Journal of Nuts

Journal homepage: ijnrs.damghaniau.ac.ir

ORIGINAL ARTICLE

Nutritional Value and Physical Properties of Syrian Pine Nuts

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A R T I C L E I N F O

Keywords:

Chemical composition;

Fatty acid;

Physical properties;

Pinus species

A B S T R A C T

This investigation aims to determine the nutritional value and physical traits of Syrian pine nut kernels and shells over time. Furthermore, the pine nut's composition and nutritional content are assessed concerning the latest climatic conditions. For each prepared sample, chemical analyses were done in two and physical analyses in three replicates, all according to a completely randomized design. The Homs District Agricultural Development Cooperative provided the pine nut shell samples used in this study. The sampling was conducted in May and June, taking subsamples of in-shell nuts from 25 kg bags. Every year, 15 subsamples were taken from various bags, and 33, 35, and 38 aggregate samples were generated. The in-shell nut quality showed seasonal variations concerning cracked and defective nuts, with crack rates spanning from 21 to 46% and 3 to 5%, respectively. The composition of the pine nut kernel was determined to have the following proportions: carbohydrates 12.19%, protein 32.18%, fat 43.2%, ash 4.93%, water activity 0.412, and moisture 4.31%. The elements with the greatest abundance were magnesium, phosphorus, and potassium. Additionally, kernels contain a high concentration of the minerals zinc and iron. The findings show that, compared to other Mediterranean pine nut sources, pine nut kernels cultivated in the Homs region are a rich source of several essential elements that positively impact public health.

Introduction

A few *Pinus* species produce delicious and very nutritious kernels. The Mediterranean and Far-eastern Asian countries are the leading producers of pine nuts (Zuleta *et al*., 2018; Polemis *et al*., 2019; El Khoury *et al*., 2021). With a significant (17,220 metric tons) and profitable ($570 million) global market in 2019–20, pine

[*]**Corresponding author**: Email address: hamza_radhi@yahoo.com
Received: 1 October 2022; Received in revised form: 5 November 2022; Accepted: 8 January 2023
DOI: 10.22034/jon.2022.1968627.1199

nuts are one of the most expensive fruits and nut species (Rahman *et al*., 2021; Adelina *et al*., 2022). Fig. 1 displays the annual global production of pine kernels from 2010/11 to 2019/20 (Zhang and Zhang, 2019). Natural forests produce most marketable pine nuts, but production varies greatly from year to year (Derzhapolskaya *et al*., 2021).

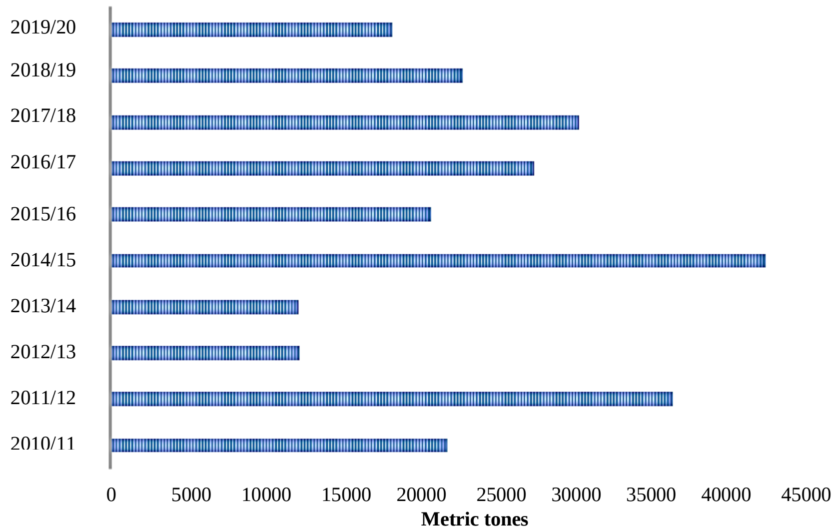


Fig. 1. World pine nut production from 2010 to 2019.

