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Chemical composition and thermal properties of *Pistacia atlantica* subsp. *Kurdica* gum

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Abstract

Pistacia atlantica subsp. *Kurdica* (PAK) is distributed throughout the Zagros Mountains and is indigenous to Kurdistan province in western Iran. This study focused on the composition and thermal properties of gum extracted from female and male trees from six regions of Kurdistan province. Significant differences were detected in the total protein, total ash, total carbohydrate and monosaccharaide contents according to gender and geographic region, but no significant difference was found for moisture content. Analysis of the monosaccharide composition using HPLC showed the presence of arabinose, galactose, glucose, rhamnose and xylose. Significant differences were observed for the amino acid contents of the various PAK gum samples. The most abundant amino acids were glutamic acid, aspartic acid, serine, proline and histidine; however, the relative proportions of amino acids varied considerably between samples. The results indicate that the volatile components (VoC) were significantly different between samples according to gender and region, with the predominant VoC being α-Pinene. The results of thermogravimetric analysis showed that the onset of the initial and main decomposition of the samples was at 80 °C and above 240 °C, respectively. The differential scanning calorimetry results showed that nearly all gum samples included two glass transition temperatures and heat capacity values and that nearly all of the values for the female gum samples were lower than for the male samples.

Keywords: Chemical composition, Gum, *Pistacia atlantica* subsp. *Kurdica*, Thermal properties

Introduction

There are 11 species of *Pistacia* globally [1]. *Pistacia atlantica* is widely distributed from the Canary Mountains in Spain to the mountains of Iran [2]. Iran is a major source of *Pistacia* diversity in pistachio cultivation and production [3]. *P. atlantica* has four subspecies (*mutica*, *cubolica*, *atlantica* and *kurdica*) [4]. *P. atlantica* subsp. *Kurdica* (PAK) is distributed throughout the Zagros Mountains and is indigenous to Kurdistan province in western Iran [5].

Herbal medicine has been used to treat diseases because of its therapeutic potential [6]. The different products of PAK (leaves, fruit and gum) are valuable for their medicinal, cosmetic and food value. They are used to treat digestive disturbances and as moisturizers, antimicrobials, antioxidants, edible oil, feed and chewing gum [7, 8]. The quality and quantity of the gum, or oleoresin (*jajka talla* in Kurdish), depends on the species of plant, gender and geographic origin [9]. Several studies have examined the chemical composition of *P. atlantica* essential oil [4, 10]. The optical rotation and nitrogen, ash, moisture and tannin contents are the parameters that are frequently used to recognize the properties of gums used as food additives. The unique fundamental properties of this gum are its high water solubility and low viscosity [11].

Knowledge about the thermal properties of food and food components is important. Thermogravimetric analysis (TGA) continuously determines the weight of a sample as a function of temperature over time. It detects changes in the mass of a sample (gain or loss)

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and determines the temperatures that characterize a step in mass loss and gain curves to monitor food processes [12]. Several researchers have used thermal properties to calculate the energy of activation based on the Broido model. An increase in the energy of activation indicates a higher thermal stability, so that an activation energy of above 100 represents high polymer stability and suggests the presence of synthetic polymers as compared to the lower activation energy of biopolymers. The difference in the energy of activation can be influenced by the origin and species of the gum [10].

Differential scanning calorimetry (DSC) measures the heat flow of samples as a function of temperature or time. This method determines physical transition and chemical reactions quantitatively [13]. The glass transition temperatures (T_g) of synthetic polymers and biopolymers have been measured using DSC. At the glass transition temperature, materials convert from very viscous glassy to rubbery form, the molecular mobility increases and the viscosity decreases. This may result in structural changes such as stickiness and collapse [14].

Materials and methods

Gum extraction

The oleoresin of PAK was extracted by piercing the trunk of the tree with a specialized tool and collected in a clay bowl attached to the trunk [15]. To keep minimum damage during oeloresin extraction and maximum consistency among samples, a sampling strategy introduced by Karamshahi et al. [16] was employed. Trees with 30–50 cm trunk diameter were selected and 20 horizontal grooves (2 cm length) were pierced to collect the resinous exudates from male and female trees at the beginning of July 2016 in six regions of Kurdistan province in Iran (Armardeh, Kanisoor, Marivan, Sarvabad, Dezli, Hawraman).

Moisture, total ash and protein contents

The moisture and total ash contents of the oleoresin samples were determined using the AOAC method [17]. The total protein content was determined by analyzing the nitrogen content using the semi-micro Khjeldahl method [17]. On the basis of early determinations, a conversion factor of 6.6 was used to calculate the crude protein content [18].

Total carbohydrate content

In order to determine the total carbohydrates (TC) content, 4 g of crude gum was dissolved in a final volume of 100 mL of distilled water at 50 °C and then filtered through Whatman no. 1 filter paper [19]. The total carbohydrate content of the 4% solution was determined by the phenol–sulfuric acid colorimetric method with D-glucose as the standard at 490 nm [20].

Amino acid composition

Oleoresin samples were hydrolyzed with 0.2 mL of 5.5 N in constantly boiling HCl in a sealed tube at 110 °C for 18 h [21]. The hydrolyzed liquid was neutralized with bicarbonate and centrifuged at 13,500*g* for 10 min. Then 200 µL of the supernatant was mixed with 50 µL of 4-(4,dimethylamino) phenyl azobenzene sulfonyl chloride (20 mg mL^{-1}) at 60 °C for 60 min to convert the amino acids into dabsyl chloride derivatives. The acetone then was evaporated and the final solution was injected into the HPLC [21, 22].

Monosaccharide composition

The sample was labeled by adding 30 µL of NaOH (0.3 M) and 20 µL of PMP (1-phenyl-3-methyl-5-pyrazolone) solution (0.5 M in methanol). Fucose was added as an internal standard to each sample before derivatization. The mixtures were incubated at 70 °C for 60 min, cooled to room temperature and neutralized with 30 µL of HCl (0.3 M), 1 mL of trichloromethane was added. After vigorous shaking and layering, the organic phase was carefully removed and discarded. The aqueous layer was passed through a 0.45 µm syringe filter before HPLC analysis.

The PMP-labeled monosaccharides were analyzed using an Unicam Crystal 200 HPLC system consisting of a G1311C quaternary pump, G1329B autosampler (0.1–100 µL), G1316A pre-column oven (273–333 K) and G1315D-DAD detector (190–950 nm). The analytical column was a TC-C18 column (4.6 × 250 mm; 5 µm). The injection volume was 20 µL with an eluent flow rate of 1.0 mL min^{-1} at 35 °C. Mobile phase A was 100% acetonitrile and mobile phase B was a mixture of distilled water and acetonitrile (90: 10, v/v) with 0.045% KH_2PO_4–0.05% triethylamine buffer (pH 7.5). Gradient elution was performed at 94%–94%–88%–88% B with linear decreases at 0–4–5–20 min. The UV detection wavelength was 245 nm [23].

Volatile components

To prepare the sample extracts, the oleoresin (75 g) was firstly extracted with 300 mL of ethanol (90%) by sonication. The n-hexane fraction was saponified with 0.5 N methanolic NaOH solution by heating in a steam bath until fat globules entered the solution (approximately 5 min) and then boiled for 2 min. After cooling, saturated NaCl solution was added to each solution. The mixtures were transferred to a separatory funnel individually and each was extracted with 30 mL of petroleum ether and

converted to their methyl ester forms with 20 mL of boron trifluoride-methanol complex reagent [6].

Chromatographic analysis was carried out on Agilent 6890N network GC system combined with an Agilent 5973 network mass selective detector (GC–MS). The capillary column used was an Agilent 19091N-136 (HP Innowax capillary: 60.0 m × 0.25 mm × 0.25 μm). Helium was used as a carrier gas at a flow rate of 0.8 mL min^{-1} with a 1 l injection volume. Samples were analyzed with the column held initially at 60 °C for 1 min after injection with a 10 min hold time, then increased to 220 °C with 4 °C min^{-1} heating ramp and kept at 220 °C for 10 min. The final temperature was increased to 240 °C with 1 °C min^{-1} heating ramp. The injection was performed in splitless mode. Detector and injector temperatures were 280 and 250 °C, respectively. The run time was 80 min [6].

Fourier transform infrared spectroscopy

The IR spectra of the oleoresin samples were determined using Fourier transform infrared spectrometry (FTIR) (Perkin-Elmer; 16 PC spectrometer; USA). The samples were ground with spectroscopic grade potassium bromide powder and then pressed into 1 mm pellets for FTIR measurement at wavenumber ranges of 400 and 4000 cm^{-1} [24].

Thermogravimetric analysis

The thermal behavior of the oleoresin samples was analyzed by TGA (Mettler Toledo; TGA1, RT-800, STAR SW 10.00) at a heating rate of 10 °C min^{-1} at a temperature range of 0–600 °C in air. Samples of about 10 mg were weighed in an aluminum pan. Derivatograms of the TGA curves (derivative mass loss) were also recorded [25].

