

## A New Stilbene Tetramer from *Caragana rosea*

Guo Xun YANG, Chang Qi HU\*

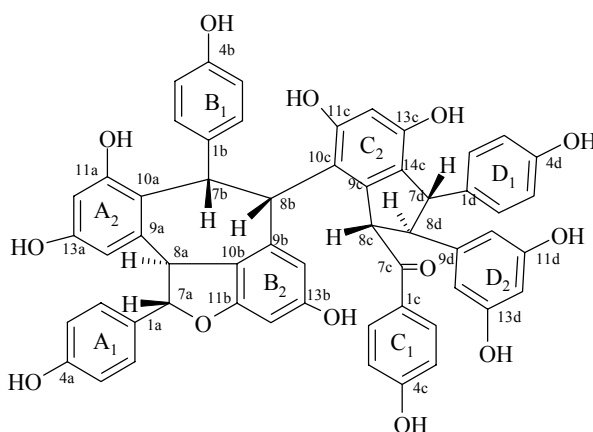
School of Pharmacy, Fudan University, Shanghai 200032

**Abstract:** Cararosinol A, a new stilbene tetramer, was isolated from *Caragana rosea*. Its structure has been established on the basis of spectroscopic evidence.

**Keywords:** *Caragana rosea*, Leguminase, stilbene tetramer.

*Caragana rosea* is widely distributed in China. Its root has been used as a folk medicine to treat asthma, cough, some kinds of women diseases, etc, a long time before<sup>1</sup>. Our research group have studied the components of *C. sinica* and found nine oligostilbenes that demonstrated interesting pharmacological activities<sup>2</sup>. But the chemical constituents of *C. rosea* have never been reported. We studied its aerial parts and found a novel stilbene tetramer from the ethanol extract, it was named cararosinol A. Here we report the structure elucidation of cararosinol A.