Since product prices in the overall industry fluctuate by region and season of harvest, calculating margins based on pine nut retail final prices is not indicative (Sharashkin and Gold, 2004; Awan and Pettenella, 2017). The most expensive pine nuts in European markets are often those from the Mediterranean (Jaouadi *et al*., 2021). The annual exports of pine kernels and production fluctuations in Syria are similar to those in other producing nations. Particularly in China and Russia, there is a significant increase in demand for pine nuts worldwide, and prices are rising as a result (Guàrdia *et al*., 2021). The Democratic People's Republic of Korea (DPRK or North Korea), Pakistan, Russia, and China are the leading producers of *Pinus Chinensis*, which makes up the majority of the global pine nut market (Awan and Pettenella, 2017).

On the other hand, the most important producers of the Mediterranean pine nut, also known as *Pinus pinea*, are Italy, Portugal, Spain, and Turkey (Calama *et al*., 2020). A significant species of the natural flora in the Mediterranean basin is *Pinus pinea*. Due to its importance for the region, it is also primarily farmed in plantations in Syria, Greece, Italy, Portugal, Spain, and Turkey (Casas-Agustench *et al*., 2011; Al-Bachir and Koudsi, 2019; Mutke *et al*., 2019). In recent years, the number of kernels produced in Syria ranged from 115 MT in 2019 to 725 MT in 2021 (Bays *et al*., 2022). Over 60% of the country's supply of pine nuts is currently produced in Syria's western region of Homs plain. For 15000 households in the area, cultivation of pine nuts is their primary source of income (Al-Bachir, 2015; Baho, 2015). With their white color and huge diameters, the pine nuts cultivated in the Homs plain are also of higher quality than those grown in other places. They are primarily exported to countries like Italy, Spain, Switzerland, and the United States (El Khoury *et al*., 2021). With their white color and huge sizes, the pine nuts cultivated in the Homs plain are also of higher quality than those grown in other places. They are primarily exported to countries like Iran, Iraq, Egypt, and Lebanon.

In Mediterranean cooking, pine nuts are traditionally used in meat dishes and salads as whole or ground, roasted, raw, cakes, sauces, bread, sweets, and candies (Evaristo *et al*., 2010). Pine nut kernels are excellent providers of mono-unsaturated fatty acids, antioxidants, protein, and minerals, especially phosphorus, potassium, and vitamin B1 (Xie *et al*., 2016; Babich *et al*., 2017). Unsaturated fatty acids comprise a larger portion of the kernels' lipid content. More than 85% of all fatty acids come from linoleic and oleic acids (Ryan *et al*., 2006; Destaillats *et al*., 2010). Numerous nuts are antioxidant-rich. Pine nuts generally have large levels of total antioxidants, even though the antioxidant content of chestnut, pecan, and walnut, is the highest among tree nuts (Hoon *et al*., 2015). The protective impact of dietary antioxidants on oxidative stress, a prevalent cause of chronic degenerative illnesses, is confirmed (Lorenzon dos Santos *et al*., 2020; Pinto *et al*., 2020). According to several studies, antioxidants in nuts may help prevent chronic diseases such as cardiovascular disease (Goyal and Kaur, 2019; Amarowicz and Pegg, 2020). This impact is attributed to the makeup of fatty acids, particularly the large amount of linoleic acid. Depending on the climatic and geographic conditions, the quality of the pine nut's kernel or in-shell may vary between subspecies or species. There is a shortage of information and research on the chemical and physical characteristics of *P. pinea* kernels, particularly those that are in-shell. The chemical and physical makeup of pine nut kernels cultivated in Syria has not been studied concerning the effects of yearly conditions or the climate. The objective of this research is to determine the chemical and structural characteristics of the kernels and shells of Syrian pine nuts over a period of time. Additionally, variations in the pine nut's composition and nutritional value are assessed in light of the current climate.

Material and Methods

Homs experiences hot, dry, clear summers and chilly, generally clear winters. The temperature rarely falls below -2°C or rises over 38°C throughout the year, often fluctuating between 2°C and 35°C (Fig. 2). The difference in precipitation from January, when it was at its peak, to August, when it was at its lowest, is 107mm.

