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Effect of Roasting Hass Avocado Kernels on Nutritional Value and Volatile Compounds

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Abstract: Because of the lack of commercial food applications of Hass avocado (*Persea americana* Mill) kernel, which are a useful agricultural waste and a good source of bioactive compounds, this study investigated the influence of roasting on the chemical composition, antinutritional factors, antioxidant activity, colour, and GC-MS profile in avocado kernels after roasting at 180 °C for 30 min. The nutritional data revealed a significant increase ($p < 0.05$) in the oil extract, crude fibre, total phenolic compounds, Ca, K, P, Na, Zn, browning index, and redness/greenness after roasting. Conversely, a significant decrease ($p < 0.05$) was noticed in crude protein, total flavonoids, Fe, antinutrients, lightness, and yellowness/blueness after roasting. The 94 volatile compounds separated by GC-MS included 51 compounds from raw Hass kernels and 65 compounds from roasted kernels. The identified compounds constituted 96.21% and 93.25% in raw and roasted Hass kernels, respectively. The most compounds in the roasted Hass kernels were 3,7,11, trimethyl-8,10-dodecedienylacetate (6.28%), 2-methylbutan-1-ol (5.89%), 2-decanone, O-methyloxime (3.73%), 2-methyl-pyrazine (3.62%), and n-hexane (3.51%). Esters were the most common volatile compounds present in both raw and roasted Hass avocado kernels extract, we found 15 and 14 of these compounds (27.53 and 20.36%), respectively. This indicates that roasted Hass kernel flour is nutritionally and organoleptically suitable for food applications, including pastries and beverages, especially coffee drinks.

Keywords: Hass avocado kernels; roasting; nutritional value; GC-MS profile

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1. Introduction

Many countries around the world seek to embed the principles of sustainability in food systems and make them part of their strategic plans. To achieve this, the search for discovering the benefits of horticultural by-products and converting them into environmentally friendly products has increased [1]. The production and consumption of avocado have expanded drastically in the past 150 years because these fruits are highly valued for their high variety of vital compounds, especially phenolic compounds [2,3]. A large amount of by-product, such as the peel and kernel, is obtained. Of these, the kernels stand out for their wonderful properties, which may have a pharmacological effect because of the fatty acids, polyphenols, and sterols. The kernels have been used since antiquity against diseases such as muscle pain, parasites, and onychomycosis [4,5]. According to the FAO, the global production of avocado fruits exceeded 8.05 million metric tons in 2020 (FAOSTAT Report, 2020 Avocado Production Indices, https://www.fao.org/faostat/en/#data/QCL, accessed on 23 June 2022). Many scientists have reported that the seed represents 18–24% of the avocado fruit [4]. A simple arithmetic operation reveals that the amount of avocado kernel residues ranges from 1.49 to 1.93 million tons. This is a large amount that poses an environmental risk, although there are not enough studies to address this risk. Egypt is primarily an agricultural country, and because of the spread of many food factories that suffer from the accumulation of waste and the consequent environmental problems, it is necessary for researchers to find solutions to make safe use of these wastes. Our research

team investigating the utilization of avocado kernels concluded that fermentation of avocado kernels using *Lactobacillus plantarum* increases the nutritional value of the resulting flour, which was used to make biscuits enriched with fermented avocado kernel flour [5]. Currently, the effect of roasting on avocado kernels is being studied. The roasting process is a heat treatment that has been introduced as an effective technological treatment to maintain the stability of the components of various seeds, including sunflower, mango kernels, coffee, and poppy seeds, in addition to improving the aroma and taste [6], as well as reducing or eliminating the antinutritional factors [5] and microbes [7] to levels that are commensurate with the standard specifications. During roasting, many physicochemical changes occur because of dehydration and chemical reactions [8] depending on the roasting time and temperature [9]. One of the most significant chemical processes that takes place during roasting is the Maillard reaction, which is responsible for many changes that include increasing the bioavailability, breaking down some antioxidant components, creating new ones with free radical scavenging activity, and producing a derivative aroma favoured by consumers [10,11]. Hundreds of chemicals can now be identified simultaneously using new analytical methods such as GC-MS, allowing researchers discover the effects of different treatments. To the best of our knowledge, no studies of the GC-MS profile of avocado kernels after roasting have been conducted. Thus, the current study aimed to explore the influence of roasting on the chemical composition, antinutritional factors, antioxidant activity, colour, and flavour compound profile in avocado kernels to complement our previous study on the benefits of avocado kernels for sustainable food systems.

