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Two New Phenolic Glycosides from *Magnolia rostrata*

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Abstract: Two new phenolic glycosides, 3, 4-dihydroxy-allylbenzene-3-O-α-L-rhamnopyranosyl (1→6)β-D-glucopyranoside (**1**) and 3, 4-dihydroxy-allylbenzene-3-O-α-L-rhamnopyranosyl (1→2) β-D-glucopyranoside (**2**), were isolated from the barks of *Magnolia rostrata.* Their structures were elucidated by spectroscopic and chemical methods, specially 2D NMR techniques.

Keyword: *Magnolia rostrata*, Magnoliacea, Phenolic glycosides.

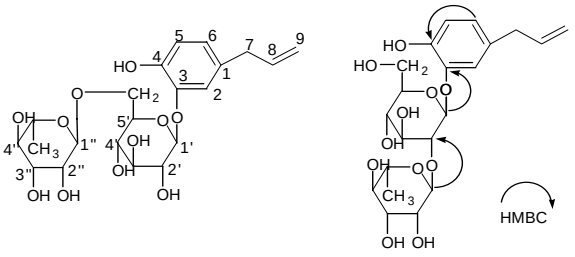
For a long time *Magnolia rostrata* has been used as a substitute of *Magnolia officinalis* which is a precious traditional Chinese medicine[1]. The aqueous constituents of *M. rostrata* have not been studied[2]. During our studies on the n-Bu-OH extract, two new phenolic glycosides (**Figure 1**) were isolated. Here, we report their structural elucidation.

Compound **1**, white amorphous powder, mp 180-182°C exhibited a molecular formula $C_{21}H_{30}O_{11}$ based on its quasi-molecular ion peak at *m/z* 457 $[M-H]^-$ in neg. FABMS and 457.1755 $[M-H]^-$ in neg. HR-FABMS. By means of ^1H NMR, ^{13}C NMR and DEPT spectra, compound **1** was readily deduced to contain a benzene ring, a rhamnose and a glucose moieties. This was confirmed by exhaustive acidic hydrolysis of **1**. It gave two sugars which were identified to be glucose and rhamnose by TLC comparison with authentic samples. In addition, the coupling constants of two anomeric proton signals at δ 5.33 (1H, d, 7.6Hz) and 5.49 (1H, d, 1.1Hz) suggested that the linkage of glucose was β form and that of rhamnose as α form. The proton signals at δ 7.51 (1H, d, 2.0 Hz), 7.16 (1H, d, 8.0 Hz) and 6.88 (1H, dd, 2.0, 8.0 Hz) were typical characteristics of a 1, 3, 4-trisubstituted phenyl. The carbon signals at δ 39.8 (CH_2), 115.7 (CH_2) and 138.5 (CH) indicated the presence of an allyl group. The carbon signals at δ 148.1 and 146.7 for two quaternary carbons, suggested the presence of two oxygen substitution on the benzene ring. By the aids of HMQC, ^1H-^1H COSY and HMBC spectra, it is easily to assign C-1, 2, 5, 6, 7, 8 and 9. The correlation of H-6 (δ 6.88, dd, 2.0, 8.0Hz) and C-4 (δ 148.1s) in HMBC spectrum resolved the assignment of C-3 and C-4. In the neg. FABMS spectrum, besides the quasi-molecular ion peaks at *m/z* 457 $[M-H]^-$, typical fragment ions at *m/z* 311 $[M-rha+H]^-$ and 149 $[M-rha-glc+H]^-$ were observed. The glycosylation shift of C-6' (δ 68.0 CH_2) due to glucose showed the linkage of rha (1→6) glc. The position of the sugar chain on the aglycone was determined by the correlation of H-1' (δ 5.33, d, 7.6Hz) and C-3 (δ 146.7s) in the HMBC spectrum. Thus, compound **1** was identified as 3, 4-dihydroxy-allylbenzene-3-O-α-L-rhamnopyranosyl (1→6)-β-D-glucopyranoside.

Compound **2** also a white amorphous powder, possessed the same aglycone and sugars by comparing its ^1H and ^{13}C spectra with those of compound **1**, this was supported

by exhaustive acidic hydrolysis of **2**. It also had the same FABMS (neg.) ion peaks at *m/z* 457 $[M-H]^-$, 311 $[M\text{-}rha+H]^-$, and 149 $[M\text{-}rha\text{-}glc+H]^-$. The main difference between **1** and **2** is the linkage of the two sugars. Comparison of the ^{13}C NMR data of the sugar moieties, showed that in **2** the C-2' signal was downfield shifted to δ79.3,due to C-2' glycosylation, so the rhamnopyranosyl group should be linked to C-2' of the glucose. The correlation of the anomeric proton H-1' (δ 5.60, d, 7.6Hz) and H-2' (δ 4.35, m) in ^1H-^1H COSY spectrum was helpful for assigning C-2'. Therefore, the structure of compound **2** was identified as 3,4-dihydroxy-allylbenzene-3-O-α-L-rhamnopyranosyl-(1→2)-β-D-gluco-yranoside.

Figure 1. Structures of compound **1** and **2**



1 **2**

Table 1. ^1H and ^{13}C NMR data for compound **1** and **2** (400MHz, C_5D_5N, δ)

	1		**2**			**1**	**2**
C	^{13}C	^1H	^{13}C	^1H	C	^{13}C	^{13}C
1	131.9s		131.8s		1'	105.7d	102.9d
2	121.2d	7.51, d, 2.0Hz	119.0d	7.47, s	2'	74.2d	79.3d
3	146.7s		146.5s		3'	78.4d	78.9d
4	148.1s		147.4s		4'	71.5d	71.4d
5	117.2d	7.16, d, 8.0Hz	117.3d	7.16, d, 8.1Hz	5'	77.5d	78.7d
6	125.1d	6.88, dd, 2.0, 8.0Hz	123.6d	6.83, d, 8.1Hz	6'	68.0t	62.2t
7	39.8t	3.35, d, 6.7Hz	39.8t	3.26, d, 6.7Hz	1"	102.5d	102.3d
8	138.5d	5.99, m	138.4d	5.94, m	2"	72.3d	72.4d
9	115.6t	5.03, dd, 1.6, 10.0Hz	115.5t	4.98, d, 10.0Hz	3"	72.8d	72.7d
		5.11, dd, 1.7, 17.8Hz		5.06, d, 17.0Hz	4"	75.0d	74.3d
					5"	69.9d	70.5d
					6"	18.6q	18.7q

References

1. C. L. Yu, T. K. Huang, Z. Z. Ding *et al.,'Zhongyaocihai'* , China Medical Science and Technology Press, Beijing, **1993**, *1*, 261.
2. W. M. Yan, *Acta Botanica Sinica*, **1979**, *21*(1), 54

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