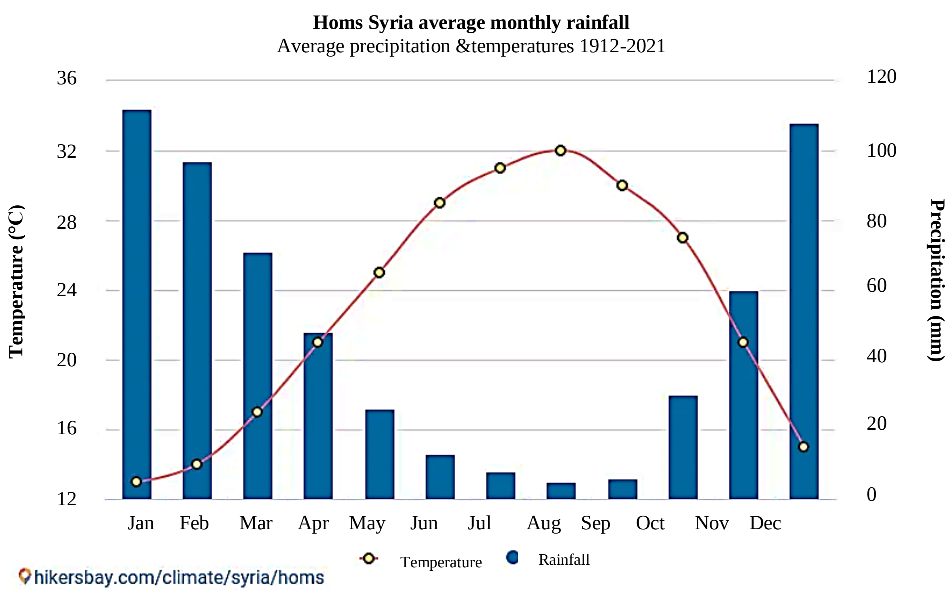


Fig. 2. The Average precipitation and temperature of Homs city, Syria.

From the Homs District Agricultural Development Cooperative, samples of the pine nut (*Pinus pinea L.*) shell were acquired throughout three crop years. The scanning electron microscope (SEM) image of a pine nut shell are shown in Fig. 3. According to the cross-section image, the perfect pine nut shell was granular and had no pores.

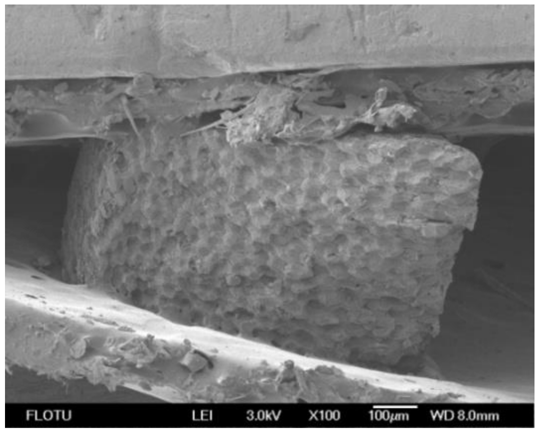


Fig. 3. SEM images of the pine nut shell.

A week following the removal of the nuts from the cones in May and June, a subsample of in-shell nuts from 25kg sealed jute bags was taken for the sampling. Annually, 15 subsamples were taken from various bags, and 33, 35, and 38 aggregate samples were generated. For each prepared sample, three replicates of physical analyses and two replicates of chemical analyses were carried out. Within a month of the harvest, the kernel samples were tested while stored at 5°C and in complete darkness. Using a visual inspection, 100 g of in-shell nuts from each sample were divided into six quality categories: cracked and kernel ready for germination with the crack length being 3/3, 2/3, or 1/3 of the length of the nut, cracked on both sides, cracked on one side, uncracked; and the proportion of nuts in each category was calculated as percent. The quantity of in-shell nuts in 100 g was computed after the in-shell nuts were weighed (XB-320M, Presica Instruments Ltd., Switzerland). The skins, kernels, and shells of these in-shell pine nuts were carefully separated after being manually cracked. The kernel ratio (the weight of the kernel to the weight of the in-shell nut) and the number of kernels in 100 g were then computed. The defective kernel ratio was calculated by visually examining the kernels taken from 100 in-shell nuts. The ratios were calculated after classifying the kernels into six categories, and the ratios were calculated: discoloration of the tip, green, black, visible mold, yellow, and white (intact). The primary axes' dimensions were also measured to establish the size. Utilizing a digital caliper with a sensitivity of 0.01 mm, we measured the main diameters of 20 kernels chosen at random.