2. Materials and Methods

2.1. Materials

2.1.1. Hass Avocado Kernels

Fruits from Hass avocado trees were harvested from PICO Modern Agriculture Company's farms in the El Beheira governorate of Egypt (30.53 N, 30.794 E). The orchard is laid out so that each row is separated from the next by 6 m, with a 4 m space separating the trees, and the soil is light and well-aerated clay. The area has a humid, hot to moderate climate. Fresh ripe avocados (harvested 190–200 days after full bloom) with good characteristics were picked in November 2021. The fleshy part of Hass avocado fruits was removed, and the seeds were retained and directly sundried to obtain a moisture content of 12–14% (about 4 days) before being sealed in polyethylene bags under nitrogen.

2.1.2. Chemicals and Reagents

Folin–Ciocalteu reagent was obtained from Sisco Research Laboratories Chemicals (India), DPPH reagent was obtained from Sigma-Aldrich Ltd. (Irvine, UK), and the other chemicals were obtained from El-Gomhouria Co. (Cairo, Egypt).

2.2. Methods

2.2.1. Roasting Process

Several preliminary laboratory experiments were conducted to roast the avocado kernels at various temperatures and times (160, 180, 200, and 220 °C; 10, 20, and 30 min) in a hot air oven (model Memmert Gmbh and Co. KG, Schwabach, Germany), with the goal of producing an alluring aroma and colour, which were judged by an expert sensory panel (12 members aged 28–57). The tasters all agreed that roasting for 30 min at 180 °C produced the finest scent. Immediately after roasting, the thin crust was gently peeled off the surface of the kernel, and the remainder was finely ground using a multi-speed electric grinder (model No. MB-355, Beijing, China) at Speed 4 to allow the obtained powder to pass through a sieve with a 50 mm mesh size. The output was immediately frozen in liquid nitrogen prior to laboratory experiments and isolation of the volatiles.

2.2.2. Chemical Analysis

On the basis of the [12] standards, the moisture, protein (N × 6.25), ash, crude fibre, and oil extract contents in raw Hass Kernel flour (HKF) and roasted Hass kernel flour (RHKF) were estimated. Carbohydrate content was calculated by subtracting the sum of moisture, protein, ash, crude fibre, and oil extracts percentage from 100.

The content of Ca, P, K, Na, Fe, Zn, Mn, and Mg were identified in the resulting ash after dissolving it in 6 N HCl acid, followed by filtering into a volumetric flask (100 mL). Deionized water was added to the filtrate to the gauge line to constitute the measurement solution. The concentration of the minerals above was estimated by using atomic absorption spectroscopy (model 2380, Perkin-Elmer, Waltham, MA, USA) in the line with Approved Methodology No. 967.21 of the [13].

2.2.3. Preparation of Aqueous Extracts

According to Kumaran [14], the phenolic, tannin, and flavonoid compounds in HKF and RHKF were extracted by aqueous methanol. One gram of each sample was extracted with 20 mL of methanol (80%, v/v), with agitation for 20 h at room temperature by using Axygen® Microtube shakers (Union City, CA, USA). The solution was filtered and centrifugated (model EBA280, Hettich (Kirchlengern, Germany)) at 19,000 rpm for 5 min at 4 °C for extraction of the phenolics and tannin, and at 9000 rpm for 10 min for extraction of the flavonoids. Finally, the aqueous extract was used for direct estimation.

