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COMPOSITION OF *Tamarix hokenakeri* AND *T. ramosissima*

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The qualitative composition and quantitative content of certain groups of natural compounds of Tamarix hokenakeri *and* T. ramosissima *growing in the Republic of Kazakhstan were studied.*

Key words: *Tamarix hokenakeri*, *T. ramosissima*, Tamaricaceae, chromatography, spectroscopy, new flavonoid, 7-O-sinapoylkaempferide.

We investigated stems and leaves of *Tamarix hokenakeri* Bgi and *T. ramosissima* Lbd. (Tamaricaceae), which are widely distributed in the deserts and alkaline regions of Kazakhstan and Middle Asia [1].

Green twigs of *T. hokenakeri* contain up to 9.2% tanning agents, the maximum content of which occurs in spring and summer [2]. The content of tanning agents in *T. ramosissima* was determined in the organs (%): roots, 4.5; stems, 39; leaves, 8-9; bark, 4.1-9.09; flowers, 12.7; fruit, 14.4. Leaves also contain *p*-coumaric acid and coumarins; bark, 0.16 coumarins, 1.64 flavonoids, and anthocyans; flowers, 0.1 coumarins, 2.4 flavonoids represented by quercetin, kaempferol, isoquercitrin, tamarixetin, and tamarixin; fruit, 0.15 coumarins, 1.64 flavonoids, 2.3 anthocyans; green twigs, 0.19 coumarins and 1.66 flavonoids [3-7].

Other species of *Tamarix* contain isoferulic, gallic, dehydrodigallic, 3,3′-dimethoxyellagic acids, alkanes, alkaloids, steroids, anthocyans, coumarins, mono-, di-, and trisulfates of flavonoids, tamarixinol, tamarixone, hirtellins T_1-T_3, tamarixins B, C, T_1, and T_2, and other dimeric and trimeric hydrolyzed tanning agents [8-10].

Tamarisks have been used since antiquity in folk medicine and practice. Their industrial sustainability has been noted. Chemical investigation of tamarisk composition could facilitate its incorporation into official medicine.

A comparative analysis of stems and leaves of two species showed that they contain the same groups of compounds, differing only in components and amounts.

Table 1 shows that stems of both species are rich in alkaloids, amino acids, and tanning agents. Leaves contain slightly more coumarins, flavonoids, and phenolic acids.

Comparison with standards identified five carbohydrates (glucose, arabinose, xylose, galactose, and saccharose), two flavonoids (keampferol and quercetin), six phenolic acids (*p*-coumaric, gallic, ellagic, ferulic, sinapic, 3-hydroxy-5-methoxybenzoic), two coumarins (coumarin and umbelliferone), eight amino acids (tryptophane, cysteine, threonine, glutamic acid, methionine, asparagine, glutamine, arginine), and a glucoside of emodine. Three other substances were identified based on chemical and physicochemical data and comparison with literature data for other *Tamarix* species. Two substances, kaempferide and 2,3-digalloylglucose, have been described. The third substance is new. The chromatographic behavior and qualitative reactions of the third substance are identical to kaempferide. However, the chromatographic mobility is greater in aqueous systems. Kaempferide and sinapic acid were identified in the hydrolysate after acid hydrolysis by HCl (1 N) for 1 h at 85-90°C.

UV spectrum (MeOH, λ_{max}, nm): 384, 266 (MeOH), 396, 289 (+NaOAc), 404, 288 (+$AlCl_3$).

PMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.63 (3H, s), 6.22 (d, J = 2.2), 6.46 (d, J = 2.5), 6.61 (2H, d, J = 8.4), 7.29 (2H, d, J = 8.5).

The 3H-singlet at 3.63 ppm in the PMR ($CDCl_3$) of **1** corresponds to one methoxy. The two 2H-doublets at 6.61 (J = 8.4 Hz, H-3′,5′) and 7.29 (J = 8.5 Hz, H-2′,6′) with *ortho* splitting constants are consistent with 4′-methoxy substitution in ring B. Two doublets with *meta* splitting constants of 2.2 and 2.5 Hz at 6.22 (H-6) and 6.46 (H-8) ppm are consistent with

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TABLE 1. Qualitative Composition and Content of Substances in Two *Tamarix* Species (Substances/Total Content of These Substances, %)