Following the completion of the physical examinations, the in-shell nuts that were still present were cracked using specialized machinery. Their skins, kernels, and shells were then meticulously separated by hand. For mineral and proximate analyses, kernels were pulverized in a Waring blender. To determine a sample's moisture content, samples were dried in an oven at 75°C to a constant weight, and then the weight loss percentage was computed. At 30°C, a water activity meter was used to monitor the water activity. A muffle furnace estimated the total ash content after samples were dried for 15 hours at 65°C in an oven. For 24 hours, the samples were ashed at a temperature gradually increasing to 600°C. The Kjeldahl method was utilized to examine the protein content of pine nut kernel samples (Jung *et al*., 2003). The total amount of carbs was computed by deducting the total proportion of the other components from 100. The pine nut kernel's total fat was discovered using the petroleum ether and Soxhlet extraction method (López-Bascón and De Castro, 2020; Tykheev *et al*., 2020; Nogales-Bueno *et al*., 2021). Using an atomic absorption spectrophotometer, the absorbances of the extract were calculated (Ferreira *et al*., 2018). The standard curves were used to compute the mineral quantities (Lee *et al*., 2021). Vanadium phosphomolybdate, a type of phosphorus, was examined spectrophotometrically (Shyla and Nagendrappa, 2011). For the purpose of determining the amount of phenolic compounds, an Aquity Ultra-High Pressure Liquid Chromatography (UPLC) apparatus was utilized (Waters, Manchester, MA, USA).

An entirely random design was used to conduct the experiment. Using Duncan's multiple range tests at $P \leq 0.05$, significant differences between groups were identified. The replicates were used to calculate the standard deviation (SD) of the mean. Using the statistical program SPSS version 22, analyses of variance (ANOVA) were performed on all data.

Results

Corresponding with the years, the proportion of in-shell nuts with cracks varied significantly ($P \leq 0.01$), and a 31% average was determined as the overall average. Lengthwise (3/3) in-shell cracking along one side was found to be the primary mode of cracking.

Compared to the previous two years, the third year had the greatest cracked ratio. The cracks where the kernels are about to germinate, the cracks on both sides, and the lengthwise cracks on one side of the in-shell had higher cracking ratios (Fig. 4).

The qualities of in-shell pine nuts and kernels may be significantly influenced by environmental factors, such as temperature, precipitation frequency, and timing. Higher day-to-night temperature swings throughout the drying stage of cones in stacks were shown to be the main cause of the third-year crack ratios being higher than in the first year. Compared to the first two study years, the third study year's March through July period saw diurnal temperature ranges within larger boundaries (14.2%). The quality of the kernel was unaffected by cracking despite increased cracked ratios. This might have happened as samples of in-shell nuts weren't kept for a long time. In-shell nuts can be kept for more than a year in a typical storage environment. The average amount of healthy and unbroken kernels ($P \leq 0.05$) was calculated to be 94.23%, while the number varied according on the yearly conditions. According to (Zhang *et al*., 2017), a good crop of pine nuts only occurs about every seven years in the United States due to the crop's great susceptibility to unpredictable plant and weather cycles that cause drastic seasonal changes. It was discovered that yellow kernels were the main defect. Due to a higher proportion of yellow kernels (4.73%), the ratio of whole and sound kernels was lowest during the first year of sampling. In the three years of the study, the other faults (tip discoloration, green, black, or moldy) were relatively modest and comparable (<0.95) (Fig. 5).