Differential scanning calorimetry

DSC measurement was carried out in N_2 atmosphere (Mettler Toledo; DSC1, −130 to 600, STAR SW 12.00; Switzerland) calibrated with indium as a standard. Analysis started at −120 °C and continued up to 80 °C at a heating rate of 10 °C min^{-1}. Samples were weighed (10–15 mg) in aluminum DSC pans (aluminum crucible = 40 μL) and an empty pan was used as a Ref. [13].

Statistical analysis

All chemical analyses were performed in triplicate. All data was analyzed using a two-way general liner model design analysis of variance (ANOVA) with the factors of geographic region and gender. Tukey's multiple range test was used to compare the treatment means (SAS 9.3). Non-parametric Spearman rank correlation coefficients of chemical components and environment characteristics were calculated using the SPSS software version 22.0.

Results and discussion

Chemical composition analysis

The results of compositional analysis for all PAK oleoresin samples are summarized in the Tables 1, 2 and 3. Significant differences were observed in the total protein ($P < 0.01$) and total ash ($P < 0.05$) contents for gender and geographic region, but no significant difference in moisture content was found. The values for moisture was 16.03% to 19.26%, for total ash was 0.86% to 0.94% and for protein was 3.97% to 5.05%.

Table 1 Chemical composition of the extracted gum samples for factors under investigation

Sample	Gender		Geographic regions					
	Female	Male	Kanisoor	Armardeh	Hawraman	Dezli	Sarvabad	Marivan
Moisture (%)	18.30 ± 1.28 a	18.60 ± 1.31 a	18.81 ± 0.93 a	18.89 ± 1.35 a	18.58 ± 0.50 a	16.03 ± 0.19 a	19.12 ± 2.20 a	19.26 ± 0.16 a
Ash (%)	0. 93 ± 0.002 a	0. 88 ± 0.003 b	0. 94 ± 0.002 a	0. 92 ± 0.003 ab	0. 86 ± 0.003 b	0. 91 ± 0.003 ab	0. 93 ± 0.002 ab	0. 87 ± 0.002 ab
Totalcarbohydrates (%)	40.51 ± 2.35 b	44.74 ± 2.53 a	45.56 ± 2.12 a	41.23 ± 3.04 a	43.36 ± 1.63 a	44.01 ± 2.63 a	39.83 ± 1.33 a	41.76 ± 1.76 a
Arabinose[a]	73.63 ± 6.09 a	66.88 ± 5.32 b	78.00 ± 4.13 b	74.00 ± 0.85 c	60.50 ± 1.51 e	69.00 ± 0.85 d	53.50 ± 1.66 f	86.50 ± 2.20 a
Galactose	53.42 ± 5.55 a	49.42 ± 5,66 b	50.00 ± 2.47 d	69.00 ± 0.97 a	36.50 ± 0.69 f	59.63 ± 0.81 b	41.38 ± 1.38 e	52.00 ± 1.38 c
Rhamnose	20.96 ± 3.18 a	19.08 ± 2.47 b	20.33 ± 0.40 c	13.08 ± 0.48 f	28.85 ± 1.50 a	17.63 ± 0.29 d	24.15 ± 0.93 b	15.40 ± 0.31 e
Fucose	3.58 ± 1.45 a	3.27 ± 1.06 b	1.73 ± 0.33 d	1.38 ± 0.01 e	6.15 ± 0.49 b	2.37 ± 0.15 c	7.43 ± 0.32 a	1.49 ± 0.10 e
Xylose	24.00 ± 4.98 b	25.5 ± 4.35 a	21.50 ± 1.16 c	17.00 ± 0.38 e	36.50 ± 0.59 b	19.00 ± 0.38 d	38.00 ± 0.85 a	16.50 ± 0.59 e
Glucose	5.07 ± 1.05 a	4.69 ± 1.25 b	4.63 ± 0.13 c	2.40 ± 0.19 e	7.58 ± 0.29 b	3.35 ± 0.14 d	8.08 ± 0.35 a	3.25 ± 0.49 d
Glucuronic acid	22.88 ± 2.78 a	17.47 ± 2.77 b	15.30 ± 0.59 e	15.70 ± 2.99 e	23.33 ± 2.03 b	30.13 ± 1.45 a	19.60 ± 0.85 c	16.50 ± 0.23 f
Galacturonic acid	43.63 ± 5.37 a	35.33 ± 4.98 b	34.23 ± 1.69 d	49.80 ± 2.58 b	27.80 ± 0.52 e	28.30 ± 3.18 e	44.75 ± 4.11 c	52.00 ± 1.39 a

Values with different letters are significantly different

[a] Unit for monosaccharide: milligrams (mg) per gram of carbohydrate

Table 2 Chemical composition (total Protein and amino acids) of the extracted gum samples for factors under investigation

Sample	Gender		Geographic regions					
	Female	Male	Kanisoor	Armardeh	Hawraman	Dezli	Sarvabad	Marivan
Total protein (%)	4.63 ± 0.22 a	4.23 ± 0.20 b	4.09 ± 0.12 d	4.82 ± 0.15 b	4.18 ± 0.05 d	4.47 ± 0.15 c	5.05 ± 0.13 a	3.97 ± 0.11 e
Alanine[a]	46.17 ± 5.37 a	35.33 ± 4.98 b	50.00 ± 0.35 b	40.63 ± 7.60 c	33.88 ± 1.86 e	53.00 ± 5.76 a	37.63 ± 2.82 d	29.38 ± 3.23 f
Glycine	40.29 ± 5.68 b	42.38 ± 5.83 a	37.00 ± 0.43 d	32.50 ± 0.59 e	59.00 ± 0.89 a	25.50 ± 0.53 f	43.5 ± 0.59 c	50.50 ± 0.55 b
Lysine	41.75 ± 1.87 b	46.33 ± 2.88 a	43.85 ± 0.43 cd	47.60 ± 5.75 a	44.18 ± 1.61 bc	43.57 ± 1.93 d	44.30 ± 0.68 b	40.75 ± 1.45 e
Cysteine	4.16 ± 0.88 a	3.42 ± 1.43 b	2.98 ± 0.52 d	4.05 ± 0.02 c	1.60 ± 0.74 e	5.93 ± 0.56 b	7.03 ± 0.65 a	1.15 ± 0.53 f
Threonine	35.29 ± 4.88 b	47.39 ± 6.23 a	50.25 ± 0.21 b	40.80 ± 8.06 c	34.13 ± 1.72 e	55.38 ± 6.51 a	38.05 ± 3.26 d	29.45 ± 3.65 f
Valine	34.02 ± 5.14 a	31.98 ± 4.98 b	48.75 ± 0.75 a	42.00 ± 0.85 b	33.25 ± 0.44 c	25.13 ± 0.62 e	19.90 ± 0.55 f	29.00 ± 0.35 d
Phenylalanine	24.71 ± 3.08 a	17.20 ± 2.24 b	16.75 ± 2.61 e	16.50 ± 0.59 e	23.00 ± 1.93 b	18.50 ± 1.66 d	29.47 ± 2.35 a	21.50 ± 4.39 c
Histidine	78.67 ± 6.13 b	85.17 ± 6.18 a	101.50 ± 2.20 a	71.00 ± 1.93 e	91.50 ± 1.12 b	77.50 ± 1.92 d	66.50 ± 1.66 f	83.50 ± 1.95 c
Glutamine	30.51 ± 3.35 b	32.63 ± 3.38 a	36.38 ± 0.71 b	39.85 ± 0.85 a	34.08 ± 0.51 c	28.10 ± 0.61 e	19.50 ± 0.59 f	31.50 ± 0.59 d
Isoleucine	25.98 ± 4.30 a	24.61 ± 4.31 b	21.50 ± 0.49 d	40.00 ± 0.35 a	18.00 ± 0.85 e	32.50 ± 0.59 b	23.25 ± .22 c	16.50 ± 0.23 f
Asparagine	47.00 ± 6.47 a	42.75 ± 6.47 b	33.50 ± 0.59 e	36.00 ± 3.57 d	44.50 ± 1.12 c	34.00 ± 1.48 e	53.50 ± 1.11 b	67.75 ± 1.55 a
Methionine	17.08 ± 2.22 a	22.13 ± 6.62 a	12.63 ± 2.14 a	11.00 ± 0.35 a	13.63 ± 0.35 a	20.25 ± 0.70 a	20.13 ± 1.59 a	15.00 ± 3.02 a
Serine	106.08 ± 8.13a	95.50 ± 6.25 b	78.00 ± 1.83 f	115.50 ± 2.75 b	90.75 ± 2.10 e	104.50 ± 2.75 c	118.00 ± 5.76 a	98.00 ± 2.49 d
Arginine	23.63 ± 4.29 b	24.08 ± 5.71 a	9.75 ± 0.44 f	29.50 ± 0.59 c	20.25 ± 1.24 d	15.50 ± 0.59 f	33.25 ± 3.72 b	34.88 ± 0.27 a
Proline	94.67 ± 6.90 a	103.42 ± 7.52 a	118.75 ± 2.90 a	87.25 ± 2.09 e	111.25 ± 2.63 b	94.25 ± 2.34 d	78.00 ± 1.93 f	104.75 ± 2.61 c
Tyrosine	38.75 ± 4.16 a	27.25 ± 5.16 b	35.00 ± 3.02 b	31.25 ± 3.18 d	33.75 ± 2.34 c	26.50 ± 2.75 f	27.25 ± 6.99 e	46.25 ± 3.70 a
Glutamic acid	159.50 ± 10.15b	184.00 ± 9.42a	172.80 ± 13.15 b	168.75 ± 10.00 b	181.50 ± 5.50 a	183.75 ± 11.11 a	171.50 ± 14.00 b	152.25 ± 11.91 c
Aspartic acid	118.42 ± 7.60b	103.83 ± 6.53 a	89.00 ± 3.06 f	122.25 ± 4.25 b	98.00 ± 3.57 e	117.25 ± 4.25 c	128.75 ± 4.80 a	111.50 ± 4.13 d
Leucine	30.42 ± 5.44 a	29.17 ± 4.82 b	29.75 ± 5.35 c	18.00 ± 0.05 f	28.75 ± 1.28 d	32.50 ± 3.84 b	45.25 ± 1.55 a	24.50 ± 3.30 e
Tryptophan	7.45 ± 2.25 a	5.83 ± 2.17 b	5.50 ± 1.66 d	2.88 ± 1.58 e	9.50 ± 1.12 b	12.50 ± 1.12 a	1.50 ± 0.82 f	8.00 ± 0.35 c