Figure 1

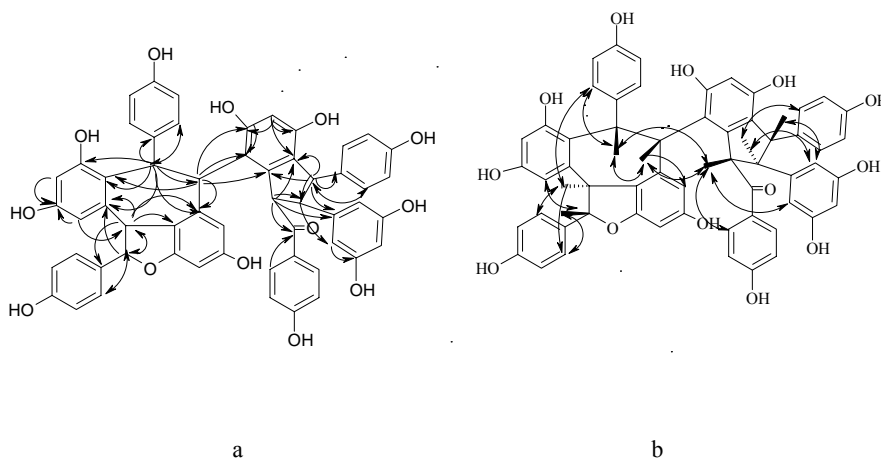


cararosinol A

\* E-mail: changqihu@online.sh.cn

Cararosinol A was obtained as white amorphous powder. It showed a quasimolecular ion peak at  $m/z$  923.2709 [ $MH^+$ ] ( $m/z$  923.2704 calcd. for  $C_{56}H_{43}O_{13}$ ) in the high resolution FABMS corresponding to the molecular formula  $C_{56}H_{42}O_{13}$ .  $[\alpha]_D^{22.9} = -70$  ( $c$  0.005, MeOH).  $^1H$ -NMR showed it was a typical stilbene tetramer. There are four sets of ortho-coupled aromatic protons: [  $\delta$ 7.05 ( $d$ , 2H,  $J=8.6$ Hz, H-2 (6) a) and 6.72 ( $d$ , 2H,  $J=8.6$ Hz, H-3 (5) a) ] ;  $\delta$ 6.52 ( $d$ , 2H,  $J=8.7$ Hz, H-2 (6) b) and 6.35 ( $d$ , 2H,  $J=8.7$ Hz, H-3 (5) b) );  $\delta$ 7.66 ( $d$ , 2H,  $J=8.8$ Hz, H-2 (6) c) and 6.72 ( $d$ , 2H,  $J=8.8$ Hz, H-3 (5) c) );  $\delta$ 7.04 ( $d$ , 2H,  $J=8.6$ Hz, H-2 (6) d) and 6.67 ( $d$ , 2H,  $J=8.6$ Hz, H-3 (5) d) ] ; a set of three aromatic protons in an  $AB_2$  system:  $\delta$ 6.27 ( $d$ , 2H,  $J=2.2$ Hz, H-10 (14) d) and 6.22 ( $t$ , 1H,  $J=2.2$ Hz, H-12d) ; two sets of meta-coupled aromatic protons:  $\delta$ 6.31 ( $d$ , 1H,  $J=2.1$ Hz, H-12a) and 6.22 ( $d$ , 1H,  $J=2.1$ Hz, H-14a) ;  $\delta$ 6.09 ( $d$ , 1H,  $J=2.0$ Hz, H-12b) and 6.49 ( $d$ , 1H,  $J=2.0$ Hz, H-14b) ; an aromatic proton in singlet  $\delta$ 5.92 (H-12c). The  $^1H$ -NMR and  $^1H$ - $^1H$ COASY spectra indicated the presence of two sets of mutually coupled benzyl methine protons:  $\delta$ 4.15 ( $d$ , 1H,  $J=11.2$ Hz, H-8a) and 5.74 ( $d$ , 1H,  $J=11.2$ Hz, H-7a) ;  $\delta$ 5.29 ( $d$ , 1H,  $J=3.0$ Hz, H-7b) and 4.65 ( $br s$ , 1H, H-8b) ; a sequence of successively coupled benzyl methine protons:  $\delta$ 5.19 ( $d$ , 1H,  $J=3.6$ Hz, H-8c) , 3.16 ( $t$ , 1H,  $J=3.4$ , 3.5Hz, H-8d) and 4.32 ( $d$ , 1H,  $J=3.3$ Hz, H-7d). All the carbon signals were assigned by HMQC and HMBC spectra. In the HMBC spectrum of cararosinol A (**Figure 2a**), the correlations between H-7a/C-2(6)a, 8a, 9a; H-8a/C-7a, 9a, 10b; H-7b/C-2(6)b, 8b, 10a; H-8b/C-9b, 10a, 10c; H-8c/C-7c, 8d, 14c; H-7d/C-2(6)d, 14c, 8d, 9d, 9c; H-8d/C-10(14)d suggested its planar structure should be like **Figure 1**. The relative stereostructure of cararosinol A was determined by the NOESY spectrum. In the NOESY spectrum, the NOEs between H-7a/H-14a, H-8a/H-2(6)a indicated a *trans* orientation of H-7a and H-8a. The NOEs between H-8a and H-2 (6)b indicated a *trans* orientation of H-8a and H-7b. The NOEs between 7b/8c, 8b/8c, 7b/8b revealed a *cis* orientation of 7b, 8b and 8c. The NOEs between H-8c/H-10 (14) d , H-7d/10 (14) d suggested a *trans* orientation between H-8c/H-8d , H-7d/H-8d. Thus, the relative stereostructure of cararosinol A was established as **Figure 1**.

**Figure 2** CH long-range correlations in HMBC spectrum(a) and NOE interactions in the NOESY spectrum(b) of cararosinol A



**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectral data for cararosinol A (in acetone-  $\text{d}_6$ )

position	$^1\text{H}$	$^{13}\text{C}$	position	$^1\text{H}$	$^{13}\text{C}$
1a		130.64	14b	6.51, d (2.0)	109.87
2 (6) a	7.05 <sup>1</sup> , d (8.6)	129.65 <sup>3</sup>	1c		129.81
3 (5) a	6.72 <sup>2</sup> , d (8.6)	116.07 <sup>4</sup>	2 (6) c	7.66, d (8.8)	131.79
4a		158.54	3 (5) c	6.72 <sup>2</sup> , d (8.6)	115.95 <sup>4</sup>
7a	5.74, d (11.2)	88.34	4c		163.09
8a	4.15, d (11.3)	49.43	7c		201.15
9a		142.34	8c	5.19, d (3.6)	61.25
10a		119.79	9c		145.45
11a		158.13	10c		118.11
12a	6.31, d (2.1)	101.66	11c		157.65
13a		157.65	12c	5.92, s	104.51
14a	6.22, d (2.1)	105.45	13c		153.49
1b		134.09	14c		124.97
2 (6) b	6.52, d (8.2)	128.05	1d		137.65
3 (5) b	6.35, d (8.7)	115.36 <sup>5</sup>	2 (6) d	7.04 <sup>1</sup> , d (8.6)	129.91 <sup>3</sup>
4b		155.81	3 (5) d	6.67, d (8.6)	115.52 <sup>5</sup>
7b	5.29, d (3.0)	41.66	4d		156.38
8b	4.65, br s	44.12	7d	4.32, d (3.3)	59.38
9b		139.68	8d	3.16, dd (3.4,3.5)	61.58
10b		118.63	9d		150.43
11b		160.61	10 (14) d	6.27, d (2.2)	105.98
12b	6.09, d (2.1)	96.82	11 (13) d		159.63
13b		159.63	12d	6.22, d (2.2)	101.92

$^1\text{H}$ -NMR were determined at 400Hz and  $^{13}\text{C}$ -NMR were determined at 100Hz. Data with the same upper labels may be interchangeable.

### Acknowledgments

This research program was supported by the National Natural Science Foundation of China (No. 30070085). The authors are grateful to professor Yingxin Liu who helped collect and identify the plant.

### References

1. Jiang Su New Medical College, *Dictionary of Chinese traditional Medicine*, Shanghai Science and Technology press, Shanghai, **1985**, p.1019.
2. H. F. Luo, L. P. Zhang, C. Q. Hu, *Tetrahedron*, **2001**, 57, 4849.

Received 1 November, 2002