Chinese Chemical Letters Vol. 10, No. 9, pp. 771–774**,** 1999 

# Paeonivayin, A New Monoterpene Glycoside from *Paeonia delavayi*

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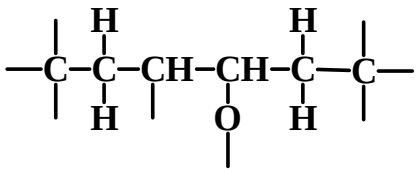
**Abstract:** A new monoterpene glycoside named paeonivayin with other seven known compounds were isolated from the roots of *Paeonia delavayi* Franch. and their structures were determined by means of spectroscopic studies.

**Keywords:** *Paeonia delavayi* Franch, paeoniaceae, monoterpene glycoside, paeonivayin.

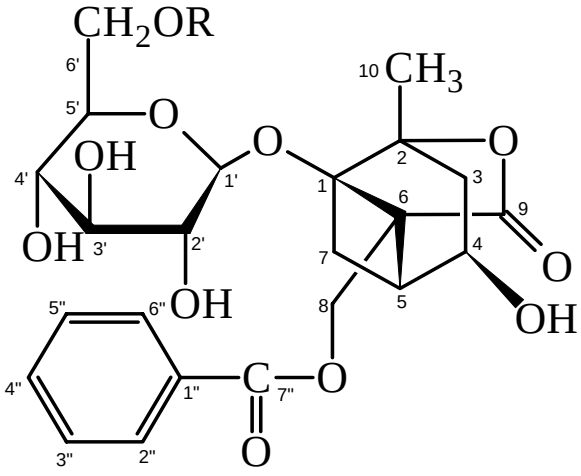
Paeonia root bark, "Dan-Pi " in Chinese, is one of the most important herbal drugs which has been used for treatment of muscular spasm, chest pains, diarrhoea, blood and liver disorders as well as a general analgesic in traditional Chinese medicine. Significant chemical and pharmacological investigations have been conducted on the different species of Paeonia [1-6], *P. albiflora*, *P. anomala*, *P. lactiflora* and *P. suffruticosa*. As one of the main sources of "Dan-Pi", the constituents of *P. delavayi* Franch. have not been studied. In the course of our study on pharmacologically active principles of Paeoniae Radix, seven known constituents paeoniflorigenone, hederagenin, benzoic acid, palmitic acid, 3,5-dihydroxy-4-methoxy-benzoic acid, 2-hydroxy-benzyl alcohol and daucosterol as well as one new monoterpene glycoside paeonivayin **1** have been isolated from the MeOH extract of the roots of *P. delavayin*. This paper describes the structural elucidation of this new monoterpene glycoside.

The roots of *Paeonia delavayi* Franch. (1130g) were pulverized and extracted 3 times with MeOH. The combined MeOH extracts were concentrated *in vacuo* to give a residue, and then partitioned between water and EtOAc. The EtOAc extract (56g) was subjected to repeated chromatography over silica gel eluting with $CHCl_3$-MeOH mixture to afford eight compounds. Seven known constituents paeoniflorigenone, hederagenin, benzoic acid, palmitic acid, 3,5-dihydroxy-4-methoxy-benzoic acid, 2-hydroxy-benzyl alcohol and daucosterol were identified on the basis of spectral evidence and comparison with the data in the literature. Paeonivayin **1**, $C_{30}H_{32}O_{12}$, mp 152.5-155.5 °C. A FAB mass spectrum showed it has MW 584 and the IR spectrum exhibited the presence of hydroxy groups ( 3440 $cm^{-1}$) and carbonyl groups (1758, 1711 $cm^{-1}$) . In the $^1H$ and $^{13}C$ NMR spectra the signals associated with two benzoyl and one glucosyl groups were readily recognized. The DEPT spectrum of the aglycone moiety exhibited signals attributed to one methyl (δ 20.9 ), three methylenes (δ 61.7, 41.8, 27.8 ), two methines (δ 67.4, 41.3 ) and four quaternary carbons (δ 175.7, 91.5, 86.4, 55.9 ). By use of

$^{1}$H-$^{1}$H-COSY techniques, the spectral data (**Table 1**) showed that paeonivayin contains the following moiety in the aglycone.