Values with different letters are significantly different

[a] Unit for amino acids: milligrams (mg) per gram of protein

Significant differences were found for TC content between samples ($P < 0.01$), with the maximum and minimum TC contents recorded for the Kanisoor (45.56%) and Sarvabad (39.83%) regions, respectively. Interestingly, the female tree samples had higher TC contents than the males. Arabinose and galactose were the most abundant monosaccharides in the samples, suggesting an arabinogalactan structure for the gum [26]. It should be noted that the presence of fairly high concentrations of xylose and rhamnose may influence the physical properties (T_g; Table 8) [27]. Substantial differences between samples from different regions ($P < 0.01$) could result from topographic and land attributes (slope, aspect, soil type, etc.) [28].

ANOVA results indicated that both geographic location ($P < 0.01$) and gender ($P < 0.01$) had significant effects on the amino acid concentrations (Table 2). Slope, geographical direction and such could influence these results [28]. The presence of high concentrations of serine and proline in all samples may be related to the arabinogalactan-protein content [26, 29].

Significant differences were observed for the volatile components (VoC) contents according to region ($P < 0.01$) and gender ($P < 0.01$). In both female and male samples, α-Pinene was determined to be the principle volatile component along with β-Pinene, longifolene, trans-verbenol, 3-carene, comphene, α-terpinolene and limonene (Table 3).

Måren [30] determined that concentrations of nitrogen, phosphorus, organic materials and moisture in the soil were high in the north and the level of soil acidity was low. These characterizations indicate that the efficiency of VoC from the samples taken in the north was higher than in the south. The samples from the south showed increased concentrations of VoC compared to samples from the north. Our results agree with these findings [30].

Fourier transform infrared spectroscopy

Chemical and covalent bonding characterization and detection of functional groups of PAK gum samples from the female and male trees of different regions was carried out using the transmittance spectra of the characteristic peaks in FTIR spectroscopy. Figure 1 shows the FTIR spectra of both female and male oleoresins.

Table 3 Volatile components of the extracted gum samples for factors under investigation

Compound	RI	Gender		Geographic regions					
		Female	Male	Kanisoor	Armardeh	Hawraman	Dezli	Sarvabad	Marivan
1,3 Octanal	873	1.15 ± 0.16 a	0.91 ± 0.25 b	1.25 ± 0.22 b	1.36 ± 0.03 a	1.00 ± 0.16 c	0.43 ± 0.23 e	1.25 ± 0.14 b	0.90 ± 0.08 d
Tricyclene	898	0.98 ± 0.08 b	1.06 ± 0.09 a	1.00 ± 0.04 a	0.85 ± 0.02 b	1.00 ± 0.03 a	1.10 ± 0.03 a	1.10 ± 0.07 a	1.08 ± 0.17 a
α-Thujene	908	1.64 ± 0.16 a	1.60 ± 0.25 b	1.70 ± 0.03 b	1.70 ± 0.19 b	1.95 ± 0.11 a	1.35 ± 0.22 c	1.95 ± 0.13 a	1.08 ± 0.04 d
α-Pinene	920	44.41 ± 2.16 a	43.39 ± 1.93 b	40.15 ± 1.07 e	41.00 ± 1.69 d	45.05 ± 2.00 b	44.80 ± 0.14 b	42.83 ± 1.63 c	49.58 ± 1.26 a
Comphene	935	2.63 ± 0.73 b	3.32 ± 0.93 a	3.48 ± 0.09 b	3.10 ± 0.95 b	3.05 ± 0.82 c	3.05 ± 0.90 c	1.43 ± 0.09 c	3.83 ± 1.51 a
verbenone	946	1.20 ± 0.17 b	0.88 ± 0.35 a	0.50 ± 0.27 e	0.96 ± 0.05 c	1.20 ± 0.05 b	1.78 ± 0.07 a	0.78 ± 0.43 d	1.00 ± 0.04 c
Sabinene	960	1.53 ± 0.22 a	1.35 ± 0.21 b	1.20 ± 0.19 c	2.10 ± 0.03 a	1.18 ± 0.07 c	1.20 ± 0.18 c	1.73 ± 0.15 b	1.25 ± 0.08 c
β-Pinene	971	4.41 ± 0.42 b	5.55 ± 0.74 a	5.20 ± 0.08 c	6.10 ± 0.74 a	4.65 ± 0.05 d	4.65 ± 0.08 d	5.55 ± 0.65 b	3.73 ± 0.55 e
Myrcene	990	1.57 ± 0.18 a	1.58 ± 0.25 a	1.75 ± 0.18 ab	1.30 ± 0.19 d	1.83 ± 0.21 a	1.63 ± 0.14 bc	1.48 ± 0.24 c	1.48 ± 0.28 c
3-Carene	1006	3.40 ± 0.63 a	1.89 ± 0.82 b	1.98 ± 0.53 cd	1.93 ± 1.06 d	2.53 ± 1.38 bc	2.68 ± 0.48 b	4.45 ± 0.04 a	2.33 ± 0.15 bcd
α-Phelandrene	1020	1.50 ± 0.19 b	1.71 ± 0.29 a	2.23 ± 0.15 a	1.68 ± 0.16 c	0.95 ± 0.02 e	1.28 ± 0.12 d	1.85 ± 0.08 b	1.65 ± 0.25 c
β-Ocimene	1031	1.49 ± 0.23 a	1.13 ± 0.13 b	1.45 ± 0.22 b	1.04 ± 0.08 d	1.48 ± 0.32 b	1.28 ± 0.15 c	1.63 ± 0.14 a	1.00 ± 0.02 d
p-Cymen	1040	1.41 ± 0.17 b	1.60 ± 0.26 a	1.53 ± 0.07 b	1.03 ± 0.02 e	1.93 ± 0.26 a	1.40 ± 0.25 c	1.25 ± 0.14 d	1.90 ± 0.08 a
Fenchone	1052	0.73 ± 0.28 b	1.35 ± 0.20 a	0.38 ± 0.20 e	1.18 ± 0.13 bc	1.08 ± 0.02 cd	1.20 ± 0.16 b	1.00 ± 0.55 d	1.43 ± 0.04 a
Limonene	1065	2.85 ± 0.47 b	3.96 ± 0.84 a	3.30 ± 0.41 d	4.65 ± 0.80 a	3.30 ± 0.14 d	3.80 ± 0.08 c	4.40 ± 0.52 b	0.98 ± 0.02 e
1,8-Cineole	1084	1.08 ± 0.09 b	1.66 ± 0.23 a	1.53 ± 0.26 b	1.00 ± 0.08 d	1.54 ± 0.32 b	1.45 ± 0.08 c	0.99 ± 0.01 d	1.72 ± 0.21 a
γ-Terpinene	1105	1.53 ± 0.23 a	1.21 ± 0.13 b	1.00 ± 0.04 c	1.75 ± 0.16 a	1.44 ± 0.06 b	1.70 ± 0.19 a	1.36 ± 0.23 b	0.98 ± 0.02 c
α-Terpinolene	1122	2.73 ± 0.71 b	3.01 ± 0.55 a	2.13 ± 0.02 c	4.81 ± 0.04 a	2.00 ± 0.33 c	3.20 ± 0.65 b	1.84 ± 0.26 d	3.24 ± 0.54 b
Citronellel	1140	1.32 ± 0.38 b	1.35 ± 0.23 a	1.95 ± 0.06 a	1.63 ± 0.37 b	1.40 ± 0.19 c	1.35 ± 0.16 c	0.90 ± 0.04 d	0.78 ± 0.43 e
Linalool	1162	1.43 ± 0.23 a	1.35 ± 0.24 b	1.60 ± 0.07 b	1.00 ± 0.08 e	1.25 ± 0.20 c	2.20 ± 0.04 a	1.14 ± 0.02 d	1.15 ± 0.16 cd
Cis-verbenol	1180	0.80 ± 0.34 b	0.89 ± 0.24 a	1.00 ± 0.04 c	0.75 ± 0.41 d	0.48 ± 0.26 e	0.38 ± 0.20 f	1.30 ± 0.33 a	1.18 ± 0.05 b
Trans-pinocarveol	1196	1.03 ± 0.23 b	1.18 ± 0.14 a	1.58 ± 0.05 a	0.93 ± 0.10 d	1.08 ± 0.14 c	1.13 ± 0.11 c	0.50 ± 0.29 e	1.40 ± 0.14 b
Trans-verbenol	1212	4.95 ± 0.61 b	5.13 ± 0.70 a	5.85 ± 0.86 a	5.93 ± 0.56 a	4.15 ± 0.30 c	4.63 ± 0.37 b	5.73 ± 0.57 a	3.95 ± 0.05 c
Terpinen-4-ol	1240	1.17 ± 0.11 a	1.03 ± 0.26 b	1.13 ± 0.10 b	1.55 ± 0.07 a	1.13 ± 0.05 b	1.15 ± 0.11 b	1.18 ± 0.07 b	0.48 ± 0.26 c
Myrtenal	1264	1.08 ± 0.11 b	1.23 ± 0.12 a	1.50 ± 0.08 a	0.93 ± 0.05 d	1.15 ± 0.11 b	1.13 ± 0.14 bc	1.13 ± 0.07 bc	1.08 ± 0.02 c
Myrtenol	1277	1.11 ± 0.14 a	0.84 ± 0.22 b	1.11 ± 0.19 b	1.34 ± 0.06 a	0.83 ± 0.01 d	1.04 ± 0.05 c	0.66 ± 0.36 d	0.88 ± 0.08 d
Trans-carveol	1297	0.92 ± 0.23 b	1.25 ± 0.19 a	1.20 ± 0.08 b	1.10 ± 0.08 c	1.23 ± 0.05 b	0.53 ± 0.23 e	0.84 ± 0.02 d	1.63 ± 0.19 a
Bornyl acetate	1339	1.15 ± 0.12 a	0.71 ± 0.26 b	1.20 ± 0.08 a	1.06 ± 0.06 b	1.25 ± 0.17 a	0.48 ± 0.26 d	1.04 ± 0.05 b	0.56 ± 0.30 c
p-Cymen-7-ol	1355	0.83 ± 0.21 b	0.94 ± 0.21 a	0.90 ± 0.02 c	0.00 d	0.93 ± 0.11 c	1.27 ± 0.02 a	1.00 ± 0.14 b	1.24 ± 0.17 a
α-Burbonene	1369	0.94 ± 0.10 b	1.13 ± 0.11 a	0.85 ± 0.02 d	1.05 ± 0.11 b	1.14 ± 0.10 a	1.19 ± 0.14 a	1.04 ± 0.15 b	0.95 ± 0.02 c
α-Terpenyl acetate	1396	1.29 ± 0.12 a	1.09 ± 0.12 b	1.43 ± 0.04 a	1.29 ± 0.18 b	1.18 ± 0.13 c	1.05 ± 0.02 d	1.14 ± 0.16 cd	1.06 ± 0.11 d
Longifolene	1440	3.91 ± 0.71 a	3.23 ± 1.02 b	5.30 ± 0.41 a	2.35 ± 0.65 f	2.70 ± 0.48 e	3.93 ± 0.37 c	4.34 ± 0.63 b	2.83 ± 1.00 d
Germacren D	1505	0.96 ± 0.11 a	0.88 ± 0.22 b	0.91 ± 0.02 d	0.80 ± 0.07 e	0.40 ± 0.22 f	1.10 ± 0.03 b	0.98 ± 0.02 c	1.35 ± 0.02 a
α-Muurolene	1537	0.64 ± 0.25 a	0.61 ± 0.25 b	0.38 ± 0.20 e	0.92 ± 0.16 b	1.01 ± 0.16 a	0.49 ± 0.26 d	0.36 ± 0.14 e	0.58 ± 0.31 c
Total volatile components (%)		27.88	27.39	26.47	26.73	28.67	27.04	28.28	28.59

