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Some Chemotaxonomic Characteristics of Local Garlic Genotypes

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Abstract

This study was carried out to determine some chemotaxonomic characteristics such as volatile sulfur compounds, mineral and protein content of 7 garlic genotypes grown in Hatay province. The results revealed that the garlic genotypes have a large variation in terms of sulfur compound, mineral and protein content. A total of 10 volatile sulfur compounds were detected, mainly diallyl disulphide and its amount in the genotypes varied between 41.51% and 59.48%. The highest value (59.48%) was detected in genotype Altınözü 2. The mineral content of determined in garlic genotypes also differed among genotypes. Samandağ 2, Samandağ 3 and Hatay 1 had higher value in terms of Cu, Samandağ 1, Hatay 1 and Hatay 2 had higher value in terms of Zn, Samandağ 2, Altınözü 2, and Hatay 1 had higher value in terms of Na, Samandağ 1, Hatay 1, and Samandağ 3 had higher value in terms of K, Samandağ 1 had higher value in Ca and Fe, Altınözü 2 had higher value in terms of Mn, and Samandağ 2, Hatay 1, and Hatay 2 had high value in terms of Mg. The protein content of the garlic genotypes varied between 4.77% and 7.71%. It is thought that this study will form a basis for the evaluation of these genotypes in breeding programs.

Key Words: Allium sativum L., Garlic, GC-MS, Mineral content, Protein, Sulfur compounds

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1. Introduction

Garlic (Allium sativum L.) belongs to the genus Allium in the family Alliaceae and is the second most cultivated vegetable crop after onion in this family. It is known its strong aromatic bulby crop worldwide (Martins et al., 2016). Garlic, which is grown in almost all regions of Türkiye, can meet the optimum temperature conditions it requires better in the Mediterranean climate. Garlic is widely cultivated in Altınözü, Center and Samandağ districts of Hatay, Center district of Kahramanmaraş and Center, Elmalı and Korkuteli districts of Antalya in the Mediterranean Region (İbret, 2013).

According to data from the Turkish Statistical Institute, garlic accounts for 5% of the total vegetable production in Türkiye; 4% of this rate is dry garlic with a production of 116840 tons and 1% is fresh garlic with a production of 28552 tons. The highest garlic production is in Gaziantep province with 33973 tons on an area of 26222 ha, Kastamonu ranks second with 22995 tons and Kahramanmaraş ranks third with 17259 tons. In Hatay province, which ranks ninth in production, cultivation is carried out on a total area of 3396 ha with 3025 tons of dry garlic and 396 tons of fresh garlic (Anonymous, 2022). Scientific and clinical research reports that garlic boosts immunity, protects against infection and inflammation, and helps reduce the risk of cancer, heart disease and dementia (Gebreyohannes and Gebreyohannes, 2013; Sehitoglu et al., 2018; Yarali Karakan, 2022). The positive effects of garlic on human health are due to its chemical composition. These biological activities are due to volatile compounds such as essential oils and mineral content (Martins et al., 2016; Turan et al., 2017; Petropoulos et al., 2018). Garlic contains 0.2-0.5% garlic oil and 94% of garlic oil is composed of sulfur compounds (4.7-8.0% diallyl sulfide, 21.9-40.0% diallyl disulphide, 39.0-41.5% diallyl trisulfide) (Akan, 2014). The compound allicin, which is found in 4-5 mg in a clove of garlic and is extremely important for human health, occurs when garlic cloves are mechanically damaged. This compound is formed by the degradation of allylins, a sulfur amino acid, by the enzyme allylinase (Tung and Chung, 1989). After allicin is produced, it contributes to the formation of allyl methyl disulphide and diallyl disulphide (Özcan Sinir and Barringer, 2020).

The macro and micro elements found in foods are important not only because of their essential nutritional value, but also because of their beneficial effects on human health. Therefore, analyzing the mineral composition of various foods is of critical importance in human nutrition (Turan et al., 2017). Increasing yield quality and quantity in garlic production is possible through the development of cultivars resistant to diseases and pests. For this purpose, studies to determine the potential of existing genotypes should be emphasized (Yarali Karakan et al., 2024). In many studies, protein, essential oil and mineral contents of garlic cultivated in different regions of our country have been investigated. However, no scientific study on local genotypes grown in Hatay province where the production is high was found in the literature. Therefore, the aim of this study was to determine the protein, mineral content and volatile sulfur compounds of garlic genotypes grown in Hatay province.