2.2.4. Determination of the Total Phenolic Content

The Folin–Ciocalteu method [15] was used to determine the total content of phenolic compounds in the aqueous extract. For this, 5 mL of the extract was thoroughly mixed in a volumetric flask with 5 mL of Folin–Ciocalteu reagent (1:5 distilled H_2O) and stirred at 750 rpm for 8 min by vortex mixer, then 5 mL of 10% (w/v) Na_2CO_3 was added to the mixture, and the contents were rested for 30 min. The absorbance at 725 nm was measured in a UV-vis spectrophotometer (model UV-1601PC, Schimadzu, Kyoto, Japan). Finally, the concentration of total phenols was determined using a calibration curve of gallic acid (0.04–0.25 mg/mL). The result was calculated as mg equivalent of gallic acid (EAG) per 1 g of avocado kernel flour.

2.2.5. Determination of the Total Flavonoid Content

The measurements were taken via the spectrophotometric methodology [16], modified in some respects. For this, 2 mL of the aqueous extract followed by 2 mL of an $AlCl_3$ (2%, w/v) solution and 2 mL of CH_3CO_2K (120 mM) were added into a test tube and kept at 20 °C for 1 h. The absorbance was measured at 425 nm by UV-vis spectrophotometry against a blank solution. The yield of flavonoids was estimated from the standard curve of quercetin (0.04–0.25 mg/mL). The results were calculated as mg equivalent of quercetin (QE) per 1 g of avocado kernel flour.

2.2.6. Extraction and Analysis of Radical DPPH Scavenging Activity

To obtain the extracts, 1 g of each sample was weighed and diluted with 25 mL of 80% (w/w) methanol in a 50 mL conical flask and subjected to continuous stirring for 180 min in a magnetic shaker bath at 100 rpm. Subsequently, the mixture was centrifuged in a thermoelectronic CL40R centrifuge at 4500 rpm for 30 min. The solution was filtered using filter paper (BOECO, pore size: 10 µm). This procedure was performed in triplicate. For determination of the antioxidant capacity, the Tris base radical was used ($(HOCH_2)_3CNH_2$) with 2,2-diphenyl1-picrylhydrazil (DPPH). Subsequently, 1 mL of the extract solution and 3 mL of the DPPH solution were placed in a 10 mL volumetric flask and the product was brought to the full volume with 99% (w/w) methanol. This was carried out for both the raw and roasted Hass avocado extracts. The flasks were protected from light for 30 min. The absorbance was measured in a UV-vis spectrophotometer (model UV-1601PC, Schimadzu,

Japan) at 517 nm; methanol 99% (*w*/*w*) was taken as the blank [17]. The DPPH free radical inhibition data were recoded as μM Trolox equivalents (TE)/1 g of avocado kernel flour.

2.2.7. Determination of the Antinutrients

The main antinutrients were determined in HKF and RHKF as follows.

The tannin content was determined according to Tamilselvi [18]. For this, a 100 μL aliquot of the extract was added to 750 μL of distilled water, 500 μL of Folin–Ciocateu reagent, and 1000 μL of Na_2CO_3 (35%, *w*/*v*). The mixture was diluted by distilled water upon 10 mL, shaken well, and incubated for 30 min at 20 °C and read at 725 nm using a UV-vis spectrophotometer. A calibration curve for tannic acid (0.02–0.1 mg/mL) was prepared. The total tannin content was expressed as mg tannic acid/100 g.

Saponins were extracted by Soxhlet units using methanol as the solvent for 4 h, then the mixture was filtered, the solvent was evaporated from the extract, and the residue was distributed in a mixture of water and dichloromethane (1:1). The aqueous phase was extracted with 1-butanol and then the organic phase was separated to be concentrated in a rotary evaporator (model 0003740800, IKA, Königswinter, Germany). The residue was dissolved with distilled water in a 100 mL beaker, and 1 mL of this solution was mixed with 1 mL of sulfuric acid and 1 mL of 0.2% (*w*/*v*) cobalt chloride. The mixture was left to stand for 10 min, and the absorbance was recorded by a spectrophotometer at 284 nm [19]. A calibration curve for saponin solutions (0.025 to 0.15 mg/mL) was prepared.