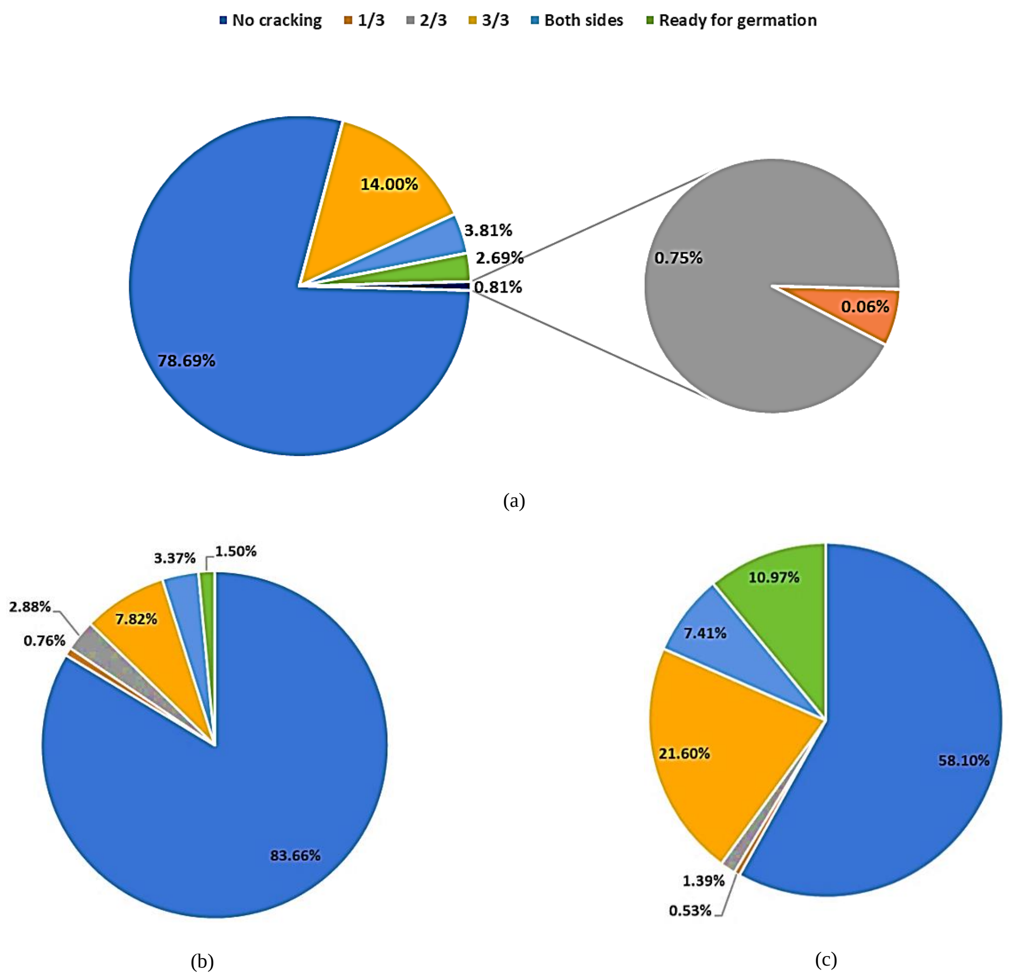
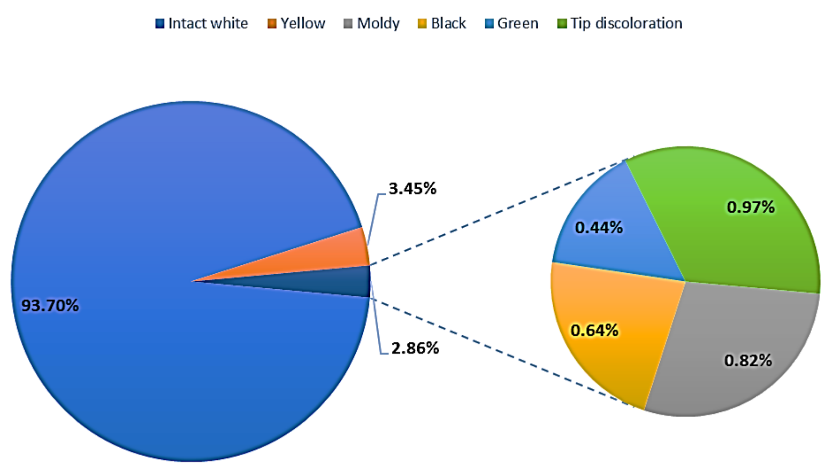
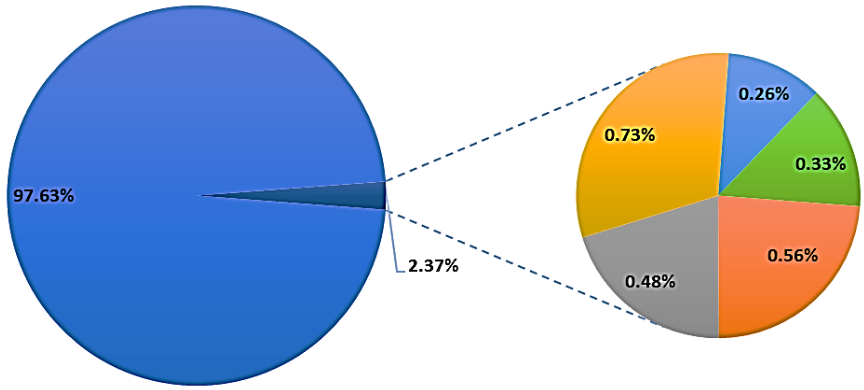


