phytochemistry, Henan College of Traditional Chinese Medicine,
Zhengzhou 450003

Abstract: Two new gallotannins, pistafolins A (**1**) and B (**2**), were isolated from the leaf extract of *Pistacia weinmannifolia*. Their structures were determined by spectral methods.

Keywords: *Pistacia weinmannifolia*, Anacardiaceae, gallotannin, pistafolin A, pistafolin B.

Pistacia weinmannifolia J. Poisson ex Franch. (Anacardiaceae) is a shrub or an arbor that is widely found in Yunnan province of China. The leaves of this plant have the functions of “expelling toxin by cooling and astringing to stop bleeding”, and can be used against dysentery, enteritis, influenza, traumatic bleeding, headache and lung cancer¹. However, its chemical constituents have never been studied. In a survey on them, we found that beside the essential oil, this medicinal plant was also rich in tannins and polyphenols. This result led to the isolation of two new gallotannins named pistafolin A (**1**) and B (**2**). In this paper, the structure elucidation of **1** and **2** is reported.

Pistafolin A (**1**) was obtained as an off-white amorphous powder and gave a dark blue color with ferric chloride characteristic of gallotannins. The molecular formula was established as C₂₈H₂₄O₁₈ based on negative HRFABMS (obsd 647.0880, calcd 647.0884). The presence of galloyl groups was revealed by the analysis of the ¹H NMR and ¹³C NMR spectra. The ¹³C NMR and DEPT spectra also showed seven carbon signals due to two methylenes (δ 37.9, 38.6), three oxygen-bearing methines (δ 71.3, 72.8, 73.3), a quaternary carbon (δ 73.6) and a carboxyl signal (δ 176.8), which corresponded to a quinic acid moiety.

In the ¹H NMR spectrum, besides the signals of galloyl groups in the aromatic region and two methylenes at δ 2.00–2.30, three broad 1H singlets were observed. One bearing the galloyl groups appeared in the lowfield (δ 5.41), the other two free from ester functions were shown upfield (δ 3.82, 4.21). So, when these three signals were assigned, the location of the galloyl groups on the quinic acid nucleus would be determined. Based on the ¹H-¹H COSY spectrum, the methine at δ 3.82 was ascribable to H-4 of the quinic acid moiety. The assignment of H-3 and H-5 was achieved through the half-width values². Because H-3, H-4 and H-5 possess axial, axial and equatorial orientations respectively, H-3 should have a large half-width, while H-5 should have a small one.

Accordingly, the lowfield proton (δ 5.41, br s, $J_{\text{wh}/2} = 20$ Hz) and the upfield signal (δ 4.21, br s, $J_{\text{wh}/2} = 8$ Hz) were assigned to H-3 and H-5 respectively, indicating the gallic acid ester at C-3. Simultaneously, the carbon signals of the quinic acid moiety were also assigned by the HMQC spectrum.

From the molecular formula, the occurrence of three galloys linked through depside bonds could be deduced. Depsidically linked galloyl groups have been reported to occur in solution as an equilibrium mixture of *m*- and *p*-depside forms³. The complication of the signals due to galloyl groups in the ¹H NMR and ¹³C NMR spectra of **1** indicated that it actually existed as an equilibrium mixture of *m*- and *p*-isomers. Thus, pistafolin A (**1**) was characterized as 3-O-trigalloylquinic acid.

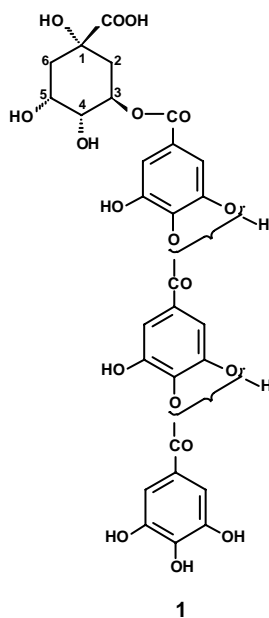
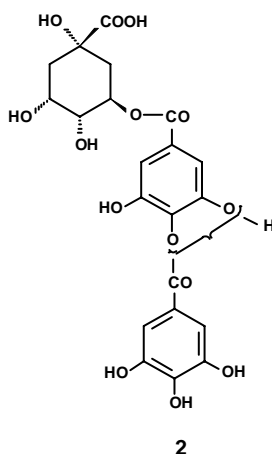


