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Two New Iridoid Glycosides from *Caryopteris mongholica*

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Abstract: Two new iridoid glucosides were isolated from the whole plant of *Caryopteris mongholica* Bunge. On the basis of chemical and spectral evidence, they were determined as 8-acetyl-6'-O-(*p*-coumaroyl)harpagide and 6'-O-(*p*-coumaroyl)antirrinoside, respectively.

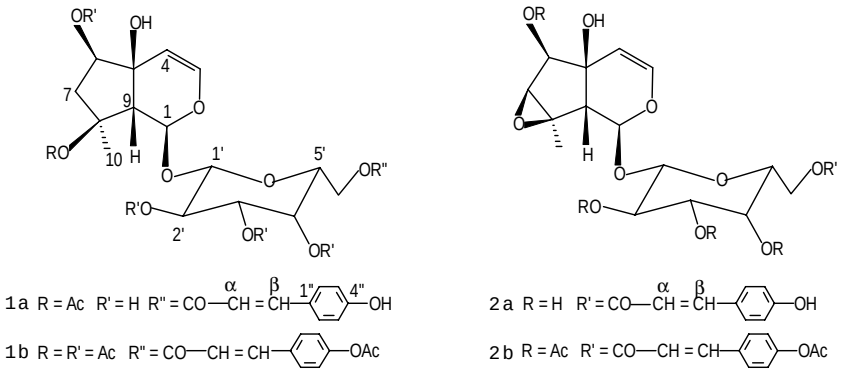
Keyword: *Caryopteris mongholica*, verbanaceae, 8-acetyl-6'-O-(*p*-coumaroyl)harpagide, 6'-O-(*p*-coumaroyl)antirrinoside.

The whole plant of *Caryopteris mongholica* Bunge was used in China as a herbal medicine which relieves cold, cough and rheumatic pains[1]. In previous paper, a hypolactin-7-glucoside was reported from this plant[2]. In this paper, we wish to report the isolation and structure elucidation of two new iridoid glucosides, 8-acetyl-6'-O-(*p*-coumaroyl)harpagide (**1a)** and 6'-O-(*p*-coumaroyl) antirrinoside (**2a)** from the whole plants of *C. mongholica* Bunge.

Compounds **1a** and **2a** were isolated as an inseparable mixture which showed a single spot in TLC with several eluents. It showed UV bands at 315 and 222 nm and IR bands at 1706 and 1630 cm-1 (conjugated ester), 1600 and 1510 cm-1 (phenyl group), along with a strong hydroxyl absorbent band (3350 cm-1). Acid hydrolysis of the mixture afforded glucose as the sole sugar. Alkaline hydrolysis of the **1a+2a** yielded p-coumaroyl acid, besides a mixture of 8-acetylharpagide3 and antirrinoside4, identified by their physical and spectroscopic data and by direct comparison with authentic samples, these facts established that **1a+2a** were a mixture of the p-coumaroyloates of 8-acetylharpagide and antirrinoside and that they occured in ca 1:1 ratio indicated by integration of the olefinic protons corresponding to the iridoids in the 1HNMR spectrum. Acetylation under mild conditions formed a mixture of hexa and penta acetate, **1b+2b**, which were separated on a column of silica gel. Two compounds **1b** and **2b** were isolated in pure form.

Compound **1b** was isolated as an amorphous powder, mp 208-210°C, $[\alpha]_D^{24}$ -35 ($CHCl_3$, c=0.72). It has a molecular formula $C_{36}H_{42}O_{18}$ based on FAB-MS data (*m/z* 684$[M\text{-}H_2O\text{-}AcOH]^+$ and on counting carbons and hydrogens from the data of its ^1H and ^{13}C NMR DEPT spectra. The IR of compound **1b** showed typical absorption of enol ether system of an iridoid at 1630 cm^{-1}, an ester function at 1706 cm^{-1} and a phenyl

Figure 1. Structure of compounds **1a-2b**



function at 1600, 1510 cm^{-1}. The UV maximum of **1b** at 281 nm revealed the presence of an α, β-unsaturated ester; a shoulder at 220 nm was attributable to a conjugated ether system. The ^{1}HNMR spectrum of **1b** ($CDCl_3$) was strongly reminiscent of that of 8-acetylharpagide[3] with additional signals due to a *trans-p*-coumaroyl group (δ 6.48 and 7.73 (each 1H, d, J=16Hz), and 7.13 and 7.58 (each 2H, d, J=8.7Hz)). The ^{13}CNMR spectrum of **1b** (**Table 1**) showed the presence of one CH_3, one CH_2, five CH, two quaternary carbons having an oxygen function and six acetoxy carbons in addition to the signals due to a *trans-p*-coumaroyl and a sugar moiety. These spectral data suggest that **1b** might be the *trans-p*-coumaroyl ester of 8-acetyl harpagide[3]. In fact, the ^{13}CNMR signals assignable to the aglycone portion were identical to those of 8-acetylharpagide. The location of the *p*-coumaroyl group was elucidated to be at C-6' from the analytical result of HMBC: the carbonyl carbon of the *p*-coumaroyl moiety was correlated with H-6' of the sugar moiety. This assignment was further supported by the fact that the signal assignable to C-6' of **1a+2a** resonated downfield (1.84 ppm), whereas the signal assignable to C-5' was shifted upfield (1.93 ppm), compared to that of 8-acetylharpagide in the ^{13}CNMR spectrum. On the basis of these findings, the structure of **1b** was elucidated as 8-acetyl-6'-O-(*p*-coumaroyl)harpagide hexaacetate. Compound **1a** should be 8-acetyl-6'-O-(*p*-coumaroyl) harpagide. Its molecular formula was deduced as $C_{26}H_{32}O_{13}$ based on FAB-MS data (*m/z* 553 $[M+1]^+$) and the NMR spectral data of **1a**+**2a**.