Values with different letters are significantly different

The results of FTIR show that the pattern of the fingerprint region (500–1500 cm^{-1}) is similar for nearly all gum samples. This spectrum causes complex deformation of transmittance, which is unique for each compound, and this range cannot be used for recognition of uncertain components [31]. In the PAK spectrum, the band range at 4000–3750 cm^{-1} represents the existence of water vapor [32]. The characteristic transmission band at 3500–3200 cm^{-1} relates to the O–H stretch vibration, strong dimer O–H stretching vibration, N–H stretching vibration and aromatic secondary (2°) amine [33]. The results of FTIR spectra for nearly all PAK gum samples indicate a band at 3000–2900 cm^{-1} that was assigned to aliphatic C–H stretching related to the existence of galactose,

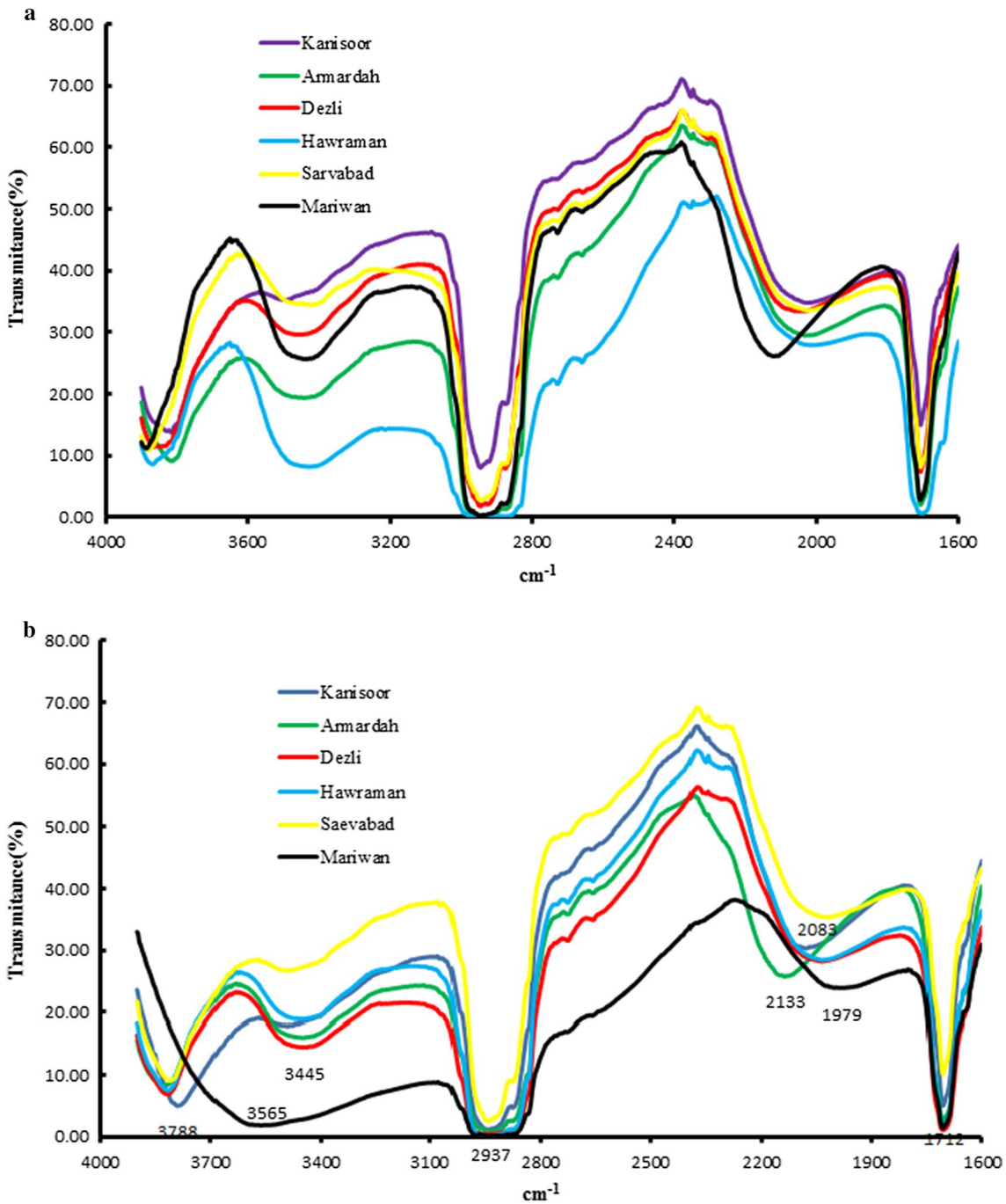

Fig. 1 FTIR spectra of kurdica gum samples from the female (**a**) and the male (**b**) trees of different regions in Kurdistan province, Iran

arabinose and rhamnose [34]. The spectra of nearly all PAK samples showed a band at 2150–1900 cm^{-1} can be assigned to aromatic cyanide and cyanate. The spectra of nearly all PAK gum samples showed a band at 1725–1700 cm^{-1} which can be assigned to the presence of carboxylic acid stretching and ketone [35]. FTIR results for female samples of the content and intensity of functional groups were higher than for the male samples in all regions.