Oxalate content was determined by the titration method of Nwinuka [20]. Two grams of the sample was digested with 50 mL of H_2SO_4 (0.75 mol/L) for 2 h, stirred, and filtered using Whatman No. 1 filter paper. The filtrated solution was heated to 80–90 °C and a known volume was titrated against a $KMnO_4$ (0.5 mol/L) solution. The equivalence point was reached when the titrated solution acquired a pale pink colour that did not disappear upon agitation. The titration was repeated two more times.

The phytic acid content in the HKF and RHKF was determined using Vaintraub and Lapteva's colorimetric method [21]. Approximately 0.5 g of the sample was placed in 50 mL centrifuge tubes with 20 mL of 3.5% (*w*/*w*) HCl. The tubes were shaken for 1 h at 20 °C. At the end of the stirring time, the extracts were recovered by centrifugation (5000 rpm, 10 min). Next, 1 mL of Wade reagent (30 mg of $FeCl_3 \cdot 6H_2O$ + 300 mg of sulfosalicylic acid + 100 mL of distilled water) was added. The tubes were shaken and the absorbance at 500 nm was assessed against distilled water. The results were expressed as mg of phytic acid/100 g of the sample.

The alkaloid content in the HKF and RHKF was measured by the method of Mulder-Krieger [22].

2.2.8. The Browning Index

The browning index of the HKF and RHKF was measured according to Chung et al. [23], using a UV-vis spectrophotometer (UV-1601PC, Schimadzu, Japan) at 420 nm.

2.2.9. Colour Measurements

The L*, a*, and b* parameters for the colour of the HKF and RHKF were assessed using the CIE L* a* b* method [24].

2.2.10. Estimation of Volatile Compounds

The compounds of a methanolic extract of the HKF and RHKF were identified using a Gas Chromatography System model 7890B coupled to a mass spectrometry (GC-MS) system model 5977A (both from Agilent Technologies, Santa Clara, CA, USA). Exactly 1 μL of each sample was injected at 250 °C into a capillary column (type HP-5, 30 m × 0.25 mm i.d. 0.25 μm), using helium gas at a flow rate of 1 mL/min as a carrier and 0.26187 psi in splitless mode. The oven temperature was gradually raised to 150 °C at the rate of 5 °C/min, then to 280 °C at the rate of 12 °C/min, as previously explained by Wang et al. [25]. The chemical components of the extracts were identified by their retention

time and total ion counts (TICs), by comparing the mass spectra with those of the NIST 14 and Wiley 11 database libraries. The individually listed compounds were re-confirmed through the online databases of AMDIS (National Institute of Standards and Technology, US Department of Commerce, Gaithersburg, MD, USA), PubChem (NCBI, 2020), ChemSpider (www.chemspider.com), and the Chinese Chemical database (cciss.cirs-group.com).

2.2.11. Statistical Analysis

The statistical analysis was achieved with the SPSS 16 program, and the results are provided as the mean ± SD and were compared using one-way ANOVA. All experiments were carried out in triplicate. The significance level was set at $p < 0.05$.

3. Results

3.1. Chemical Composition

The changes that occurred in the chemical composition (on a dry weight basis) during the roasting of avocado kernels are shown in Table 1. The data revealed that there were significant differences ($p < 0.05$) in the chemical composition produced by the roasting treatment, except for the crude fibre content. Raw Hass had a significantly greater ($p < 0.05$) moisture content (12.33%) than the RHKF (6.54%); the same trend was found for crude protein, which decreased after roasting to 5.31% and 5.04% for raw and roasted Hass avocado kernels, respectively.

Table 1. The chemical composition of raw (HKF) and roasted Hass avocado kernel flour (RHKF).