Table 1. ¹³C NMR Data for Compounds **1** and **2** (100 MHz, δ in ppm)

carbon	1 ^a	2 ^b
Quinic acid moiety		
1	73.6 (s)	73.7 (s)
2	38.6 (t)	37.2 (t)
3	72.8 (d)	70.6 (d)
4	73.3 (d)	72.3 (d)
5	71.3 (d)	68.4 (d)
6	37.9 (t)	36.3 (t)
COOH	176.8 (s)	175.2 (s)
Galloyl moiety		
1'	121.8, 120.6, 120.5 (s)	120.1, 118.8 (s)
2', 6'	118.2-110.1 (d)	116.1-108.6 (d)
3', 5'	151.8-144.2 (s)	150.5-143.1 (s)
4'	140.4, 140.2, 140.0 (s)	139.3, 139.1 (s)
CO	167.1, 166.6, 165.9 (s)	165.2, 164.5, 164.0 (s)

^aRecorded in MeOH-d₄. ^bRecorded in DMSO-d₆

Pistafolin B (**2**), off-white amorphous powder, afforded a dark blue color with ferric chloride, indicating the presence of galloyl group. The signals in the ^1H NMR and ^{13}C NMR spectra were very similar to those of pistafolin A (**1**), suggesting the same structural skeleton as **1**. From ^1H - ^1H COSY and the half-width values, the location of the galloyl groups was considered to be at C-3. The molecular formula, $\text{C}_{21}\text{H}_{20}\text{O}_{14}$ established by negative HRFABMS (obsd 495.0834, calcd 495.0775), determined that **2** was a quinic acid digallate, where the two galloyls were linked by depside bond. Accordingly, pistafolin B (**2**) was identified as 3-O-digalloylquinic acid.



Pistafolin A (**1**): $\text{C}_{28}\text{H}_{24}\text{O}_{18}$, off-white amorphous powder, $[\alpha]_D^{24}$ -9.9 (*c* 0.68, MeOH); UV (MeOH) λ_{max} (log ϵ) 217.5 (4.79), 271.5 (4.43) nm; IR (KBr) ν 3382, 1715, 1611, 1534, 1446, 1323, 1195, 1086, 1025 cm^{-1} ; FABMS m/z 647 $[\text{M}-\text{H}]^-$ (100); negative HRFABMS m/z 647.0880 (calcd for $\text{C}_{28}\text{H}_{23}\text{O}_{18}$, 647.0884); ^1H NMR (MeOH- d_4 + D_2O , 400 MHz) δ 7.58-7.13 (galloyl H), 2.30-2.00 (4H, m, H-2, 6), 5.41 (1H, br s, $J_{\text{wh}/2}$ = 20 Hz, H-3), 3.82 (1H, br s, H-4), 4.21 (1H, br s, $J_{\text{wh}/2}$ = 8 Hz, H-5); ^{13}C NMR data, see **Table 1**.

Pistafolin B (**2**): $\text{C}_{21}\text{H}_{20}\text{O}_{14}$, off-white amorphous powder, $[\alpha]_D^{24}$ -67.9 (*c* 0.24, MeOH); UV (MeOH) λ_{max} (log ϵ) 217.5 (4.53), 278.0 (4.11) nm; IR (KBr) ν 3378, 2927, 2855, 1711, 1611, 1533, 1446, 1324, 1205, 1129, 1086, 1032 cm^{-1} ; FABMS m/z 495 $[\text{M}-\text{H}]^-$ (57); negative HRFABMS m/z 495.0834 (calcd for $\text{C}_{21}\text{H}_{19}\text{O}_{14}$, 495.0775); ^1H NMR (DMSO- d_6 , 400 MHz) δ 7.30-6.99 (galloyl H), 2.10-1.18 (4H, m, H-2, 6), 5.14 (1H, br s, $J_{\text{wh}/2}$ = 20 Hz, H-3), 3.62 (1H, br s, H-4), 3.96 (1H, br s, $J_{\text{wh}/2}$ = 8 Hz, H-5); ^{13}C NMR data, see **Table 1**.

Acknowledgments

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