Table 4 Matrix of Spearman's correlation coefficient for protein, amino acids and environment factors, upper triangle

	Ala	Gly	Lys	Cys	Thr	Val	Phe	His	Gln	Ile	Asn	Met	Ser	Arg	Pro	Tyr	Glu	Asp	Leu	Trp	SI	EI	MAT	TAP	SLO
Pr[a]	0.406	−0.510	−0.110	*0.823*	−0.004	−0.287	0.427	−*0.816*	−0.302	*0.775*	−0.112	0.455	*0.818*	0.203	−*0.879*	−0.175	−0.140	*0.839*	0.229	−0.450	0.399	0.112	0.036	−0.137	−0.039
Ala		−0.615	−0.515	0.346	−0.320	0.210	−0.420	−0.070	−0.035	0.449	−0.273	0.203	0.091	−0.538	−0.077	0.210	−0.259	0.224	0.250	0.193	−0.427	−0.413	0.512	−0.263	−0.221
Gly			−0.004	−0.633	−0.480	−0.490	0.252	0.326	−0.042	−*0.828*	0.644	−0.175	−0.385	0.336	0.382	0.186	−0.021	−0.392	0.123	−0.060	0.182	0.252	−0.551	0.235	0.410
Lys				0.210	*0.777*	−0.600	0.002	0.166	0.016	0.127	−0.518	0.007	−0.123	−0.152	−0.110	−0.643	0.663	−0.250	−0.149	−0.170	0.071	−0.233	−0.004	−0.055	−0.124
Cys					0.365	−0.498	0.283	−0.671	−0.489	*0.764*	−0.267	0.470	0.643	0.042	−*0.795*	−0.444	0.081	0.693	0.424	−0.174	0.131	−0.272	0.406	−0.308	−0.124
Thr						0.074	−0.329	0.270	0.097	0.369	−*0.811*	−0.042	−0.235	−0.508	0.098	−0.653	0.676	−0.308	−0108	0.002	−0.284	−0.588	0.505	−0.302	−0.477
Val							−0.434	0.557	*0.877*	−0.014	−0.441	−0.650	−0.441	−0.420	0.585	0.382	−0.077	−0.517	−0.519	−0.025	−0.196	0.112	−0.231	0.088	−0.424
Phe								−0.382	−0.635	−0.126	0.410	*0.727*	0.392	0.294	−0.438	−0.007	−0.287	0.490	0.561	−0.162	0.070	0.091	−0.174	−0.168	0.462
His									0.397	−0.580	−0.256	−0.417	−*0.970*	−0.609	0.972	0.033	0.336	−*0.963*	−0.178	0.389	−0.613	−0.431	0.121	−0.047	−0.184
Gln										0.107	−0.459	−*0.779*	−0.288	−0.200	0.467	0.206	0.049	−0.470	−0.694	−0.145	0.168	0.340	−0.399	0.348	−0.401
Ile											−0.598	0.105	0.642	−0.098	−0.640	−0.327	0.074	0.565	−0.120	−0.224	0.309	0.021	0.157	0.049	−0.267
Asn												0.161	0.126	0.662	−0.137	0.453	−0.466	0.252	0.336	−0.060	0.193	0.357	−0.267	−0.007	0.433
Met													0.399	0.042	−0.487	−0.235	−0.021	0.510	0.515	−0.039	−0.112	−0.245	0.306	−0.294	0.298
Ser														0.510	−*0.942*	−0.007	−0.399	−*0.951*	0.106	−0.330	−0.601	0.483	−0.192	0.158	0.249
Arg															−0.525	0.095	−0.217	0.510	−0.053	−0.446	−*0.692*	*0.720*	−0.508	0.102	0.137
Pro																0.170	0.203	−*0.949*	−0.228	0.389	−0.543	−0.291	0.039	0.047	−0.132
Tyr																	−*0.830*	0.063	−0.019	0.132	−.182	0.326	−0.185	−0.012	0.095
Glu																		−0.448	−0.236	−0.151	−0.028	−0.399	0.174	−0.070	−0.347
Asp																			0.243	−0.243	0.427	0.357	−0.046	−0.021	0.224
Leu																				0.053	−0.254	−0.490	0.405	−0.440	0.201
Trp																					−0.605	−0.309	0.239	0.278	0.431
SI																						*0.741*	−0.689	0.501	0.158
EI																							−*0.842*	0.567	0.270
MAT																								−0.694	−0.384
TAP																									0.618

[a] Pr, Protein; Ala, Alanine; Gly, Glycine; Lys, Lysine; Cys, Cysteine; Thr, Threonine; Val, Valine; Phe, Phenylalanine; His, Histidine; Gln, Glutamine; Ile, Isoleucine; Asn, Asparagine; Met, Methionine; Ser, Serine; Arg, Arginine; Pro, Proline; Tyr, Tyrosine; Glu, Glutamic acid; Asp, Aspartic acid; Leu, Leucine; Trp, Tryptophan; SI, solar illumination during 1 year (W m^{-2}); EI, elevation (m); MAT, mean annual temperature (°C); TAP, total annual precipitation (mm); SLO, slope (%); underline---d numbers: $P < 0.05$; italics numbers: $P < 0.01$

Underlined numbers denote $P < 0.05$

Italic numbers denote $P < 0.01$

Table 5 Matrix of Spearman's correlation coefficient for volatile components and environment factors, upper triangle

	VoC2	VoC3	VoC4	VoC5	VoC6	VoC7	VoC8	VoC9	VoC10	VoC11	VoC12	VoC13	VoC14	VoC15	VoC16	VoC17	VoC187	VoC19	VoC20	VoC21	SI	EI	MAT	TAP	SLO
VoC1	−0.604	−0.021	−0.214	0.097	−0.629	−0.254	0.023	−0.013	0.450	−0.488	−0.148	−0.117	−0.141	−0.302	−0.055	0.458	0.328	0.123	−0.346	−0.023	−0.075	−0.374	0.400	−0.476	−0.367
VoC2		−0.039	0.233	−0.391	*−0.933*	0.271	−0.197	0.460	−0.484	0.489	0.173	0.021	−0.263	0.214	−0.179	*−0.862*	−0.312	−0.283	0.234	−0.049	−0.147	0.119	−0.064	0.193	0.536
VoC3			−0.064	−0.539	−0.011	−0.058	0.436	0.451	−0.077	0.462	−0.261	0.039	0.134	−0.258	0.464	−0.304	−0.034	0.233	−0.226	−0.509	−0.428	−0.091	0.169	−0.018	0.002
VoC4				0.103	−0.255	0.348	−0.335	−0.219	0.074	0.147	0.607	−0.215	−0.133	0.263	−0.356	−0.110	−0.002	−0.241	−0.064	−0.345	0.131	0.046	−0.283	0.606	*0.756*
VoC5					0.242	−0.012	−0.069	*−0.841*	−0.005	−0.676	0.374	0.000	0.025	−0.309	−0.333	0.697	0.182	−0.262	0.180	0.041	0.637	0.433	−0.270	0.108	−0.118
VoC6						−0.249	0.120	−0.319	0.625	−0.236	−0.297	0.049	0.224	−0.104	0.236	*0.772*	0.286	0.369	−0311	0.144	0.133	−0.228	0.111	−0.172	−0.622
VoC7							−0.048	0.093	−0.423	0.269	0.114	−0.257	0.455	0.083	−0.261	−0.238	−0.368	0.018	0.272	−0.076	−0.316	−0.418	0.418	−0.012	0.074
VoC8								0.041	0.115	0.163	−0.343	0.084	0.034	−0.169	0.108	0.086	0.053	0.094	0.135	−0.134	−0.025	−0.035	0.032	−0.349	−0.289
VoC9									−0.158	0.616	−0.279	0.284	−0.188	0.086	0.104	*−0.731*	−0.181	−0.071	−0.218	−0.092	−0.470	−0.256	0.269	−0.213	−0.037
VoC10										0.011	0.030	0.189	−0.195	0.075	−0.168	0.304	0.631	0.037	−0.254	−0.079	0.323	−0.158	−0.121	0.132	−0.125
VoC11											−0.292	0.120	−0.063	0.309	0.276	−0.599	−0.278	0.173	−0.093	−0.058	−0.316	−0.232	0.079	0.118	0.070
VoC12												0.343	0.060	0.029	*−0.719*	−0.099	0.545	*−0.801*	0.303	−0.435	0.407	0.453	−0.484	0.677	0.520
VoC13													−0.039	−.107	−0.362	−0.133	0.471	−0.694	−0.050	−0.267	0.497	0.587	−0.551	0.389	−0.179
VoC14														0.050	0.129	0.112	0.098	0.210	0.444	−0.026	−0.337	−0.242	0.244	0.109	−0.293
VoC15															0.183	−0.072	−0.094	0.051	0.354	0.624	0.336	−0.264	−0.189	0.050	0.089
VoC16																0.143	−0.420	*0.754*	−0.105	0.409	−0.538	−0.239	0.232	−0.354	−0.350
VoC17																	0.108	0.218	−0.106	0.301	0.340	0.077	−0.135	−0.158	−0.435
VoC18																		−0.484	0.280	−0.297	0.290	0.149	−0.191	0.255	−0.106
VoC19																			−0.226	0.337	−0.496	−0.595	0.538	−0.420	−0.266
VoC20																				0.311	−0.258	−0.092	0.099	−0.115	−0.152
VoC21																					−0.270	−0.302	0.144	−0.522	−0.466
SI																						*0.741*	−0.689	0.501	0.158
EI																							*−0.842*	0.567	0.270
MAT																								−0.694	−0.384
TAP																									0.618