2. Material and Methods

2.1. Material

In the study, 7 garlic genotypes (Altınözü 1, Altınözü 2, Hatay 1, Hatay 2, Samandağ 1, Samandağ 2, Samandağ 3) cultivated in Altınözü, Center and Samandağ districts of Hatay province and Taşköprü garlic, cultivated commercially in Türkiye, as reference were used. The cloves of garlic genotypes obtained from the cultivation regions.

2.2. Methods

2.2.1. Determination of volatile sulfur compounds of garlic genotypes

Garlic cloves were peeled and crushed and 5 g of garlic sample placed in 10 ml GC vials. The extraction of the volatile components of garlic cloves was carried out using a headspace unit in an oven at 80 °C for 45 minutes (Calvo-Gomez et al., 2004). After extraction, the volatile components were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) model Agilent mvda 7890B GC-5977 MSD. HP-5 MS (30 m x 0.25 mm i.d., film thickness 0.25 m; Hewlett-Packard) was used as capillary column and mass detector was used as detector. According to the arrival times of the fragmented ions at the mass the percentages detector, of volatile components were calculated using the NIST and WILEY libraries.

2.2.2. Determination of mineral content of garlic genotypes

The garlic cloves were peeled and cut into slices, the samples were dried in a compressed air oven at 72 °C and the dried samples were powdered with a mortar and pestle. Powdered 0.25 g of sample was taken, mixed with 9 ml nitric acid (HNO₃)

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and 3 ml hydrogen peroxide (H₂O₂) and burned in a microwave oven under 200 W power for 30 minutes. The digested samples were filtered through 42 Whatman filter papers with a diameter of 125 mm and placed in 50 ml plastic tubes and diluted by adding distilled water to a final volume of 25 ml (Petropoulos et al., 2018). Calcium (Ca), Magnesium (Mg), Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu) contents were determined by Atomic Absorption Spectrometry (AAS, Perkin Elmer 1100B, Waltham, MA, USA) and Sodium (Na) and Potassium (K) contents were determined by Flame Photometer (Sherwood Model 410, Cambridge, UK).

2.2.3. Determination of protein content of garlic genotypes

Protein analysis of garlic genotypes was performed using the Kjeldahl method according to Jung et al., (2003). 0.25 g of sample was weighed, then 15 ml sulfuric acid and a catalyst tablet (Pro-Pac Tablets N. TT-57; Alfie Packers Inc., Omaha, NE) was added to the samples and burned in a fume hood for about 3.5 hours. Distillation of the combusted samples was carried out in a VELP mvda UDK 159 model distillation unit. A 40% NaOH solution was used to produce an alkaline distillation medium and a 4% boric acid solution was used to collect the distilled ammonia. Titrations were performed with standardized 0.1 N HCl. Indicator was used to determine the end point of the titration (0.375 g methyl red and 0.250 g methylene blue in 300 ml %95 ethanol). Nitrogen and protein content were calculated according to the AOAC (2016) procedure.

2.2.4. Statistical analysis

Results obtained from mineral and protein content analyses were evaluated by analysis of variance using JMP pro version 14 (SAS Institute, NC, USA) statistical software. The difference between means was compared with Tukey test at 0.05 significance level. Hierarchical cluster analysis (HCA) were used to determine the distribution of genotypes according to volatile sulfur compounds, mineral and protein contents. Heatmaps were performed using Clustvis software (http://biit.cs.ut.ee/ clustvis/).

3. Results and Discussion

3.1. Volatile sulfur compounds of garlic genotypes

In the essential oil of garlic genotypes, 10 sulfur compounds were detected, mainly diallyl disulphide (41.51-59.48%), disulfide, methyl 2-proplenyl (8.84-22.64%), diallyl sulfide (4.83-12.35%) and sulfide, allyl (3.75-10.38%). methvl The main component was determined as diallyl disulphide. The diallyl disulphide content of the genotypes varied between 41.51% and 59.48%. The highest value (59.48%) was found in Altınözü 2 genotype, followed by Taşköprü garlic with 55.87%, Altınözü 1 with 55.08%, Hatay 1 with 53.41%, Hatay 2 with 50.59%, Samandağ 1 with 47.48% and Samandağ 2 with 41.51% (Table 1).