The comparison of spectra of **1** with that of paeoniflorin **2** (**Table 1**) suggested the same skeleton for the both compounds[3]. The most obvious difference between **1** and **2** was that the former contained one benzoyl group more than the latter. This difference was discerned from $^{1}$H and $^{13}$C NMR spectroscopic comparisons. The possibility of 6'-O-benzoate in the former is strong since the acylation shifts of C-6' and C-5' were observed. The signal of H-6' appeared in rather low-field in comparison with ordinary value ( $\delta$ 4.3-4.5 in pyridine-$d_5$ ). By analogy of **2**, with the aid of 2D-NMR, spectra of **1** was readily assigned, part of which was showed in **Table 1**. The structures of other seven known compounds were identified by comparison of the spectral data (mass, $^{1}$H and $^{13}$C NMR) with literature values.



**1**: R = $C_6H_5CO$-
**2**: R = H

So far more than 10 monoterpene compounds have been isolted and these compounds have been showed to have anticoagulative[7], sedative[8], antiinflammatory[9] and antihyperglycemic[10] activities, as well as a block effect of neuromuscular junction[11].

**Table 1.** $^{1}H$ and $^{13}C$ NMR spectral data for **1** and **2** (in pyridine-$d_5$)

| C | **2** | **1** | H(J Hz) | H-H COSY selected | HMQC | HMBC selected |
|---|---|---|---|---|---|---|
| 1 | 91.3 | 91.5 | | | | H-3,5,7,10 |
| 2 | 86.3 | 86.4 | | | H-2 | H-3,7,10 |
| 3 | 41.8 | 41.8 | 2.28 (m) | H-4 | H-3 | H-5,10 |
| 4 | 67.4 | 67.4 | 4.40 (t, 4.8) | H-5/H-3 | H-4 | H-3,5,7 |
| 5 | 41.4 | 41.3 | 3.13 m | H-7b/H-4 | H-5 | H-3,7,8 |
| 6 | 56.1 | 55.9 | | | | H-4,5,7,8 |
| 7 | 28.3 | 27.8 | 2.05 (d, 10.3) | H-7b | H-7 | H-5 |
| | | | 3.06 m | H-7a/H-5 | | |
| 8 | 61.7 | 61.7 | 5.24 (dd,12,10) | | H-8 | H-5 |
| 9 | 175.7 | 175.7 | | | | H-8 |
| 10 | 20.7 | 20.9 | 1.70 (s) | | H-10 | |
| 1’ | 100.3 | 100.2 | 5.14 (m) | | H-1’ | |
| 2’ | 74.8 | 74.8 | 4.02 (m) | | H-2’ | |
| 3’ | 78.4 | 78.2 | 4.02 (m) | | H-3’ | |
| 4’ | 71.6 | 71.7 | 4.16 (m) | | H-4’ | |
| 5’ | 78.4 | 75.3 | 4.02 (m) | | H-5’ | |
| 6’ | 62.8 | 65.0 | 5.14 (m) | | H-6’ | |
| 1” | 130.8 | 130.8 | | | | |
| 2”6” | 130.1 | 130.1 | 8.20 (m) | | H-2”6” | |
| 3”5” | 128.7 | 128.9 | 7.24 (m) | | H-3”5” | |
| 4” | 133.2 | 133.4 | 7.46 (m) | | H-4” | |
| 7” | 166.6 | 166.6 | | | | H-8,2”,6” |
| 1’’’ | | 130.7 | | | | |
| 2’’’6’’’ | | 130.0 | 8.20 (m) | | H-2’’’6’’’ | |
| 3’’’5’’’ | | 128.7 | 7.46 (m) | | H-3’’’5’’’ | |
| 4’’’ | | 133.1 | 7.52 (m) | | H-4’’’ | |
| 7’’’ | | 166.3 | | | | H-6’,2’’’,6’’’ |

## Acknowledgment

The authors are grateful to Dr. T. Henkel (Bayer AG, Life Science Center Natural Products, Wuppertal, Germany) for kind help in the work and the colleagues of the Department of Instrument Analysis of our Institute for the measurement of the spectra. We also wish to acknowledge financial support from Natural Science Foundation of Yunnan Province (98C086M) and Laboratory of Phytochemistry, Kunming Institute of Botany, the Chinese Academy of Sciences.

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Received 29 March 1999