Chemical Composition	HKF	RHKF (180 °C/30 min)
Moisture %	12.33 ± 0.45 [a]	6.54 ± 0.35 [b]
Crude protein %, db	5.31 ± 0.13 [a]	5.04 ± 0.2 [b]
Oil extract %, db	3.94 ± 0.1 [b]	4.22 ± 0.1 [a]
Crude fibre %, db	7.31 ± 0.34 [a]	7.46 ± 0.24 [a]
Ash %, db	2.19 ± 0.1 [b]	2.46 ± 0.1 [a]
Carbohydrates %, db	68.92 ± 0.67 [b]	74.28 ± 0.74 [a]
Total Phenolics (mg GAE/g)	22.93 ± 0.41 [b]	23.82 ± 0.66 [a]
Flavonoids (mg QE/g)	1.58 ± 0.07 [a]	0.89 ± 0.05 [b]
DPPH (μ mol TE/g)	152.3 ± 2.36 [b]	181.7 ± 4.1 [a]

Data represent the mean ± standard deviation of triplicate readings. Values with the same letter within the same row are not significantly different ($p < 0.05$).

HKF and RHKF have an oil extract content of 3.94% and 4.22%, respectively. Furthermore, the crude fibre content in HKF and RHKF on a dry weight basis was 7.31% and 7.46%, respectively, without significant differences ($p < 0.05$). The ash content increased significantly from 2.19% to 2.46% in HKF and RHKF, respectively. As a result of the changes that occurred in the protein, fat, fibre, and ash contents after roasting, the carbohydrate content increased significantly from 68% to 74% after roasting. The outcomes of the current study illuminate the impact of roasting on some vital compounds in RHKF (Table 1), as the content of total phenolic substances increased significantly ($p < 0.05$) from 22.93 for raw Hass kernel flour to 23.82 mg GAE/g after roasting. The content of flavonoids decreased significantly ($p < 0.05$) from 1.58 to 0.89 mg QE/g after roasting. The antioxidant activity increased from 152.3 to 181.7 μmol Trolox/g after roasting.

3.2. Mineral Content

The overall mineral profiles of HKF and RHKF on a dry weight basis are presented in Figure 1. Potassium, phosphorus, and calcium constituted the major minerals in HKF. The concentrations of the elements in RHKF were significantly ($p < 0.05$) higher than those

in HKF, except for zinc, manganese, and magnesium, which did not show a significant difference in their content, as well as a statistically significant ($p < 0.05$) reduction in the iron content after roasting. Potassium was the predominant element in HKF (75.8 mg/100 g) and RHKF (81.38 mg/100 g). The phosphorus content ranged between 28.53 and 33.63 mg/100 g in HKF and RHKF, respectively. The calcium content was 17.13 and 18.39 mg/100 g for raw Hass kernels and RHKF, respectively. The sodium content slightly increased from 25.11 to 26.92 mg/kg after roasting at 180 °C for 30 min. The iron content varied from 12.69 to 11.45 mg/kg in HKF and RHKF, respectively. As shown in Figure 1, there was a slight increase in zinc content without significant effect after roasting, which reached 3.36 mg/kg but was 2.96 mg/kg in HKF.

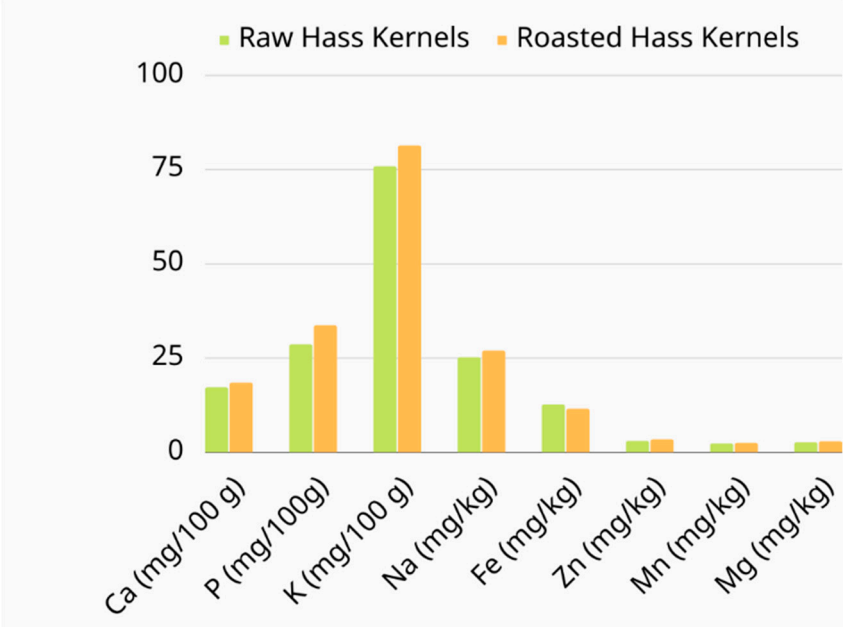

Figure 1. Mineral content in raw and roasted Hass kernels (dry weight basis).