A heatmap was obtained to reveal the similarities and differences between garlic genotypes in terms of volatile sulfur compounds (Figure 1). In the heatmap, the colors changing from dark blue to dark red the proportion of indicate sulfur compounds. The darkening of the blue color indicates that the amount of the component decreases and the change of color towards red and darkening indicates that the amount component of the increases. The constellation graph with obtained with twoway hierarchical clustering analysis (HCA) revealed that garlic genotypes were divided into two main groups in terms of volatile sulfur compounds. Accordingly, the first group consisted of Samandağ 1 and Samandağ 3 genotypes, while in the second group, Taşköprü garlic was separated from the other genotypes and branched alone; Altınözü 1, Hatay 2, Samandağ 2, Altınözü 2, Hatay 1 genotypes were in the same group (Figure 2).



Table 1. Volatile sulfur compounds in essential oil of garlic genotypes

	Genotype															
Sulfur compounds	Altınö	özü 1	Altınö	özü 2	Hata	ny 1	Hata	iy 2	Saman	dağ 1	Saman	idağ 2	Saman	dağ 3	Taşki	öprü
	RT	%	RT	%	RT	%	RT	%	RT	%	RT	%	RT	%	RT	%
1-Allyl-2- isopropyldisulfane	10.792	0.55	10.795	0.26	10.793	0.64	10.793	0.34	-	-	10.795	0.36	-	-	-	-
(E)-1-Allyl-2-(prop- 1-en-1-yl)disulfane	11.539	2.41	11.546	5.27	11.533	3.31	11.537	2.01	11.537	3.15	11.540	2.05	11.531	4.97	-	-
Diallyl sulfide	6.828	12.35	6.836	9.94	6.829	10.93	6.834	12.22	6.835	4.83	6.841	9.81	6.835	7.42	8.580	7.36
Diallyl disulphide	11.483	55.08	11.491	59.48	11.465	53.41	11.479	50.59	11.465	47.48	11.484	41.51	-	-	13.498	55.87
Disulfide, dimethyl	5.839	0.82	5.848	0.54	5.842	0.80	5.846	1.29	-	-	5.855	1.72	-	-	7.442	2.67
Disulfide, methyl 2- propenyl	8.765	16.08	8.769	15.28	8.764	16.58	8.766	17.73	8.769	8.84	8.771	16.79	8.761	9.65	10.671	22.64
(Z)-1-Methyl-2- (prop-1-en-1- yl)disulfane	8.893	0.37	8.897	0.60	8.894	0.61	8.892	0.39	-	-	8.896	0.46		-	-	-
1-((E)-Prop-1-en-1- yl)-2-((Z)-prop-1- en-1-yl)disulfane	16.366	0.24	-	-	-	-	16.366	0.21	-	-	-	-		-	-	-
Sulfide, allyl methyl	4.507	7.67	4.512	5.44	4.507	6.59	4.506	9.81	4.516	3.75	4.507	10.38	4.504	5.15	5.728	6.42
Trisulfide, methyl 2-propenyl	-	-	-	-	-	-	-	-	15.037	0.21	-	-	-	-	-	-

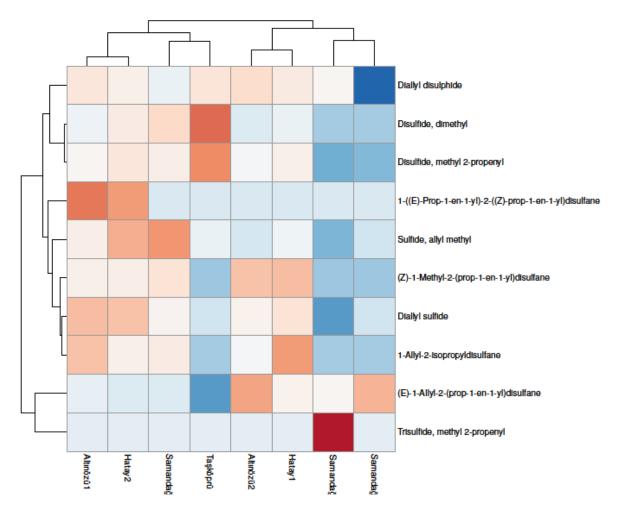
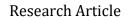