VoC1: α-Thujene; VoC2: α-Pinene; VoC3: Comphene; VoC4: verbenone; VoC5: sabinene; VoC6: β-Pinene; VoC7: Myrcene; VoC8: α-Phelandrene; VoC9: p-cymen; VoC10: Limonene; VoC11: 1,8-cineole; VoC12: γ-terpinene; VoC13: α-terpinolene; VoC14: Citronellel; VoC15: Linalool; VoC16:Trans-pinocarveol; VoC17: trans-verbenol; VoC18: Terpinen-4-ol; VoC19: myrtenal; VoC20:α-terpenyl acetate; VoC21: longifolene

Underlined numbers denote $P < 0.05$

Italic numbers denote $P < 0.01$

Table 6 Matrix of Spearman's correlation coefficient for ash, moisture, carbohydrates and environment factors, upper triangle

	Ash	TS	Ara	Gal	Rha	Fuc	Xyl	Glc	GlcA	GalA	SI	EI	MAT	TAP	SLO
MO	−0.175	0.287	0.476	−0.070	−0.126	−0.462	−0.382	−0.021	−0.218	0.165	−0.133	0.224	−0.298	0.021	−0.298
Ash		−0.196	−0.102	0.161	0.280	0.081	0.239	0.273	0.295	−0.042	−0.441	−0.517	0.494	−0.469	−0.207
TS			0.308	−0.105	−0.098	−0.420	−0.046	−0.091	*−0.710*	−0.217	−0.371	−0.357	0.270	−0.343	−0.497
Ara				0.599	−0.708	*−0.912*	*−0.898*	−0.648	−0.306	0.488	−0.259	0.312	−0.025	−0.139	−0.358
Gal					*−0.839*	−0.676	*−0.754*	*−0.804*	0.018	0.347	0.028	0.217	0.188	−0.039	−0.403
Rha						*0.781*	*0.881*	*0.916*	0.309	−0.455	−0.224	−0.455	0.028	−0.074	0.403
Fuc							*0.852*	0.630	0.403	−0.386	0.130	−0.242	−0.021	0.207	0.600
Xyl								*0.775*	0.183	−0.543	−0.007	−0.502	0.125	−0.012	0.322
Glc									0.211	−0.294	−0.112	−0.378	−0.014	−0.263	0.175
GlcA										−0.239	−0.144	−0.095	0.063	0.276	0.590
GalA											0.350	0.630	−0.247	−0.193	−0.102
SI												*0.741*	−0.689	0.501	0.158
EI[a]													*−0.842*	0.567	0.270
MAT														*−0.694*	−0.384
TAP															0.618

MO, moisture; TS, total sugar; Ara, arabinose; Gal, galactose; Rha, rhamnose; Fuc, fucose; Xyl, xylose; Glc, glucose; GlcA, glucuronic acid; GalA, galacturonic acid

Underlined numbers denote P < 0.05

Italic numbers denote P < 0.01

Statistical relationships

Spearman rank correlation coefficient results among oleoresin properties and environment factors (slope, annual solar illumination, elevation, mean annual temperature and total annual precipitation) are shown in Tables 4, 5 and 6. Fucose, glucuronic acid and β-pinene ($P<0.05$) and verbenone ($P<0.01$) contents display significant positive correlation with terrain slope. Solar illumination showed significantly negative correlations with histidine and serine at $P<0.05$ ($r=(-0.613)$–(-0.558)) and with arginine at $P<0.01$ ($r=-0.692$). Except for sabinene, no significant correlation observed between volatile components and solar illumination. Elevation significantly correlates with arginine at $P<0.01$ ($r=0.720$) and with galacturonic acid and α-terpinolene at $P<0.05$ ($r=0.630$ and 0.587, respectively). Also, elevation is found to be negatively correlated with threonine ($r=-0.588$). The significant correlation between chemical components and total annual precipitation was observed only for verbenone and α-terpinene at $P<0.05$ ($r=0.606$ and 0.677, respectively).

Previous studies have showed clear evidence that amino acid compositions have high correlation with environment characteristics (solar illumination, elevation, mean annual temperature and total annual precipitation) [36–42]. It is well-established in the literature that environmental factors (solar illumination, total annual precipitation) plays a fundamental role in the control content of carbohydrates production by photosynthesis [43–47]. According to Maxwell [49], changes in climate will strongly affect environmental factors. These changes in turn will affect availability of important resources for plants such as degree days, light, soil moisture, soil nutrients and soil oxygen that will potentially result in large alterations, both qualitatively and quantitatively, in production of secondary compounds [39, 48–51].

Thermogravimetric analysis

TGA is a simple and precise method used to assay the decomposition model and the thermal stability of polymers. The results of TGA and derivative mass loss measurements of PAK gum samples are shown in Table 7.

The primary and derivative thermograms for the PAK gum samples in the TGA curves showing the details of thermal behavior are given in Table 7. Nearly all samples of the various regions exhibited double major stage decomposition patterns, except for the female trees of the Dezli and Hawraman regions (which have three stages). The first stage occurs at 80 °C and can be attributed to the desorption of volatile essential oils and the loss of moisture and structural water, which in turn is associated with the hydrochloric nature of the functional groups of the PAK gum samples (mass loss of 20% to 25%) [52].

The second stage of the samples from Dezli and Hawraman occurred at 200 to 300 °C (mass loss of 45% to 53%) and the main decomposition of samples started above 240 to 360 °C (mass loss of 80% to 92%), both due to polysaccharide and polypeptide thermal decomposition [12,

Table 7 Thermo-gravimetric data of PAK gum samples from the female and the male trees of different regions in Kurdistan province, Iran

Gender	Regions	No. of decomposition stage	Temprature range (°C)	Derivative mass loss peak (°C)	Mass loss%	Activation energy (kJ mol^{-1})[a]
Female	Armardeh	1	27.11–162	93.68	22.53	52.24
		2	162–275	–	32.60	–
		3	275–402	362.3	91.15	56.42
		4	402–600	–	99.54	–
	Kanisur	1	30.71–149	86.47	21.96	55.96
		2	149–241	–	29.75	–
		3	241–379	339.80	80.02	39.77
		4	379–600	405.76	99.48	47.81
	Dezli	1	26.79–164.82	77.21	24.86	47.64
		2	165.133–207.31	–	28.84	–
		3	207.70–286.67	257.99	43.39	14.94
		4	287.22–399.33	359.46	92.19	50.96
		5	399.43–600	–	99.5	–
	Hawraman	1	29.60–142.74	84.07	19.82	68.92
		2	143.20–201.06	–	25.99	–
		3	201.83–309.75	289.67	52.65	28.08
		4	310.40–388.08	352.17	90.52	48.98
		5	388.89–600	–	99.52	–
	Sarvabad	1	29.67–149.85	93.07	19.05	66.98
		2	150.21–278.82	–	33.91	–
		3	279.17–402.36	354.315	90.34	52.28
		4	402.36–600	–	99.71	–
	Marivan	1	29.80–160.92	80.28	22.42	64.06
		2	161.26–276.08	–	32.87	–
		3	276.12–402.73	357.59	90.22	52.78
		4	403–600	–	99.52	–
Male	Armardeh	1	26.67–156.23	84.20	23.43	62.51
		2	157.19–241.49	–	29.49	–
		3	242.638–409.53	344.14	87.10	39.62
		4	410.18–600	–	99.51	–
	Kanisur	1	26.49–171.38	85.20	23.46	58.93
		2	172.273–256.47	–	29.49	–
		3	320.131–395.24	350.73	87.1	48.83
		4	395.64–600	–	99.51	–
	Dezli	1	26.79–164.82	80	27.72	45.22
		2	165.133–207.31	–	51.48	–
		3	207.70–286.67	270.69	91.18	28.5
		4	287.22–399.33	349.85	99.62	54
	Hawraman	1	31.38–124.21	93.15	14.07	53.02
		2	124.66–292.79	–	33.55	–
		3	292.80–401.55	363.23	90.97	57.97
		4	402.315–600	–	99.71	–
	Sarvabad	1	32.60–179.97	97.65	23.25	59.22
		2	180.36–273.40	–	30.75	–
		3	273.56–402.68	358.69	90.09	57.59
		4	402.98–600	–	99.52	–
	Marivan	1	26.86–197.66	83.30	28.15	64.06
		2	198.40–309.77	278.21	56.12	–
		3	309.83–385.38	350.73	90	52.78
		4	385.68–600	–	99.57	–