Compound **2b** was isolated as an amorphous powder, mp 198-200°C, $[\alpha]_D^{24}$ 25 ($CHCl_3$, c=0.12), and showed in the UV spectrum (MeOH) λ_{max} at 218 and 284 nm. Compound **2b** has a molecular formula $C_{34}H_{38}O_{17}$ based on FAB-MS data (*m/z* 580 $[M-H_2O-2AcOH]^+$) and the NMR spectral data. The ^{1}HNMR data of **2b** ($CDCl_3$) were similar to those of antirrinoside[4] except for the signals of the coumaric acid residue. The ^{1}HNMR spectrum of **2b** contained signals for two *trans* olefenic protons(δ 7.72 and 6.42, 2×1H, d, J=15.8Hz), four protons of an aromatic ring (δ 7.57, 2H, d, J=8.7Hz, H-2'', 6''; 7.14, 2H, d, J=8.7Hz, H-3'', 5''). As the signals for C-6' of **1a**+**2a** resonated downfield (1.07 ppm), whereas the signal of C-5' was shifted upfield (2.4 ppm), the relative

position of the coumarate was established. The assignment was further supported by the fact that the carbonyl carbon of the *p*-coumaroyl moiety was correlated with H-6' of the sugar moiety in HMBC. Therefore, the structure of **2b** was proven to be 6'-O-(*p*-coumaroyl) antirrinoside pentaacetate. Compound **2a** should be 6'-O-(*p*-coumaroyl) antirrinoside. Compound **2a** has a molecular formula $C_{24}H_{28}O_{12}$ based on FAB-MS (*m/z* 509[m+1]$^+$) and the NMR spectral data of **1a**+**2a**.

Table 1 ^{1}H and ^{13}CNMR spectral data of compounds **la-2b** (400MHz, CD_3OD or $CDCl_3$) *

C	1a	1b	2a	2b	H	1b	2b
1	94.2	94.O	94.1	94.l	1	6.02 s	5.99 s
3	143.5	141.6	142.8	141.4	3	6.35d(6.5)	6.31d(6.0)
4	107.7	107.0	107.2	106.7	4	5.49d (6.5)	5.16d (6.0)
5	72.9	71.4	73.6	73.1	6	5.39d(3.9)	4.97d(3.8)
6	78. 4.	77.6	77.5	78.0	7	1.94 d(16)	3.51 s
						2.36 d(15.9)	
7	45.8	43.3	66.O	63.1	9	3.17 s	3.18 s
8	87.7	86.O	65.9	62.7	10	1.46 s	1.49 s
9	55.5	54.5	53.1	52.0	1'	4.88 d(7.8)	4.94 d(7.8)
10	22.l	22.1	17.6	17.O	2'-4'	5.04-5.30	4.96-5.31
C=0	173.3	173.3			5'	3.85 m	3.82 m
Me	22. 5	22.4			6'	4.38 dd(12.3,4.7)	4.33 dd(12.3,4.2)
						4.41 dd(12.3,2.6)	4.39 dd(21.2, 2.3)
1'	99.8	96.4	99.4	96.2	2''	7.58 d(8.7)	7.58 d(8.7)
2'	74.6	71 .O	74.3	70.8	3''	7.13 d(8.7)	7.14 d(8.7)
3'	77.5	72.O	77.5	72.3	5''	7.13 d(8.7)	7.14 d(8.7)
4'	71.6	68.7	71.5	68.5	6''	7.58 d(8.7)	7.58 d(8.7)
5'	75.6	72.0	75.4	72.3	α	6.48 d(16.2)	6.42 d(16.0)
6'	64.7	62.1	63.9	61.7	β	7.73 d(16.0)	7.70 d(15.6)
1''	127.1	132.1	127.1	131.4			
2''	131.1	129.3	131.1	129.4			
3''	116.7	122.1	116.8	122.2			
4''	161.1	152.1	161.0	152.2			
5''	116.7	122.1	116.7	122.2			
6''	131.1	129.3	131.1	129.4			
α	146.7	144.4	146.7	144.8			
β	115.1	117.5	115.1	117.2			
C=0	168.8	166.3	166.8	166.3			

* Assignment from ^{1}H-^{1}H COSY, HMQC, HMBC and NOESY

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