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CHEMICAL COMPOSITION OF CERTAIN *Sedum* SPECIES OF KAZAKHSTAN

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The chemical composition of seven Sedum *species growing in Kazakhstan was studied by chromatography. The contents of seven groups of natural compounds were determined. Comparison with markers and literature data identified 24 compounds including 9 that have not been described previously in* Sedum *species.*

Key words: *Sedum*, Crassulaceae, chromatography, spectroscopy, new flavonoid quercetin 3-O-β-D-galactopyranosido-(6→1)-O-β-D-xylopyranoside.

Investigations of the chemical composition of plants of the *Sedum* genus and experience using various species of this plant in folk medicine of various countries as antitumor, anti-inflammatory, radioprotective, vasodilating, wound-healing, hypotensive, and other agents [1] indicate that incorporation of *Sedum* plants into official medicine is promising and advisable.

At present the chemical composition of 92 *Sedum* species has been studied to some degree, including 9 species growing and described in Kazakhstan [3]. *Sedum acre* L. was most thoroughly studied. It has not been described although it is commonly grown as a decorative. The chemical composition of *Sedum* species growing in Kazakhstan has not been previously studied. Therefore, we investigated comparatively the aerial part and roots of seven *Sedum* L. species: *S. acre* L., *S. aizoon* L., *S. ewersii* Lbd., *S. hybridum* L., *S. kamtczaticum* Fisch., *S. purpureum* (L.) Schult., and *S. telephium* L., which are native to Kazakhstan and are cultivated in the State Botanical Garden. *Sedum hybridum* L., which grows in industrial quantities according to information from the Institute of Botany of the Republic of Kazakhstan, was selected for more complete investigation.

Analysis of the published chemical compositions of 92 *Sedum* species indicates that flavonoids and their 3-O-glycosides (more rarely their methyl esters), phenolic acids (mainly gallic), coumarins and their 6,7-substituted derivatives, alkaloids, and carbohydrates dominate in all species [2].

The flavonoid composition is most thoroughly studied for *Sedum acre* L.; alkaloids, in practically all species.

A comparative investigation of Kazakhstan species revealed the absence of methylated flavonoids and a lesser degree of hydroxylation.

Phenols, phenolic, amino, and other carboxylic acids, alkaloids, carbohydrates and polysaccharides, hydrolyzed and condensed tanning agents, and anthocyans were observed in all Kazakhstan species.

It should be noted that anthocyans, tanning agents, and polysaccharides have not been described for *Sedum.*

Table 1 gives the qualitative composition of six groups of compounds identified by comparing R_f values and specific reactions with those of known compounds. Table 2 gives the quantitative content of seven groups of natural compounds.

It can be seen that the maximum content of phenolic acids and coumarins occurs in roots of *S. aizoon* L.; flavonoids, in the aerial part of *S. ewersii* Lbd.; amino acids, in roots of *S. acre* L.; alkaloids, in the aerial part of *S. purpureum* (L.) Schult.; tannins, in the aerial part of *S. telephium* L.

Published data on the chemical composition of *Sedum hybridum* L. report the presence in it of alkaloids (sedamine, sedinine, methylisopelletierine) [4], organic acids (oxalic, citric, malic, oleanolic), β-sitosterol, esculetin, carbohydrates (glucose, saccharose, fructose, and sedoheptulose) [5], gallic acid [6], arbutin [7], flavonoids (kaempferol, quercetin, kaempferol 7-O-β-D-glucofuranosyl-3-O-α-L-rhamnopyranoside, quercetin 3- and 3′-O-β-D-glucopyranosides, quercetin 3,7-dirhamnoglucoside [8], kaempferitrin and kaempferol 3,7-dirhamnoglucoside [5], and gossypetin [9].

