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Two New Compounds from *Alcea rosea*

WEIMING CHENG[1,*], XIAQIAN CHENG[2], ZHIJUN LIU[1] and YONGCHI ZENG[3,*]

[1]Department of Traditional Chinese Medicine, Zhejiang Institute for Food and Drug Control, No. 86, Lane 1, Jichang Road, Jianggan Dist. 310004, Hangzhou Zhejiang Province, P.R. China
[2]College of Pharmaceutical Science, Zhejiang Chinese Medicinal University, No. 548 Bingwen Road, Binjiang Dist. 310053, Hangzhou Zhejiang Province, P.R. China
[3]Hangzhou Innovation TCM Standarization Research Institute Co. Ltd., No. 677 Binkang Road, Binjiang Dist. 310053, Hangzhou Zhejiang Province, P.R. China

*Corresponding author: Tel: +86 158 58177067; E-mail: weiming_cheng@hotmail.com

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Five compounds had been isolated and purified from *Alcea rosea*, among which two were new compounds. The structure of the two new compounds were elucidated and characterized as 1'-hydroxy-3'-formyl-4-methylol-5-(4''-O-β-D-glucoside-3''-methoxyphenyl)-benzofuran and 1-(2'-methoxy-4'-hydroxy-5'-acetylphenyl)-3-methylbutan-1-one and named as Rosea A and Rosea B, respectively.

Key Words: *Alcea rosea*, Rosea A, Rosea B.

INTRODUCTION

A. rosea, whose entire dry plant was adopted as a traditional Chinese medicine, was widely distributed and used in China, Japan, Korea and Southeast of Asia. The traditional medicinal use of *A. rosea* was for analgesia, protection of liver and antibiosis[1-3], while modern pharmacological researches had also revealed that *A. rosea* possessed the bioactivities of antiarthritis, antiosteoporosis, protection of myocardial ischemia reperfusion, protection of kidney function, *etc*.[4-7]. A chemical components study of *A. rosea* resulted in the isolation of five compounds, among, which two were new. Structural elucidation of the new compounds was carried out on the basis of spectral data.

EXPERIMENTAL

Herbal material: Dried plant of *A. rosea* was purchased in Xi'an city, Shanxi Prov., China. Voucher specimen had been identified by Pharmacognosist Zengxi Guo and also been kept under certain conditions for future identification.

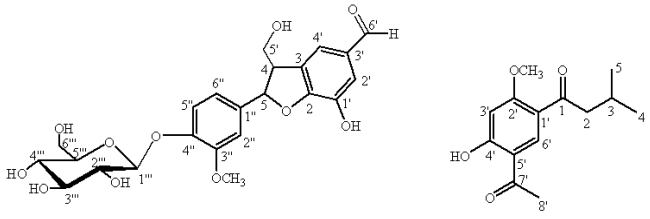
Melting point was carried out with the capillary tube method, without the calibration of temperature. NMR data were obtained by Bruker ARX-300. High Resolution MS was carried out with Bruker micrOTOFQ 125. All used reagents were of analytical grade and purchased from Hanbon Science and Tech. Co. Ltd., (Huaian, Jiangshu Prov.).

Isolation procedure: The dried fine powder of *A. rosea* (500 g) was refluxed with 60 % EtOH for 1 h, the extract was then concentrated and suspended in H_2O. After partition with $CHCl_3$, EtOAc and *n*-BuOH, the EtOAc layer then underwent isolation by silica gel column chromatography (200-300 mesh), eluting with a step gradient of $CHCl_3$ and EtOAc (20:1, 10:1, 5:1, 3:1, 1:1, 1:5, 1:10), giving 7 fractions according to TLC indication. Fraction 6 ($CHCl_3$-EtOAc=1:5, 3 g) was undergone silica gel column isolation twice and then a C_{18} open column, further purified with Sephadex LH-20 and preparative RP HPLC, yielding compound **II** (5.1 mg, Fig. 1), gossypetin (7.0 mg) and quercetin (11.3 mg). The *n*-BuOH layer underwent isolation by D-101 macroporous resin, with gradient elution of MeOH-H_2O (1:10-10:1), giving 10 fractions. Fraction 5 was then isolated on a C_{18} open column and further purified with preparative RP HPLC, which finally yielded two compounds, Compound **I** (2.7 mg, Fig. 1) and hyperoside (2.6 mg).

RESULTS AND DISCUSSION

Compound **I** was white amorphous powder. The HR MS showed that **I** had the *m/z* 479.1552 ($[M+H]^+$, calc. 479.1548) and 501.1374 ($[M+Na]^+$, calc. 501.1367), indicating the molecular formula to be $C_{23}H_{26}O_{11}$. In the ^1H NMR spectrum (Table-1), the aromatic protons signals at d 6.65 (1H, dd, J=8.2, 1.6 Hz, H-6''), 6.83 (1H, d, *J* = 8.2 Hz, H-5'') and 6.81 (1H, d,

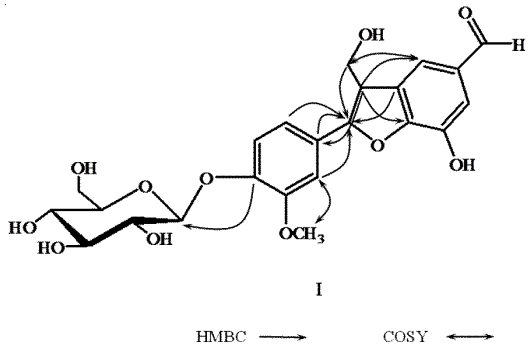
J = 1.6 Hz, H-2") indicated the presence of a ABX coupling system, while δ 7.37 (1H, d, *J* = 1.5 Hz, H-2') and 7.19 (1H, d, *J* = 1.5 Hz, H-4') formed a typical AB coupling system. A typical signal of methoxyl group at 3.55 (3H, s) could also easily be figured out. The signal at δ 5.04 (1H, d, *J* = 6.7 Hz, H-1") belonged to the anomeric proton of glycoside and the anomeric configuration was deduced to be β according to the coupling constant (6.7Hz). The sugar moiety was determined to be glucose, according to the acid hydrolysis and comparison with an authentic glucose standard through high performance TLC.