3.3. Antinutrients

RHKF had a significantly lower level of antinutrients ($p < 0.05$) after roasting for 30 min at 180 °C compared with HKF. Figure 2 reveals that after roasting for 30 min at 180 °C, the tannin content declined by 61.36% (to 2.55 mg/100 g), more than 75% of the saponin was lost, the oxalate content fell by 25% to 3.24 mg/100 g in RHKF, the content of alkaloids decreased by 70.28% to 0.63 mg/100 g in RHKF, and more than half of the phytic acid content was lost. The main antinutrients in RHKF were oxalates, followed by tannins and saponin. Traces of phytates and alkaloids were detected after roasting for 30 min at 180 °C.

3.4. Colour Characteristics

Table 2 presents the differences in the browning index, and L*, a*, and b* values of HKF and RHKF (roasted for 30 min at 180 °C). The UV-vis spectrophotometer absorption of the HKF and RHKF solutions at 420 nm demonstrated that the browning index significantly ($p < 0.05$) increased from 0.016 to 0.058. Redness (a*) rose from 7.12 in HKF to 7.58 in RHKF. The lightness (L* value) and yellowness (b* value) significantly ($p < 0.05$) decreased after roasting; specifically, lightness (L*) reduced from 67.02 in HKF to 47.31 in RHKF, and yellowness (b*) decreased from 22.2 in HKF to 14.87 in RHKF.

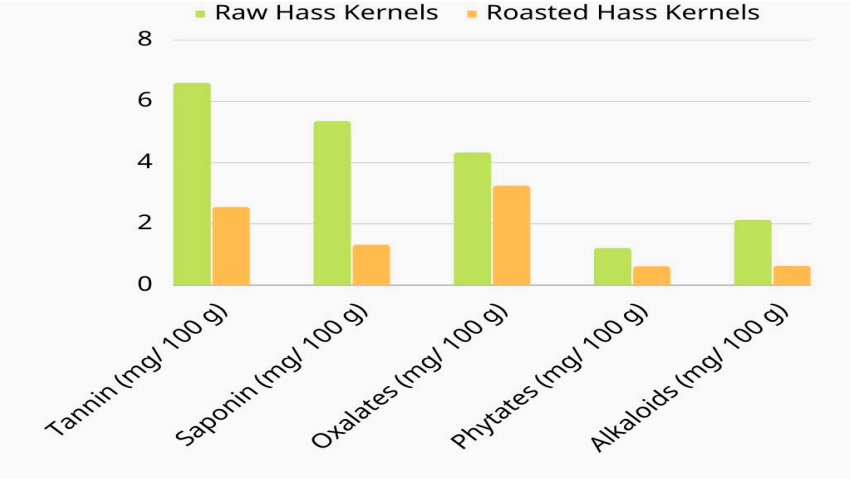

Figure 2. Antinutrients in raw and roasted Hass avocado kernels.

Table 2. Browning index and colour characteristics in raw and roasted Hass avocado kernels.

Degree		HKF	RHKF (180 °C/30 min)
Browning Index (420 nm)		0.016 ± 0.001 ^{b}	0.058 ± 0.001 ^{a}
Colour parameters	L *	67.02 ± 0.1 ^{a}	47.31 ± 0.17 ^{b}
	a *	7.12 ± 0.03 ^{b}	7.58 ± 0.04 ^{a}
	b *	22.2 ± 0.1 ^{a}	14.87 ± 0.05 ^{b}

Results are presented as the mean ± SD (n = 3). Values followed by the different letters within rows are significantly different at $p < 0.05$.