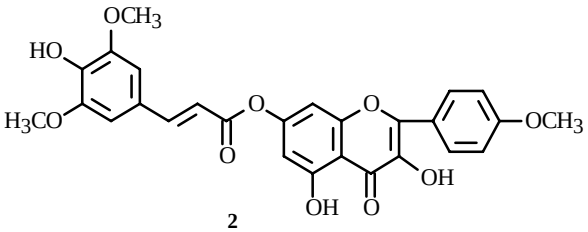
Substance	*Tamarix hokenakeri Bgi*		*Tamarix ramosissima Lbd.*	
	stems	leaves	stems	leaves
Alkaloids	++	+	++	+
Saponins	+	+	+	+
Amino acids	8/3.50	6/2.17	6/4.20	7/2.31
Phenolic acids	9/5.84	8/6.09	8/6.32	8/6.81
Anthracene glycosides	2/0.12	1/Tr.	2/0.15	1/Tr.
Flavonoids	4/3.09	3/3.27	3/3.51	4/2.76
Carbohydrates	5/2.16	3/0.91	4/0.87	3/0.97
Polysaccharides	0.64	0.59	0.71	0.68
Coumarins	3/0.22	2/0.31	2/0.29	1/0.40
Tanning agents	7.76	6.19	7.95	6.24

5,7-substitution of ring A. The characteristic bathochromic shift of both bands in the UV spectrum by $AlCl_3$ and $ZrOCl_2$ indicates that the structure includes free 3- and 5-hydroxyls. Alkaline decomposition of **1** gives phloroglucin and *p*-methoxybenzoic acid, which suggests that **1** is kaempferol, 3,5,7-trihydroxy-4′-methoxyflavone.

Compound **2** accompanies **1** in chromatograms. Their qualitative reactions are identical. The mass spectrum shows *m*/*z* (70 eV) 481.

PMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.65 (3H, s), 3.82 (6H, s), 6.49 (d, J = 2.5), 6.81 (d, J = 2.7), 6.89 (2H, d, J = 8.4), 7.13 (2H, s), 7.38 (2H, d, J = 8.5).

Two new 1H-doublets at 4.86 and 5.03 ppm with J = 18 Hz correspond to the conjugated *trans*-α-β-CH of sinapic acid; a 6H-singlet, to two equivalent methoxyls; the remaining signals, to **1**. Acid hydrolysis (1 N HCl, 3 h, 85-90°C) gives kaempferide and sinapic acid. Bathochromic shifts by 33 and 48 nm in the UV spectrum in the presence of $AlCl_3$ and analogous behavior upon addition of $ZrOCl_2$ indicates that the 7-OH is esterified. The IR spectrum contains an ester absorption band at 1727 cm^{-1} in addition to other bands. Thus, the new compound 7-O-sinapoylkaempferide (**2**) was isolated from two *Tamarix* species growing in Kazakhstan.



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Compound **3** has R_f 0.51 (butanol—acetic acid—water, 4:1:5) and 0.63 (2% CH_3CO_2H). Acid hydrolysis (5% HCl) on a boiling-water bath for 5 h gives gallic acid and glucose.

PMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.06 (2H, s), 7.12 (2H, s), 5.78 (dd), 5.40 (d), 5.08 (dd), 4.78 (dd), 4.00-4.11 (m), 3.84-3.71 (m).

The two 2H-singlets at 7.06 and 7.12 ppm are indicative of two gallic acids bonded to glucose. The two signals at 5.78 and 5.40 are shifted to a greater extent. Therefore, the site of attachment of the gallic acids can be determined. Comparison of the spectra with those in the literature [11, 12] argues in favor of 2,3-digalloylglucose.

The structures of the other substances are under investigation.

EXPERIMENTAL

Melting points of pure compounds were determined on a Kofler block. UV spectra were recorded in absolute methanol with diagnostic additives on a Specord UV; IR spectra, on a UR-75 in KBr pellets; ^1H NMR, on a Bruker AMX-400

(400.13 MHz) instrument in $CDCl_3$.

Air-dried raw material was extracted three times for 2 h each with aqueous acetone (50%). The combined extracts were concentrated in vacua to a small volume and treated successively with $CHCl_3$, ether, ethylacetate, and butanol. The resulting extracts were concentrated to a small volume. The composition was investigated by two-dimensional chromatography using butanol—acetic acid—water (40:12.5:29) and 2% acetic acid followed by separation over columns of polyamide, silica gel, Sephadex HW-40, HW-60, and LH-20. Eluents were water, aqueous alcohol (20, 30, 50, and 70%), and aqueous acetone (50%). The sharpness of the separation over columns was checked by one-dimensional chromatography of the fractions with visualization by specific reagents for the main groups of natural compounds. Certain substances were identified by one-dimensional paper chromatography with markers.

Components of both species were investigated comparatively using paper chromatography (one- and two-dimensional) with visualization of all groups of natural compounds. Table 1 presents results of the qualitative and quantitative analyses.

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