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TABLE 1. Biologically Active Groups of Substances of Kazakh *Sedum* L. Species

Identified compound	*S. acre L.*	*S. aizoon L.*	*S. ewersii Lbd.*	*S. hybridum L.*	*S. kamtczaticum Fisch.*	*S. purpureum (L.) Schult.*	*S. telephium L.*
	1	2	3	4	5	6	7
Phenols:							
hydroquinone	+	+	+	+	+	+	+
phloroglucinol	+	+	+	+	+	+	+
pyrocatechol		+		+		+	
pyrogallol					+		+
arbutin	+	+		+		+	+
Phenolic acids:							
gallic	+	+	+	+	+	+	+
caffeic	+	+	+	+	+	+	+
ferulic	+	+	+	+		+	+
syringic	+	+	+	+	+	+	+
gentisic	+	+	+	+		+	+
vanillic	+	+	+	+	+	+	+
o-coumaric	+						
Carbohydrates:							
glucose	+	+	+	+	+	+	+
rhamnose	+	+	+	+	+	+	+
fructose	+		+	+		+	+
maltose	+						+
arabinose	+						
xylose			+	+			
Amino acids:							
cysteine	+	+	+	+	+	+	+
tryptophan	+	+	+	+	+	+	+
threonine	+	+	+	+	+	+	+
glutamic acid	+	+	+	+	+	+	
aspargic acid	+	+	+	+	+	+	
methionine	+	+		+			+
asparagine	+			+			+
glutamine			+				
arginine	+	+		+	+	+	
Coumarins:							
coumarin	+			+		+	+
4,5-dihydroxycoumarin			+	+	+		
7-hydroxycoumarin	+	+	+	+		+	+
Flavonoids:							
kaempferol	+	+	+	+	+	+	+
quercetin	+	+	+	+	+	+	+
gossypetin		+	+	+			
kaempferol 3-O-α-L-rhamnopyranoside	+		+	+		+	+
quercetin 3-O-α-L-rhamnopyranoside		+	+	+	+	+	+
quercetin 3-O-β-D-(2″-O-galloyl)glucopyranoside				+	+		
quercetin 3-O-β-D-galactopyranosido-(1←6)-O-β-D-xylopyranoside			+	+			
quercetin 3-O-rutinoside		+	+	+	+		
quercetin 3-O-β-D-glucopyranoside	+	+	+	+		+	+

TABLE 1. (Continued)

Identified compound	*S. acre L.*	*S. aizoon L.*	*S. ewersii Lbd.*	*S. hybridum L.*	*S. kamtczaticum Fisch.*	*S. purpureum (L.) Schult.*	*S. telephium L.*
	1	2	3	4	5	6	7
gossypetin 7-O-β-D-xylopyranoside			+	+			
peonidin 3-O-β-D-glucopyranoside		+		+		+	+
pelargonidin 3-O-β-D-glucopyranoside			+	+		+	
Hydrolyzed tannins:							
2,3-digalloyl-D-glucose		+	+	+	+		
3,6-hexahydroxydiphenoyl-D-glucose			+	+			+

TABLE 2. Content of Certain Groups of Biologically Active Compounds in *Sedum* L. of Kazakhstan (% of air-dried mass)

Species, studied part	Carbohydrates	Amino acids	Alkaloids	Phenolic acids	Flavonoids	Tannins	Coumarins
S. acre L.,							
roots	5.3	4.3	0.02	0.07	0.8	13.9	0.4
aerial part	1.8	0.7	0.05	0.09	1.5	13.0	0.4
S. aizoon L.,							
roots	14.1	1.4	0.35	0.12	1.2	22.8	1.2
aerial part	2.5	1.3	0.20	0.07	1.6	11.5	0.3
S. ewersii Lbd.,							
roots	6.0	1.1	0.26	0.09	2.3	21.3	1.1
aerial part	2.1	3.4	0.10	0.03	3.1	14.8	0.3
S. hybridum L.,							
roots	3.0	1.7	0.23	0.08	0.9	14.8	0.8
aerial part	2.4	1.4	0.11	0.11	1.2	14.1	0.6
S. kamtczaticum Fisch.,							
roots	14.0	1.1	0.25	0.08	1.1	7.5	0.4
aerial part	2.6	1.1	0.11	0.07	1.5	10.0	0.3
S. purpureum (L.) Schult.,							
roots	2.6	1.2	0.07	0.04	1.3	10.3	0.2
aerial part	13.6	1.2	0.46	0.03	1.8	6.9	0.3
S. telephium L.,							
roots	1.5	2.9	0.33	0.11	1.1	16.7	0.8
aerial part	2.3	1.2	0.18	0.88	1.1	24.8	1.0