[a] Activation energy for the major stage of decomposition according to the Borido method

Table 8 DSC thermo-gram data of PAK gum samples from the female and the male trees of different regions in Kurdistan province, Iran

Regions	Gender	Glass transition temperature (T_g1)		Glass transition temperature (T_g2)		Peak of melting temperature (T_m) (°C)	Enthalpy changes (DH) (J g^{-1})	Heat capacity [C_p (J g^{-1} k^{-1}]
		T_g (°C)	ΔC_p (J g^{-1} k^{-1})	T_g (°C)	ΔC_p (J g^{-1} k^{-1})			15 (°C)
Armardeh	Female	−34.08	0.19	49.95	44.11	–	–	1.71
	Male	−29.21	0.16	–	–	–	–	1.78
Kanisoor	Female	−25.86	0.22	49.25	11.03	–	–	1.67
	Male	−24.95	0.08	65.18	46.59	–	–	1.77
Dezli	Female	−27.28	0.25	39.48	27.47	61.52	−0.30	1.70
	Male	−31.43	0.23	72.27	81.00	51.19	−0.24	1.74
Hawraman	Female	−27.49	0.24	46.24	3.43	63.85	−0.17	1.68
	Male	−27.84	0.24	64.80	30.63	–	–	1.79
Sarvabad	Female	−24.16	0.21	49.81	6.37	–	–	1.72
	Male	−27.60	0.24	60.70	0.11	–	–	1.70
Marivan	Female	−26.15	0.263	42.07	33.01	–	–	1.71
	Male	−27.46	0.24	58.23	2.71	–	–	1.76

52]. The peaks of the derivative mass loss curves of female trees occurred at 362.3, 339.80, 359.46, 352.17, 355.64 and 357.59 °C for Armardeh, Kanisoor, Dezli, Hawraman, Sarvabad and Marivan, respectively. The peaks of the derivative mass loss curves of the male trees appeared at 344.14, 350.73, 349.85, 363.23, 358.69 and 350.73 for Armardeh, Kanisoor, Dezli, Hawraman, Sarvabad and Marivan, respectively.

The stimulation of thermal decomposition can be quantitatively shown by determining the apparent activation energy (E_a) for the main steps of decomposition of the samples. The Borido method is effective for the evaluation of the activation energy [53]. The Borido equation is:

$$\ln\left(\ln\left(\frac{1}{y}\right)\right) = \ln\left(\ln\left(\frac{W_0 - W_\infty}{W_t - W_\infty}\right)\right) = -\left(\frac{E_a}{RT}\right) + c \quad (1)$$

where W_t denotes the mass of the PAK gum samples at time t and W_0 and W_∞ denote the initial and final masses, respectively. From the slope of graphs of $\ln\left(\ln\left(\frac{1}{y}\right)\right)$ versus $\frac{1000}{T}$ (T denotes absolute temperature), the E_a of any stage of decomposition could be evaluated ($Y = -6.0083X + 9.5883$; $R^2 = 0.9958$). According to the data of the plots, the E_a of the samples from female trees were lower than for male trees. In other words, the gum from female trees decomposed faster than from male trees (Table 7).

Differential scanning calorimetry

This method was used to determine the glass transition temperature, melting point, heat capacity and enthalpy of all PAK gum samples. The DSC thermograms of the PAK gum samples are shown in Table 8 along with the thermal transition behavior of the female and male gum samples. Nearly all gum samples had two glass transition temperatures, except for the male sample from the Armardeh region, which had only one T_g. The results showed that the T_g for the male samples were higher than for the female samples. T_m (Melting temperature) values occurred only for the Dezli and Hawraman regions and the exothermic enthalpy values for these samples showed an overall decrease in enthalpy by the generation of heat. The low glass transition temperature of all gum samples could relate to their low molecular weights signifying that glass to rubber transition occurs readily as a result of water sorption and can cause physical properties such as stickiness [54]. This is consistent with the apparent properties of the compound under consideration.

The DSC plots were also used to determine the heat capacity (C_P) of the samples. Table 6 shows the heat capacity behavior of the female and male gum samples. As seen, the C_P values of the female gum samples are lower than for the male samples, except for the samples from the Sarvabad region. The C_P values at 15 °C show that they varied by region. Table 8 also shows that the male samples from the Hawraman region and the female samples from the Kanisoor region, recorded the maximum and minimum C_P values, respectively.

The chemical composition and thermal properties of PAK gum samples determined from the female and male trees of different regions of Kurdistan province revealed that the female tree samples had higher TC contents than the male samples. Arabinose and galactose were the most abundant monosaccharides in the samples, suggesting an arabinogalactan structure of the analyzed gums. High concentrations of serine and proline may influence the arabinogalactan-proteins in the gum samples. In both the

female and male samples, α-Pinene was determined to be the principle volatile component. The PAK gum samples showed different thermal properties due to the functional group differences.

The TGA results indicated two-stage decomposition with the main decomposition of samples beginning above 240 to 360 °C. The results of E_a indicate that the female tree gums decomposed faster than the male tree gums and the minimum value of E_a was observed for the samples collected from the Dezli region. The results of DSC indicated that the T_g of nearly all the gum samples included two glass transition temperatures. The T_g values of the male samples were higher than for the female samples. The C_P value of all the female samples were lower than for the male samples. The maximum and minimum C_P values were determined for samples from Hawraman and Kanisoor, respectively. The FTIR results showed that the content and intensity of the functional groups from the female samples were higher than for the male samples in all regions investigated. These results can improve our understanding about the optimization of PAK gum usage from different geographic regions.

Authors' contribution

FM, carried out gum sampling, spatial analyses, chemical and thermal analyses of gum samples, statistical analyses and drafted the manuscript. MM, carried out thermal analyses (DSC and TGA), interpreting obtained thermograms and participated in drafting the manuscript. RS, carried out FTIR and GC-Mass analyses and interpreting the obtained results. MHG, analysis of sugars and amino acids using HPLC and interpreting the obtained results. All authors read and approved the final manuscript.

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Competing interest

The authors declare that they have no competing interests.