Figure 1. Heatmap clustering of garlic genotypes based on volatile sulfur compounds





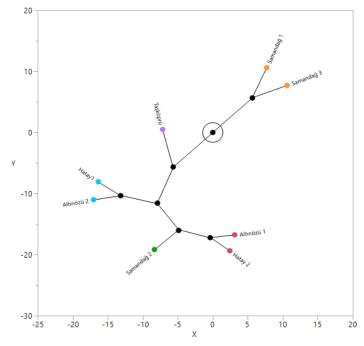


Figure 2. Constellation graph of garlic genotypes based on volatile sulfur compounds

Disulfides and trisulfides are known as characteristic aroma compounds of garlic (Molina-Calle et al., 2016; Satyal et al., 2017). As we found in this study, Lee and Shibamoto, (2002), Calvo-Gomez et al., (2004), Casella et al., (2013), Keles et al., (2014), Özcan Sinir and Barringer (2020), Akan, (2022), Beşirli et al., (2022), Yarali Karakan (2022), Beşirli et al., (2024) reported that diallyl disulphide is the main component of garlic essential oil. Contrary to these findings, Jirovetz et al. (1992), Rohani et al. (2011), Dziri et al. (2014), Hassaan and Soltan (2016) reported that the main component of garlic essential oil is diallyl trisulfide, Kozan (2012) and, Sufer and Bozok (2019) reported that the main component of garlic essential oil is allyl trisulfide, while Dery et al. (2010) found that 3-vinyl-4H-1,2-dithiin (31.89%). It is thought that these results found in different studies may vary depending on factors such as geographical location (soil content, climate difference, etc.), genetic diversity and extraction techniques (Sufer and Bozok

2019). As a matter of fact, Keles et al. (2014) reported that the main component of the

essential oil of Kastamonu and Chinese garlic was diallyl sulfide; the ratio of this component was 41.87% in Kastamonu garlic and 34.95% in Chinese garlic.

3.2. Mineral content of garlic genotypes

The K, Ca, Mg, Na, Mn, Fe, Cu and Zn contents of garlic genotypes varied between 507.68 mg kg⁻¹ and 433.80 mg kg⁻¹, 5.85 mg kg⁻¹ and 3.23 mg kg⁻¹, 14.59 mg kg⁻¹ and 14.12 mg kg⁻¹ ¹, 11.46 mg kg⁻¹ and 6.12 mg kg⁻¹, 0.31 mg kg⁻¹ ¹ and 0.17 mg kg⁻¹, 1.07 mg kg⁻¹ and 0.13 mg kg⁻¹, 0.15 mg kg⁻¹ and 0.03 mg kg⁻¹, 0.62 mg kg⁻¹ and 0.34 mg kg⁻¹, respectively (Table 2). The genotypes with the highest copper (Cu) content were Samandağ 2, Samandağ 3 and Hatay 1; with the highest zinc (Zn) content were Samandağ 1, Hatay 1 and Hatay 2; with the highest sodium (Na) content were Samandağ 2, Altınözü 2 and Hatay 1; with highest potassium content were the Samandağ 1, Hatay 1 and Samandağ 3; with the highest calcium (Ca) and iron (Fe) content were Samandağ 1; the highest manganese (Mn) content were Altınözü 2; and with the highest magnesium content were Samandağ 2, Hatay 1 and Hatay 2 (Figure 3).

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Constrans	Mineral content										
Genotype	К	Са	Mg	Na	Mn	Fe	Cu	Zn			
Altınözü1	433.80h	3.87g	16.13f	7.23g	0.17h	0.64f	0.11f	0.38f			
Altınözü 2	440.71f	3.23h	17.84e	8.65d	0.31a	0.13h	0.03h	0.35g			
Hatay 1	451.83c	4.24c	19.70b	8.54e	0.18e	0.71c	0.14b	0.48c			
Hatay 2	438.22g	4.03e	19.27c	7.77f	0.18f	0.67e	0.12d	0.46d			
Samandağ 1	456.76b	5.14b	17.89d	11.46a	0.19d	0.94b	0.09g	0.62a			
Samandağ 2	444.86e	4.01f	19.76a	9.80b	0.20c	0.64g	0.15a	0.41e			
Samandağ 3	447.27d	4.20d	14.12h	6.12h	0.18g	0.70d	0.13c	0.34h			
Taşköprü	507.68a	5.85a	14.59g	9.35c	0.21b	1.07a	0.11e	0.50b			