I II

Fig. 1. Structures of two new compounds

The ^{13}C NMR signals (Table-1) provided 23 signals, belonging to methoxyl carbon at δ 56.1, methylene at δ 61.8, *etc*. HMQC and DEPT spectrum helped to distinguish out the protons to each carbon, respectively. The HMBC correlation from H-1" to C-4" revealed that the sugar moiety was linked to the aglycone position at C-4". The key HMBC signals indicated the correlations from H-5 to C-1", C-2", C-6", C-3, C-5', from H-4 to C-1", C-4', C-2, from H-5' to C-5, indicated the presence of the benzofuran moiety. In the ^1H-^1H-COSY spectrum, the correlations of H-2" to 3"-OCH_3, H-5' to H-4' further strengthened the confirmation about ascription results. Therefore, **I** was elucidated to be 1'-hydroxy-3'-formyl-4-methylol-5-(4"-O-β-D- glucoside-3"-methoxyphenyl)-benzofuran and named as Rosea A. The key correlations of HMBC and COSY of **I** were shown in Fig. 2.



I

HMBC ⟶ COSY ⟷

Fig. 2. Selected HMBC and COSY correlations of I

Compound **II** was yellow needle crystal, with the melting point at 163-164 ºC. The HR MS showed that **II** had the *m/z* 251.1271 ($[M+H]^+$, calc. 251.1278) and 273.1091 ($[M+Na]^+$, calc. 273.1097), indicating the molecular formula to be $C_{14}H_{18}O_4$. In the ^1H NMR spectrum (Table-2), the low field signal at δ 13.05 (1H, s) suggested the existence of hydroxyl group and this signal disappeared after the D_2O was added in, which confirmed it to be a reactive H. The aromatic protons signals at δ 6.32 (1H, s, H-3'), 7.99 (1H, s, H-6') indicated the presence of a AX coupling system. In the high field of spectrum, the signals at δ 1.13 (6H, d, *J* = 6.0Hz, H-4, 5), 2.53 (2H, d, *J* = 6.4Hz, H-2) and 2.22 (1H, m, H-3) could be seen as the characteristic symbol of isobutyl group.

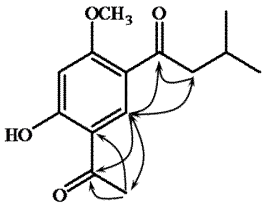
TABLE-1
^1H AND ^{13}C NMR DATA FOR **I** (300 MHz, ppm in DMSO-d_6)

No	^1H NMR (*J* in Hz)	^{13}C NMR
2		151.3
3		126.1
4	3.21 (1H, m)	53.6
5	5.32 (1H, m)	83.7
1'		147.3
2'	7.37 (1H, d, 1.5)	111.0
3'		133.3
4'	7.19 (1H, d, 1.5)	116.4
5'	3.52 (2H, m)	61.8
6'	9.25 (1H, s)	179.4
1''		133.9
2''	6.81 (1H, d, 1.6)	111.5
3''		152.4
4''		146.1
5''	6.83 (1H, d, 8.2)	115.1
6''	6.65 (1H, dd, 8.2, 1.6)	120.3
3''-OCH_3	3.55 (3H, s)	56.1
1'''	5.04 (1H, d, 6.7)	103.2
2'''	3.53 (overlapped)	71.3
3'''	4.11 (overlapped)	73.4
4'''	4.06 (overlapped)	68.8
5'''	3.73 (overlapped)	73.9
6'''	3.43, 3.49 (overlapped)	58.9

The ^{13}C NMR spectrum (Table-2) showed 14 carbon signals, including one methoxyl carbon at δ 56.3, two carbonyl carbons at δ 202.1, 202.6, six SP^2 carbons of an conjugated benzene ring, *etc*. The key correlations showed in HMBC spectrum between H-2 and C-1, 9'-Me and C-5', C-8' and H-6' with C-1, C-8' revealed the relative location of two carbonyl groups. In the ^1H-^1H-COSY spectrum, H-6' produced COSY effect with H-2 and 9'-Me also confirmed the assignment of the above groups. Therefore, **II** was determined as 1-(2'-methoxy-4'-hydroxy-5'-acetylphenyl)-3-methylbutan-1-one and named as Rosea B. The key correlations of HMBC and COSY of **I** were shown in Fig. 3.

TABLE-2
^1H AND ^{13}C-NMR DATA FOR II (300 MHz, ppm in DMSO-d_6)

No	^1H NMR (J in Hz)	^{13}C NMR
1		202.1
2	2.53 (2H, d, 6.4)	47.3
3	2.22 (1H, m)	25.3
4	1.13 (3H, d, 6.0)	21.1
5	1.13 (3H, d, 6.0)	21.1
1'		115.3
2'		155.6
3	6.32 (1H, s)	105.6
4'		159.3
4'-OH	13.05 (1H, s)	
5'	8.23 (1H, s)	115.2
6'	7.99 (1H, s)	137.1
2'- OCH_3		56.3
7'	2.64 (3H, s)	202.6
8'		27.8



II

HMBC ⟶ COSY ⟷

Fig. 3. Selected HMBC and COSY correlations of II

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