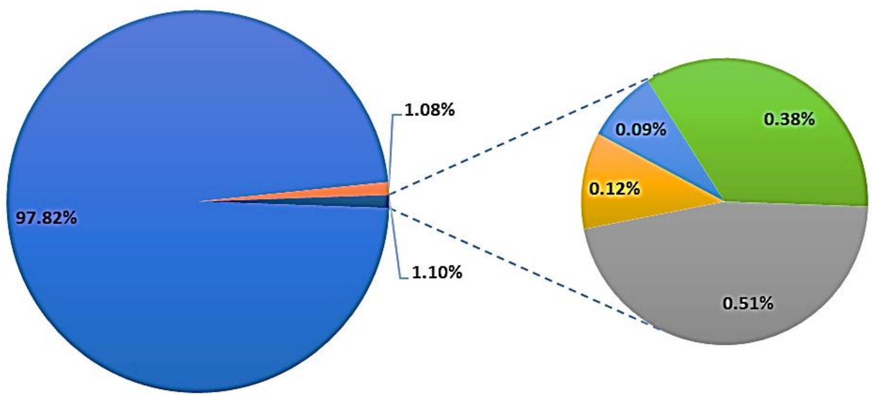
Fig. 4. The percentage of in-shell nut cracking modes in each year's samples. (a) 1-year, (b) 2-year, and (c) 3-year.



(a)



(b)



(c)

Fig. 5. Defected and intact white pine nut kernel ratios examined during various crop years.

Lipid oxidation which occurs by either enzymatic or nonenzymatic catalysis are linked to the yellowing or blackening of the kernel. In all three years, there were nearly the same amounts of in-shell nuts per 100 g. In comparison to the other sampling years, the third year's kernels were the smallest. The impact of yearly weather on kernel length was minimal, but it had a substantial impact on kernel width ($P \leq 0.05$). Compared to the third year's crop, the first year's kernels were wider. This outcome is consistent with the kernel ratio and kernel size (Table 1).

Table 1. Some of the physical properties of pine nut kernels over several distinct crop years.

Year	Kernel width (mm)	Kernel length (mm)	Kernel ratio (%)
1	6.42	16.46	33.24
2	6.34	16.64	32.04
3	6.15	16.07	30.39

The Aquity Ultra-High Pressure Liquid Chromatography (UPLC) was used to determine the concentration of phenolic compounds. Phytochemicals known as phenolic compounds are a class of nut components that have a wide range of pharmacological effects, including anti-inflammatory, anti-cancer, antioxidant, antibacterial, and antiviral effects. One of the most important roles of phenolic acids, especially caffeic, cinnamic, ferulic and vanillic acids derivatives is their antioxidant activity. Table 2 lists the amounts of phenolic compounds present in pine nuts, including phenolic acids and Caffeic acid phenethyl ester (CAPE).

Table 2. The quantity of CAPE and phenolic acids in pine nuts.

Concentration (µg g^{-1} Fresh Weight)	
Caffeic acid	0.171 ± 0.031
Cinnamic acid	Not detected
Coumaric acid	Not detected
Ferulic acid	Not detected
Hydroxycinnamic acid	0.302 ± 0.015
Sinapinic acid	0.101 ± 0.011
Syringic acid	5.396 ± 0.157
Vanillic acid	2.167 ± 0.138
Sum of phenolic	8.3
CAPE	0.124 ± 0.016

Between the three research years, there were no appreciable changes in the water activity or moisture content. The average water activity is calculated to be 0.412 and the moisture content to be 4.31%, respectively (Fig. 6). Additionally, the lipid oxidation process was slowed down by the detected water activity values.

With the exception of phosphorus (P), all three years of the study's mineral contents of the pine nut kernels were comparable. When compared to the first year of the study, the P content of the kernels collected throughout the second year was greater (Fig. 7).