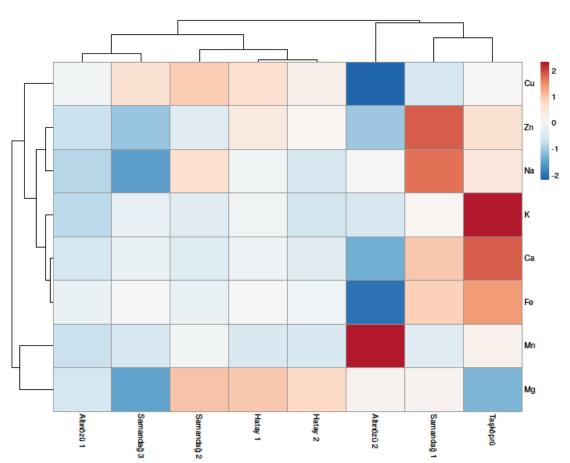
Table 2. Mineral content of garlic genotypes

Means followed by different letters are significantly different (p<0.05).

When the constellation graph in Figure 4 is examined, it was seen that garlic genotypes were divided into two main groups in terms of mineral contents. The first group consisted of Samandağ 1 and Taşköprü genotypes, while in the second group, Altınözü 2 garlic was separated from the other genotypes and branched alone. The second subgroup was also divided into two groups, the first group consisted of Altınözü 1 and Samandağ 2 genotypes, while the second group consisted of Hatay 1, Hatay 2 and Samandağ 2 genotypes.

In a similar study, Hacıseferoğulları et al. (2005) found high levels of K and significant levels of Mg, Ca and Na in garlic bulbs and reported 21378.84 mg kg⁻¹ K, 6009.37 mg kg⁻¹ P, 1056.15 mg kg⁻¹ Mg, 532.78 ppm Na and 363.61 ppm Ca. In another study, using local garlic genotypes originating from Greece and commercial garlic cultivars, it found that the main mineral was components of garlic material were K and Ca, and the K content ranged between 446 and 675 mg g⁻¹, and the Ca content ranged between 163 and 963 mgg⁻¹, while Fe and Zn contents were also found in considerable amounts (Petropoulos et al., 2018). In similar studies, Sajid et al. (2014), Divya et al. (2017), Yarali Karakan (2022) reported that K is the main mineral in garlic. In contrast to these findings, Akinwande and Olatunde (2015) reported that the main

mineral components of garlic were P (4777.88 mg kg⁻¹) and Zn (66.08 mg kg⁻¹), while Ca, Mg, Fe and Al were very low. Turan et al. (2017), who reported that the mineral composition of garlic varies, stated that it contains 23.81 g kg⁻¹ N, 3.90 g kg⁻¹ P, 12.33 g kg⁻¹ K, 0.42 g kg⁻¹ Ca, 10.50 g kg⁻¹ Mg, 10.23 g kg⁻¹ S, 2.49 g kg⁻¹ Zn, 11.46 g kg⁻¹ Fe, 0.72 g kg⁻¹ Mn, 1.00 g kg⁻¹ B and 2.34 g kg⁻¹ Na. Differences in the results on the mineral composition of garlic bv different researchers are thought to be due to the influence of many factors such as climatic conditions. genotype and analytical procedures (Martins et al., 2016; Turan et al., 2017). For example; Saadatu and Mshelia (2013) in their study on garlic genotypes grown in Nigeria, Senegal and Chad, found that P (1.29 mg L⁻¹) and Cu (0. 017 mg L⁻¹), Ca (8.639 mg L⁻¹) in garlic grown in Senegal and K (68.26 mg L⁻¹), Mg (51.60 mg L⁻¹) and Mn $(0.212 \text{ mg L}^{-1})$ in garlic grown in Chad.