Our results complete the data on the chemical composition of this species.

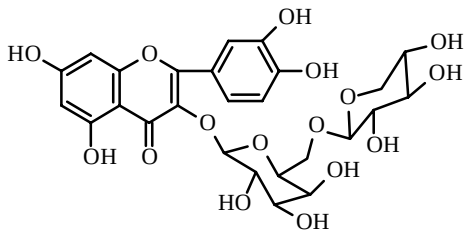
It should be noted that 17 compounds were not previously known from *S. hybridum*: gossypetin 7-O-β-D-xylopyranoside (**1**), quercetin 3-O-β-D-galactopyranosido-(6→1)-O-β-D-xylopyranoside (**2**), quercetin 3-O-β-D-(2″-O-galloyl)-glucopyranoside (**3**), quercetin 3-O-rutinoside (**4**), kaempferol 3-O-α-L-rhamnopyranoside (**5**), coumarin (**6**), 4,5-dihydroxycoumarin (**7**), 7-hydroxycoumarin (umbelliferone) (**8**), 2,3-digalloyl-D-glucose (**9**), 3,6-hexahydroxydiphenoyl-D-glucose (**10**), 5,7,4′-trihydroxyflavilium 3-O-β-D-glucopyranoside (peonidin) (**11**), 5,7,3′,4′-tetrahydroxyflavilium 3-O-β-D-glucopyranoside (pelargonidin) (**12**), 2,5-dihydroxybenzoic (gentisic) acid (**13**), 2-(3,4-dihydroxyphenylene)propenoic (caffeic) acid (**14**), 3-

methoxy-4-hydroxybenzoic (vanillic) acid (**15**), 3,5-dimethoxy-4-hydroxybenzoic (syringic) acid (**16**), and 2-(3-methoxy-4-hydroxyphenylene)propenoic (ferulic) acid (**17**). Nine of these compounds (**1**-**3**, **7**, **9**-**12**) are first observed for species of this genus. One compound (**2**) has not been previously described.

Signals of 26 C atoms confirm the presence of two carbohydrates (11C) and the absence of other C-containing substituents in the flavonoid (15C).

A singlet (18H) belongs to six aliphatic acetyls of two carbohydrates. Another singlet (12H) confirms there are four aromatic hydroxyls.

Comparison of our data with published spectra [10, 12] identifies **2** as quercetin 3-O-β-D-galactopyranosido-(6→1)-O-β-D-xylopyranoside.



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EXPERIMENTAL

Melting points of pure compounds were determined on a Kofler block; specific rotations, on a SM circular polarimeter. UV spectra were recorded in absolute methanol and with diagnostic additives on a Specord UV; IR spectra, on a UR-75 in KBr pellets, NMR (^{1}H and ^{13}C), on Bruker AMX-400 and Bruker AM-300 instruments (400.13, 75.47 MHz) in $(CD_3)_2CO$ and DMSO-d_6; mass spectra, in a MAT-311 spectrometer with computerized data processing using SS-100 MS (Varian, 70 eV). HPLC was performed in a DuPont 8800 chromatograph with a UV detector (254 and 278 nm) using reversed-phase conditions [4.6×250 mm column with Zorbax ODS and mobile phases CH_3CN—H_2O (3:7 to 1:1) (A) and KH_2PO_4—K_2HPO_4—ethanol—ethylacetate (42.5:42.5:10:5) (B)]. The flow rate was varied from 0.5 to 1.0 mL/min.

