STRUCTURE OF RHODISIN AND RHODISINOSIDE

Kim Kwan Hu, Z. A. Kuliev, A. D. Vdovin,
M. R. Yagudaev, and V. M. Malikov

UDC 547.972

With the aim of seeking new physiologically active compounds we have studied the chemical composition of the roots of Rhodiola semenovii (Rgl. et Herd), Boriss, collected in the flowering phase in the Talas Ala-Tau. Four monomeric catechins and one polymeric proanthocyanidin have been isolated from this species previously [1, 2]. Another seven individual low-molecular-mass proanthocyanidins have now been isolated from an ethanolic extract of the roots by fractionation and column chromatography on cellulose powder.

Compounds (I) and (II) have been called rhodisin and rhodisinoside, their molecular masses being, respectively, ~920 and ~1450 (gel filtration). It was established by spectral (UV, IR, ^{13}C NMR) and chemical (methylation, acid and enzymatic cleavage, etc.) methods that rhodisin is a galloylated dimeric proanthocyanidin and is the aglycon of rhodisinoside.

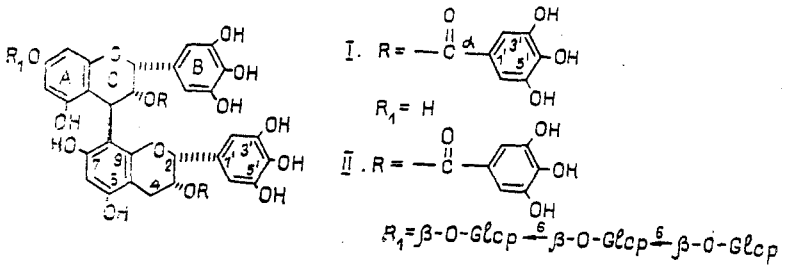
The ^{13}C NMR spectra of (I) and (II) (see Table 1) showed only the signals of epigallocatechin and of gallic acid residues. The chemical shifts of the C-2, C-3, and C-4 carbon atoms of the epigallocatechins are characteristic for galloylated epigallocatechins [3, 4]. The chemical shifts of the C-10 carbon atom (101.3 and 102.9 ppm) showed the C-4 → C-8 type of interflavan bond [5].

TABLE 1. ^{13}C NMR Parameters of Rhodisin and Rhodisinoside, ppm, 0 – HMDS [acetone–water (1:1)]

Compound	Carbon atom							
	2	3	4	5	6	7	8	9
Rhodisin								
"upper"	75,5	73,5	34,8	155,9	98,7	155,9	98,7	155,9
"lower"	78,7	70,1	—	155,9	98,7	155,9	106,7	155,9
Rhodisinoside								
"upper"	74,2	74,2	34,8	156,2	97,1	156,2	94,1	156,2
"lower"	77,5	69,2	—	156,2	97,1	156,2	109,6	156,2
Rhodisin								
"upper"	102,9	130,6	110,3	146,0	133,6	146,0	110,3	
"lower"	101,3	130,0	110,8	146,0	133,6	146,0	110,8	
Gallic acid								
"upper"		130,6	110,3	146,0	139,0	146,0	110,3	166,4
"lower"		130,6	110,3	146,0	139,0	146,0	110,3	166,8
Rhodisinoside								
upper"	100,7	130,6	109,0	146,0	133,9	146,0	109,0	
"lower	103,9	129,5	109,6	146,0	133,9	146,0	109,6	
Gallic acid								
"upper"		127,8	110,2	146,0	138,9	146,0	110,2	166,4
"lower"		127,8	110,2	146,0	138,9	146,0	110,2	168,4
Glucose								
I		103,9	74,2	77,5	69,3	76,0	66,6	
II		100,7	74,2	77,5	69,3	76,0	64,5	
III		99,5	74,2	77,5	69,3	76,0	61,8	

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 723-725, September-October, 1989. Original article submitted January 18, 1989.

 0009-3130/89/2505-0618$12.50



A study of the products of enzymatic cleavage of rhodisinoside and of the acid hydrolysis of its permethylate showed that the sugar moiety consisted of three D-glucose residues linked with the aglycon by a β-glycosidic bond and with one another by β-C-6 ← C-1 bonds (the presence of β-glucose was confirmed by the ^{13}C NMR characteristics). In galloylated catechin glycosides the sugars are usually attached to the aglycon in position 5 or 7. Because position 5 of the "upper" and position 7 of the "lower" epicatechin blocks (II) are sterically hindered, we suggest that the most probable position of attachment of the sugar moiety is the C-5 position of the "lower" or the C-7 position of the "upper" epigallocatechin block. On the basis of the facts given above, we suggest for rhodisin and rhodisinoside the most probable structures and relative configurations (I) and (II).

The study of the structures of the other proanthocyanidins is continuing.

LITERATURE CITED

1. E. A. Krasnov, Khim. Prir. Soedin., 545 (1976).
2. V. M. Malikov, A. G. Kurmukov, É. Kh. Batyrov, M. I. Aizikov, and Z. A. Kuliev, USSR Inventors' Certificate No. 1,155,601; Otkryliya, Izobreteniya, No. 18, 90 (1985).
3. G. Nonaka, I. Nishioka, T. Nagasawa, and H. Oura, Chem. Pharm. Bull., 29, No. 10, 2862 (1981).
4. D. Sun, H. Wong, and L. Y. Foo, Phytochemistry, 26, No. 6, 1825 (1987).
5. G. Nonaka, F. Hsu, and I. Nishioka, J. Chem. Soc. Chem. Commun., 15, 781 (1981).

FLAVONOIDS OF Salsola collina

A. I. Syrchina, A. L. Vereshchagin, M. F. Larin, and A. A. Semenov

UDC 547.972

We have investigated the epigeal part of Salsola colina Pall., family Chenopodiaceae, collected in the beginning of October in Novosibirsk province.

The air-dry comminuted herbage (80 kg) was extracted with 80% ethanol. From the n-butanol-soluble part of the evaporated extract previously treated with hexane and chloroform we have isolated six flavonoid compounds by column chromatography on polyamide and silica gel.

Compound (I) was tricin, $C_{17}H_{14}O_7$, mp 282-284°C. MS (EI), m/z: 330, 178, 152. UV spectrum: $\lambda_{max}^{CH_3OH}$ 250, 271, 352 nm [1]. Acetate of (I), $C_{23}H_{20}O_{13}$, mp 248-250°C. The CSs of the protons of (I) in the PMR spectrum coincided with those given in the literature [2]. ^{13}C NMR spectrum (DMSO-d_6): 164.4 (C-2); 103.8 (C-3); 182.0 (C-4); 161.6 (C-5); 99.1 (C-6); 163.8 (C-7); 94.4 (C-8); 157.5 (C-9); 104.6 (C-10); 120.6 (C-1'); 104.6 (C-2', C-6'); 148.4 (C-3', C-5'); 140.0 (C-4'); 56.6 (OCH_3). The assignment of the signals of the carbon atoms in the ^{13}C NMR spectrum of (I) was made on the basis of a comparison with the results for apigenin and tricetin [3].

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR.

Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 725-726, September-October, 1989. Original article submitted January 5, 1989; revision submitted March 7, 1989.

0009-3130/89/2505-0619$12.50