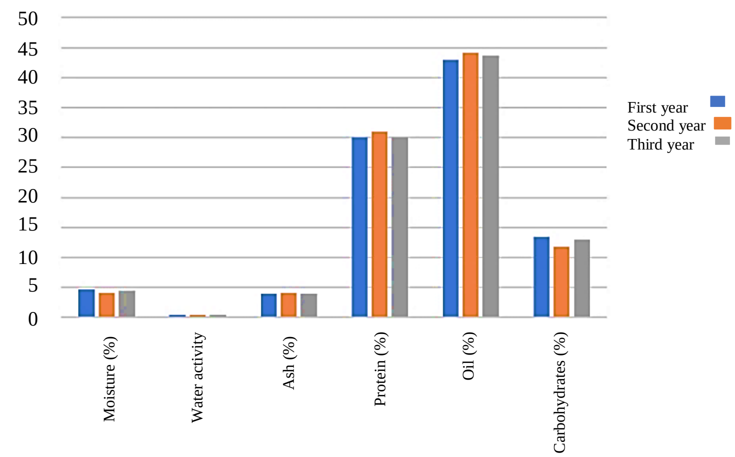


Fig. 6. Some of the chemical properties of pine nut kernels over several distinct crop years

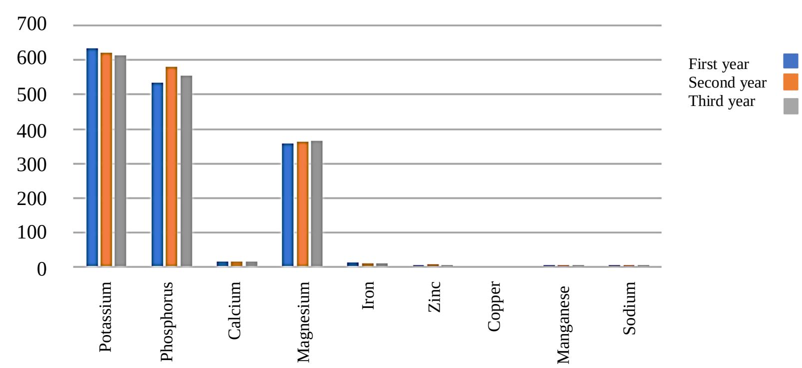


Fig. 7. Mineral composition of pine nut kernels.

Discussion

According to a number of studies, factors influencing the mineral composition of tree nuts include variety, geographic origin, harvest year, climate, soil properties, and management techniques (Habibie *et al*., 2019; Habibi *et al*., 2022; Parvaneh *et al*., 2022). With the exception of the climate, all other elements are insignificant in the Homs region. As a result, the effect on P appears to result from yearly climatic circumstances (Habibi *et al*., 2017; Najme Chatrabnous *et al*., 2018; Najmeh Chatrabnous *et al*., 2018). The most abundant mineral in pine nut kernels was potassium, which was followed by phosphorus and magnesium, which is in agreement with similar results in walnut (Pakrah *et al*., 2021, 2022; Sarikhani *et al.*, 2021; Jahanbani *et al*., 2016).

Conclusions

One of the world's most prized nuts, the Mediterranean pine nut, is utilized in traditional cuisines in many countries and has lately been separated from other pine nuts because of its bitter taste, hence popular in international markets. The study indicated that the yearly climate had a significant impact on quality, and that a high cracked ratio and yellow kernels were the main defects. Due to a larger ratio of yellow kernels, the ratio of healthy and whole kernels was lowest during the first year of sampling. According to the findings, the pine nut kernels are an abundant source of a wide variety of essential nutrients, many of which appear to have beneficial impacts on the health. Pine nuts from Homs have a high protein content as well as high levels of magnesium, phosphorus, and potassium. They also contribute to the daily intake of iron and zinc. The findings may also contribute to our understanding of nuts' chemical make-up and phenolic content, and they may be relevant to a variety of scientific disciplines, including biochemistry, food science, and nutrition.

Acknowledgements

This research was supported by the University of Ahl al-Bayt. We thank our colleagues from the University of Ahl al-Bayt who provided insight and expertise that greatly assisted the research.

Conflict of interests

The authors declare no conflict of interest.

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