Ground air-dried raw material (aerial part and roots separately) was successively treated for 5 h by soaking in benzene and $CHCl_3$ to remove lipophilic substances.

Then, it was exhaustively extracted with acetone (70%) at 55-60°C (4 times, 2 h each). The extract was concentrated in vacua to a small volume and fractionated using ether and ethylacetate.

Substances of the ether, ethylacetate, and aqueous fractions were separated over silica gel L100/160, polyamide, and LH-20 columns with subsequent purification by preparative chromatography on paper or Silufol UV-254 plates. HPLC was used for analysis.

Specific reactions were used to identify alkaloids, hydrolyzed and condensed tanning agents, and polysaccharides in the seven studied species.

The contents of the main groups of substances were determined using the USSR pharmacopoeia (XIth Ed.) and literature methods [10] (Table 2).

Quercetin 3-O-β-D-Galactopyranosido-(6→1)-O-β-D-xylopyranoside. Dark yellow substance, mp 198-199°C. Acid hydrolysis gives quercetin, D-galactose, and D-xylose. An intermediate formed during the hydrolysis was identified by comparison with quercetin 3-O-β-D-galactopyranoside [11] and D-xylose.

The type of bonding between carbohydrate units was determined from the rate of alkaline hydrolysis, a qualitative reaction with diphenylamine-*p*-anisidine reagent (blue color), and the products of periodate oxidation (dialdehyde, formic acid).

UV spectrum (MeOH, λ_{max}, nm): 356, 268 (MeOH), 388, 280 (+NaOMe), 374, 286 (+NaOAc), 384, 276 (+NaOAc/H_3BO_3), 381, 298 (+$AlCl_3$), 375, 297 (+$AlCl_3$/HCl).

IR spectrum (KBr, ν, cm^{-1}): 3450, 3280 (OH), 2740-2940 (C–H), 1660 (C=O), 1205, 1180 (C–O–C), 1070, 1056, 1018 (pyranose form), 919, 769 (6→1), 890 (β-OH).

PMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.02-4.43 (10H, m, sacch.), 4.62 (d, H-1″), 5.78 (d, H-1″), 6.18 (d, J = 2.6, H-6), 6.39 (d, J = 2.5, H-8), 6.86 (dd, J = 8.2, J = 0.7, H-5′), 7.52 (dd, J = 2.48, J = 0.7, H-2′), 7.68 (dd, J = 7.8, J = 2.46, H-6′).

^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm): 60.22 (C-6″), 65.27 (C-5′″), 67.36 (C-4′″), 69.01 (C-4″), 73.23 (C-3″), 75.49 (C-2′″), 76.42 (C-5″), 77.19 (C-3′″), 79.43 (C-2″), 93.02 (C-8), 97.50 (C-6), 98.23 (C-1″), 103.45 (C-10), 104.13 (C-1′″), 114.83 (C-5′), 115.62 (C-2′), 120.78 (C-1′), 121.51 (C-6′), 132.66 (C-3), 144.55 (C-4′), 148.11 (C-3′), 154.87 (C-2), 155.79 (C-9), 160.86 (C-5), 163.66 (C-7), 177.01 (C-4).

Peracetyl derivative:

PMR (400 MHz, DMSO-d_6, δ, ppm): 1.98 (s, 18H), 2.33 (s, 12H), 3.34 (s, 2H-6″), 3.56 (q, H-5′″a), 4.10 (q, H-5′″e), 4.76-4.89 (3H, m, H-2′″, 3′″, 4′″), 5.11-5.36 (4H, m, H-2″, 3″, 4″, 5″), 5.82 (t, H-1′″), 7.10 (d, H-1″), 7.33 (d, H-6), 7.48 (d, H-8), 7.61 (dd, H-5′), 8.06 (dd, H-2′), 8.12 (dd, H-6′).

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