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Galloylpaeoniflorin, A New Monoterpene Glucoside From Paeony Roots

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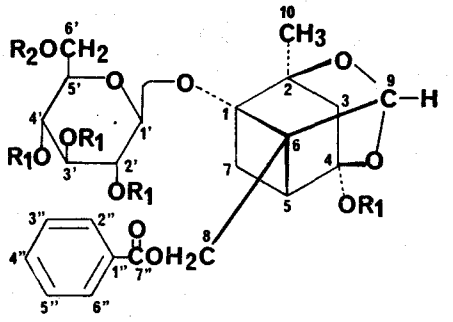
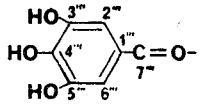
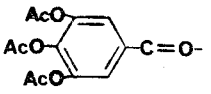
Paeony root is one of the most important crude drugs used in traditional Chinese medicine and has been used as a circulatory tonic, weakness, night sweats and lumbar pain[1]. In the course of our study on the isolation of paeoniflorin(**1**), a monoterpene glucoside of *Paeonia*, we have led to isolate a new monoterpene glucoside named galloylpaeoniflorin(**2**).

The ethylacetate soluble fraction of the MeOH extract was fractionated by silica gel column chromatography to give **2** as amorphous white together with **1**. Galloylpaeoniflorin(**2**) shows IR bands at 3420(OH), 1710(ester), 1615, 1538 (aromatic C=C), 1075, and 1035 cm^{-1}(glycosidic C—O) and UV absorption maxima at 222 and 277nm. The ^{1}H-NMR(CD_3OD) spectrum of **2** showed the presence of a methyl singlet(δ 1.25), an acetal proton(δ 5.37, s), and seven aromatic protons(δ 7.07, 2H, s; δ 7.45−7.55, 3H, m; δ 8.03, 2H, dd, J=7.8 Hz and 2.0Hz). Acetylation of **2** with Ac_2O/pyridine gave a heptaacetate(**3**), which showed the ^{1}H-NMR signals due to methyl proton singlet at δ 1.30, four aliphatic acetyl signals at δ 1.97(3H), 2.01 (3H) and 2.03(6H), three aromatic acetyl signals at δ 2.28(9H), an acetal proton singlet at δ 5.47, seven aromatic protons in the region of δ 7.25−8.07 ppm. The aforementioned spectral data were closely resembled with those of paeoniflorin(**1**) and its derivative.[2~6] Of the seven aromatic protons in the ^{1}H-NMR spectrum of **2**, two proton singlets at δ 7.07 were shifted downfield at δ 7.77 with three aromatic acetyl singlets at δ 2.28 in that of **3**. Therefore, **2** was suggested to be an acylated paeoniflorin with gallic acid. The chemical shift of methylene protons of glucose moiety at δ 4.13(2H, d, J= 4.2 Hz) was shifted downfield at δ 4.38(2H, d, J=3.8 Hz) on going from **1** acetate to **3** which suggested that galloyl residue in **2** was attached at C-6 hydroxyl group of glucose.[7] Finally, the



1 R_1 = H R_2 = H

2 R_1 = H R_2 = 

3 R_1 = Ac R_2 = 

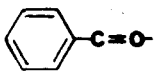
4 R_1 = H R_2 = 

Table I. ^{13}C-NMR spectral data of **2** and **4** in pyridine-d_5

Carbon	2	4[6]	Carbon	2	4[6]
1	88.79	88.8	1″	130.48	130.5
2	85.92	85.9	2″	129.68	129.8
3	44.64	44.6	3″	128.53	128.8
4	105.76	105.8	4″	133.03	133.2
5	43.67	43.7	5″	128.53	128.8
6	71.15	71.6	6″	129.68	129.8
7	22.61	22.8	7″	166.42	166.4
8	61.17	61.2			
9	101.43	101.5			
10	19.57	19.7			
1′	100.02	100.1	1‴	121.13	130.7
2′	74.64	74.7	2‴	110.09	129.8
3′	78.03	78.0	3‴	147.32	128.6
4′	71.52	71.3	4‴	140.73	133.2
5′	75.06	74.9	5‴	147.32	128.6
6′	64.32	65.0	6‴	110.09	129.8
			7‴	166.91	166.3

^{13}C-NMR spectral data of **2** confirmed the structure of galloylpaeoniflorin as shown in Table I. Thus, the structure of galloylpaeoniflorin could be formulated as formula **2**. The full details will be published elsewhere.

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Literature Cited

1. Perry, L.M.: Medicinal Plants of East and Southeast Asia, MIT Press, Cambridge, p. 336 (1980).
2. Shibata, S. and Nakahara, M.: *Chem. Pharm. Bull.* **11**, 372 (1963).
3. Shibata, S., Aimi, N. and Watanabe, M.: *Tetrahedron Lett.* (20), 1991 (1964).
4. Kaneda, M. Iitaka, Y., and Shibata, S.: *Tetrahedron* **28**, 4309 (1972).
5. Nishizawa, M., Yamagishi, T., Horikoshi, T. and Homma, N.: *Shoyakugaku Zasshi* **33**, 65 (1979).
6. Kitagawa, I., Yoshikawa, M., Tsunaga, K., and Tani, T.: *Shoyakugaku Zasshi* **33**, 171 (1979).
7. Geng, P.-W., Fukuyama, Y., Wang, R., Bao, J. and Nakagawa, K.: *Phytochem.* **27**, 1895 (1988)