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References

1. Zohary M (1952) A monographical study of the genus *Pistacia*. Palestine J Bot Jerus Ser 5:187–228
2. Martinez J-JI (2008) Impact of a gall-inducing aphid on *Pistacia atlantica* Desf. trees. Arthropod Plant Interact 2:147–151
3. Pazouki L, Mardi M, Shanjani PS, Hagidimitriou M, Pirseyedi SM, Naghavi MR, Avanzato D, Vendramin E, Kafkas S, Ghareyazie B, Ghaffari MR, Khayam Nekoui SM (2010) Genetic diversity and relationships among *Pistacia* species and cultivars. Conserv Genet 11:311–318
4. Farhoosh R, Tavakoli J, Khodaparast MHH (2008) Chemical composition and oxidative stability of kernel oils from two current subspecies of *Pistacia atlantica* in Iran. J Am Oil Chem Soc 85:723
5. Sharifi MS, Hazell SL (2011) GC-MS analysis and antimicrobial activity of the essential oil of the trunk exudates from *Pistacia atlantica* kurdica. J Pharm Sci Res 3:1364
6. Orhan I, Özçelik B, Aslan S, Kartal M, Karaoglu T, Şener B, Terzioglu S, Choudhary MI (2007) Antioxidant and antimicrobial actions of the club-moss *Lycopodium clavatum* L. Phytochem Rev 6:189–196
7. Zhu B, Wang Q, Roge EF, Nan P, Liu Z, Zhong Y (2006) Chemical variation in leaf oils of *Pistacia chinensis* from five locations in China. Chem Nat Compd 42:422–425
8. Benhammou N, Bekkara FA, Panovska TK (2008) Antioxidant and antimicrobial activities of the *Pistacia lentiscus* and *Pistacia atlantica* extracts. Afr J Pharm Pharmacol 2:022–028
9. Rahimi AR, Hadyan J, Azizi M, Abdoosi V, Larijani K (2013) Comparison of chemical compounds found in the gum essential oil of male and female *Pistacia atlantica* subsp. Kurdica. J Biodivers Environ Sci 3:174–178
10. Barrero AF, Herrador MM, Arteaga JF, Akssira M, Mellouki F, Belgarrabe A, Blázquez MA (2005) Chemical composition of the essential oils of *Pistacia atlantica* Desf. J Essent Oil Res 17:52–54
11. Karamalla K (1999) Gum arabic production, chemistry and applications. University of Khartoum, Sudan, pp 4–30
12. Zohuriaan MJ, Shokrolahi F (2004) Thermal studies on natural and modified gums. Polym Test 23:575–579
13. Bothara SB, Singh S (2012) Thermal studies on natural polysaccharide. Asian Pac J Trop Biomed 2:S1031–S1035
14. Roos YH, Drusch S (2005) Phase transitions in foods. Academic Press, Cambridge
15. Sharifi MS (2006) Fractionations and analysis of trunk exudates from *Pistacia* genus in relation to antimicrobial activity. A thesis of Docotor of Philosophy, College of Health and Science, University of Western Sydney. Sydney, Australia
16. Karamshahi A, Tahmasbi M, Najafifar A (2005) Study the best method of resin extraction from *Pistacia atlantica* trees. Paj Saz 66:78–82 **(In Persian)**
17. Thiex N (2008) Evaluation of analytical methods for the determination of moisture, crude protein, crude fat, and crude fiber in distillers dried grains with solubles. J AOAC Int 92:61–73
18. Miller GL (1959) Protein determination of large numbers of samples. Anal Chem 31:964
19. Rasouli Z, Akbari-Adergani B (2016) Assessment of aspartame exposure due to consumption of some imported chewing gums by microwave digestion and high performance liquid chromatography analysis. Orient J Chem 32:1649–1658
20. Masuko T, Minami A, Iwasaki N, Majima T, Nishimura S-I, Lee YC (2005) Carbohydrate analysis by a phenol–sulfuric acid method in microplate format. Anal Biochem 339:69–72
21. Qi W, Fong C, Lamport DT (1991) Gum arabic glycoprotein is a twisted hairy rope: a new model based on O-galactosylhydroxyproline as the polysaccharide attachment site. Plant Physiol 96:848–855
22. Krause I, Bockhardt A, Neckermann H, Henle T, Klostermeyer H (1995) Simultaneous determination of amino acids and biogenic amines by reversed-phase high-performance liquid chromatography of the dabsyl derivatives. J Chromatogr A 715:67–79
23. Ai Y, Yu Z, Chen Y, Zhu X, Ai Z, Liu S, Ni D (2016) Rapid determination of the monosaccharide composition and contents in tea polysaccharides from Yingshuang green tea by pre-column derivatization HPLC. J Chem 2016:6065813. https://doi.org/10.1155/2016/6065813
24. Postulkova H, Chamradova I, Pavlinak D, Humpa O, Jancar J, Vojtova L (2017) Study of effects and conditions on the solubility of natural polysaccharide gum karaya. Food Hydrocoll 67:148–156
25. Huang Y, Lu J, Xiao C (2007) Thermal and mechanical properties of cationic guar gum/poly (acrylic acid) hydrogel membranes. Polym Degrad Stab 92:1072–1081
26. Tryfona T, Liang H-C, Kotake T, Tsumuraya Y, Stephens E, Dupree P (2012) Structural characterisation of *Arabidopsis* leaf arabinogalactan polysaccharides. Plant Physiol 160:653–666
27. Fadavi G, Mohammadifar MA, Zargarran A, Mortazavian AM, Komeili R (2014) Composition and physicochemical properties of Zedo gum exudates from *Amygdalus scoparia*. Carbohydr Polym 101:1074–1080
28. Critto A, Carlon C, Marcomini A (2003) Characterization of contaminated soil and groundwater surrounding an illegal landfill (S. Giuliano, Venice, Italy) by principal component analysis and kriging. Environ Pollut 122:235–244

29. Khatiy Chhetri DB (1999) Comparison of forest biomass across a human-induced disturbance gradient in Nepal's Schima-Castanopsis forests. J Sustain For 9:69–82
30. Måren IE, Karki S, Prajapati C, Yadav RK, Shrestha BB (2015) Facing north or south: does slope aspect impact forest stand characteristics and soil properties in a semiarid trans-Himalayan valley? J Arid Environ 121:112–123
31. Rodrigues Filho G, de Assunção RM, Vieira JG, Meireles CdS, Cerqueira DA, da Silva Barud H, Ribeiro SJ, Messaddeq Y (2007) Characterization of methylcellulose produced from sugar cane bagasse cellulose: crystallinity and thermal properties. Polym Degrad Stab 92:205–210
32. Petrea P, Amarioarei G, Apostolescu N, Puiel AC, Ciovica S (2013) Some aspects of the characterization of vegetable gums: prunus persica (plum) and prunus domestica (cherry). Cellul Chem Technol 47:369–375
33. Cerqueira MA, Souza BW, Simões J, Teixeira JA, Domingues MRM, Coimbra MA, Vicente AA (2011) Structural and thermal characterization of galactomannans from non-conventional sources. Carbohydr Polym 83:179–185
34. Daoub RM, Elmubarak AH, Misran M, Hassan EA, Osman ME (2016) Characterization and functional properties of some natural Acacia gums. J Saudi Soc Agric Sci 17:241–249
35. Coates J (2000) Interpretation of infrared spectra, a practical approach. Ency Anal Chem 12:10815–10837
36. García del Moral LF, Rharrabti Y, Martos V, Royo C (2007) Environmentally induced changes in amino acid composition in the grain of durum wheat grown under different water and temperature regimes in a Mediterranean environment. J Agric Food Chem 55:8144–8151
37. Cao X, Ma Q, Zhong C, Yang X, Zhu L, Zhang J, Jin Q, Wu L (2016) Elevational variation in soil amino acid and inorganic nitrogen concentrations in Taibai Mountain, China. PloS One 11:e0157979
38. Song W, Yang R, Wu T, Wu C, Sun S, Zhang S, Jiang B, Tian S, Liu X, Han T (2016) Analyzing the effects of climate factors on soybean protein, oil contents, and composition by extensive and high-density sampling in China. J Agric Food Chem 64:4121–4130
39. Gambetta JM, Cozzolino D, Bastian SE, Jeffery DW (2017) Exploring the effects of geographical origin on the chemical composition and quality grading of *Vitis vinifera* L. cv. Chardonnay grapes. Molecules 22:218
40. Amelung W, Zhang X, Flach K (2006) Amino acids in grassland soils: climatic effects on concentrations and chirality. Geoderma 130:207–217
41. Assefa Y, Bajjalieh N, Archontoulis S, Casteel S, Davidson D, Kovács P, Naeve S, Ciampitti IA (2018) Spatial characterization of soybean yield and quality (amino acids, oil, and protein) for United States. Sci Rep 8:14653
42. Sidle AB (1967) Amino acid content of atmospheric precipitation. Tellus 19:128–135
43. Davis FW, Goetz S (1990) Modeling vegetation pattern using digital terrain data. Landsc Ecol 4:69–80
44. Austin M (2002) Spatial prediction of species distribution: an interface between ecological theory and statistical modelling. Ecol Modell 157:101–118
45. Lebourgeois F (2007) Climatic signal in annual growth variation of silver fir (*Abies alba* Mill.) and spruce (*Picea abies* Karst.) from the French Permanent Plot Network (RENECOFOR). Ann For Sci 64:333–343
46. Li MH, Cherubini P, Dobbertin M, Arend M, Xiao WF, Rigling A (2013) Responses of leaf nitrogen and mobile carbohydrates in different Quercus species/provenances to moderate climate changes. Plant Biol 15:177–184
47. Sperling O, Silva LC, Tixier A, Théroux-Rancourt G, Zwieniecki MA (2017) Temperature gradients assist carbohydrate allocation within trees. Sci Rep 7:3265
48. Hanover JW (1966) Genetics of terpenes I. Gene control of monoterpene levels in *Pinus monticola* dougl. Heredity 21:73
49. Maxwell JC, Pesic P (2001) Theory of heat. Courier Corporation, North Chelmsford
50. Boer G, McFarlane N, Lazare M (1992) Greenhouse gas–induced climate change simulated with the CCC second-generation general circulation model. J Clim 5:1045–1077
51. Houghton J, Ding Y, Griggs D, Noguer M, Van Der Linden P, Dai X, Maskell K, Johnson C (2001) Climate change 2001: the scientific basis. Contribution of working group I to the third assessment report of the international panel on climate change. Cambridge University Press, Cambridge, vol 36, pp 44
52. Rezaei A, Nasirpour A, Tavanai H (2016) Fractionation and some physicochemical properties of almond gum (*Amygdalus communis* L.) exudates. Food Hydrocoll 60:461–469
53. Broido A (1969) A simple, sensitive graphical method of treating thermogravimetric analysis data. J Polym Sci B Polym Phys 7:1761–1773
54. Harnkarnsujarit N, Charoenrein S (2011) Influence of collapsed structure on stability of β-carotene in freeze-dried mangoes. Food Res Int 44:3188–3194