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Figure 3. Heatmap clustering of garlic genotypes based on mineral content

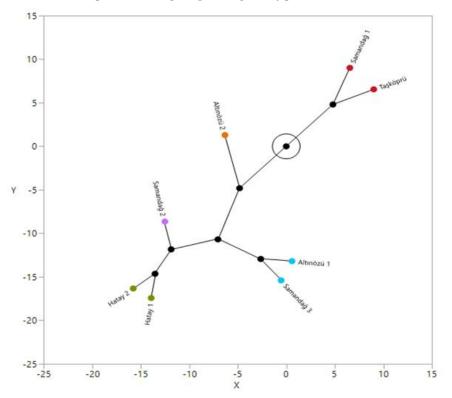


Figure 4. Constellation graph of garlic genotypes based on mineral content

3.3. Protein content of garlic genotypes

It was determined that there were statistically significant differences between the protein contents of garlic genotypes and varied between 4.77% and 7.71% (Table 3). The genotype with the highest protein content was Taşköprü garlic, followed by Samandağ 1 with 7.56%, Samandağ 2 with 6.64%, Hatay 2 with 6.29%, Samandağ 3 with 6.05%, Hatay 1 with 5.99%, Altınözü 2 with 5.63% and Altınözü 1 had the lowest protein content (4.77%).

Table 3. Prote	ein content of	garlic genotypes
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Genotype	Protein (%)
Altınözü 1	4,77h*
Altınözü 2	5,63g
Hatay 1	5,99f
Hatay 2	6,29d
Samandağ 1	7,56b
Samandağ 2	6,64c
Samandağ 3	6,05e
Taşköprü	7,71a

Means followed by different letters are significantly different (p<0.05).

When the constellation graph, the results of two-way hierarchical clustering analysis (HCA), in Figure 5 is examined, it was seen that garlic genotypes were divided into two main groups in terms of protein content. The first group consists of Samandağ 1 and Taşköprü genotypes, while in the second group, Altınözü 1 genotype separated from the other genotypes and branched alone. The second subgroup was also divided into two groups, the first group consisted of Samandağ 2 genotype, while the second group consisted of Altınözü 1, Altınözü 2, Hatay 1 and Samandağ 3 genotypes.

Tripathi (2006) reported that the chemical composition of garlic varies according to variety, cultural practices and climatic conditions and garlic contains about 6.0% protein. On the other hand, in a study conducted on garlic grown in Taşköprü region of Kastamonu, it was reported that the crude protein rate was 9.26%

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(Haciseferoğulları et al., 2005). Similarly, Sajid et al. (2014) reported that the protein content of garlic was 7.87%, Olusanmi and Amadi (2009) reported that 100 g of raw garlic contained 6.39 g protein, while Gulfraz et al. (2014) found that the total protein content of garlic genotypes originating from Pakistan was 17.5-17.6%.

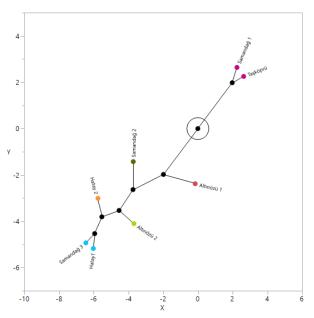


Figure 5. Constellation graph of garlic genotypes based on % protein content.

4. Conclusion

The chemical composition of garlic, which determines its quality, varies largely depending on the genotype and growing conditions. Genetic diversity among different garlic populations and genotypes provides important advantages in breeding studies to select genotypes with higher bioactive compound content. The results of the study revealed that garlic genotypes had significant variation in terms of sulfur compounds, mineral and protein contents. And also, the results of two-way hierarchical cluster analysis (HCA) also revealed that garlic genotypes were divided into different groups in terms of sulfur compounds, mineral and protein content. In conclusion, the findings of the research are important in terms of revealing the originality of garlic genotypes cultivated in Altınözü, Center and Samandağ

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The authors declare that they have no conflict

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Author Contribution

methodology, writing.

Conflicts of Interest

Mine

supervision.

writing;

of interest.

districts of Hatay province. In addition, this

study is thought to provide a basis for the

evaluation of these genotypes that stand out

in terms of sulfur compounds, mineral and

This article is based on Mine UÇAN's MSc

Faika YARALI KARAKAN: Conceptualization,

methodology,

UÇAN:

visualization.

Investigation,

thesis. The funders had no role in the study.

protein content in breeding programs.

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