3.5. Volatile Compounds

Tentatively, 51 compounds were separated from HKF by GC-MS, and 65 compounds were separated from RHKF (Table 3), of which 43 compounds appeared in RHKF but were not present in the HKF, compared with 28 compounds that were present in HKF and disappeared in RHKF. Although 23 compounds were present in both HKF and RHKF, the content of 19 compounds decreased by roasting and the content of four compounds increased.

In total, the compounds that were identified in HKF and RHKF constituted 96.21% and 93.25% of the total amount of compounds, respectively. The most abundant compounds in terms of relative content in HKF were (*E*)-hex-2-en-1-ol (7.34%), (*E*)-hept-2-enal (5.36%), pentadecane (5.33%), cyclohex-3-ene-1-carbaldehyde (4.92%), and decan-2-one (4.67%), while the most abundant compounds in terms of relative content in RHKF were 3,7,11,trimethyl-8,10- dodecedienylacetate (6.28%), 2-methylbutan-1-ol (5.89%), 2-decanone, O-methyloxime (3.73%), 2- methyl-pyrazine (3.62%), and n-hexane (3.51%).

In the preliminary experiments, the optimum roasting conditions were determined, which produced the most attractive aroma. For this, the avocado kernels were roasted at 160, 180, 200, and 220 °C for 10, 20, and 30 min. Expert judges determined that the results of treatment at 180°C for 30 min were the best in terms of odour and colour. This sample was used in the experiments to identify the flavour materials using the GC-MS system and compare the RHKF with the raw Hass kernels.

Esters were the most common chemical compound classes present in both HKF and RHKF extract, with 15 and 14 compounds identified or 27.53% and 20.36% of the total compounds detected, respectively (Figure 3). In the GC-MS profile of the RHKF extract, five chemical classes appeared that were not present in the HKF extract: pyrazines, pyrroles, imines, thiazines, and oximes. Moreover, the percentage of unsaturated aliphatic hydrocarbons, alcohols, furans, and amines increased in the extract of RHKF compared with that of HKF; in contrast, the percentage of saturated aliphatic hydrocarbons, terpenes, aldehydes, ketones, esters, and oxetanes decreased.

Table 3. Odour and relative content of the identified volatile compounds in raw and roasted avocado kernels.

No.	Compound	Molecular Formula	Odour Description *	% Content	
				HKF	RHKF
A	Saturated aliphatic hydrocarbons (SAH)			10.62	5.29
1	Undecane	$C_{11}H_{24}$	Gasoline-like to odourless	1.42	1.86
2	2,6,10-trimethyldodecane	$C_{15}H_{32}$	NF	1.08	0.52
3	Tridecane	$C_{13}H_{28}$	Hydrocarbon odour	1.25	ND
4	Tetradecane	$C_{14}H_{30}$	Mild waxy	1.54	0.36
5	Pentadecane	$C_{15}H_{32}$	NF	5.33	1.31
6	Docosane	$C_{22}H_{46}$	Odourless	ND	1.24
B	Unsaturated aliphatic hydrocarbons (UAH)			5.25	6.16
7	4-Methyl-1,4-heptadiene	C_8H_{14}	NF	ND	0.46
8	1-Ethylcyclohexene	C_8H_{14}	NF	ND	1.85
9	1-Ethyl-5-methylcyclopentene	C_8H_{14}	NF	ND	1.04
10	Dodec-5-yne	$C_{12}H_{22}$	NF	0.63	ND
11	3-[(E)-hex-1-enyl] cyclohexene	$C_{12}H_{20}$	NF	0.95	ND
12	(E)-Pentadec-3-ene	$C_{15}H_{30}$	NF	1.2	ND
13	Nonadec-1-ene	$C_{19}H_{38}$	NF	2.47	1.32
14	4′-Ethyl-4-pentyl-1,1′-bi(cyclohexan)-3-ene	$C_{19}H_{34}$	NF	ND	1.49
C	Terpenes			2.48	0.64
15	α-Cubebene	$C_{15}H_{24}$	Herbal, waxy	0.25	ND
16	β-Copaene	$C_{15}H_{24}$		0.36	ND
17	Caryophyllene oxide	$C_{15}H_{24}O$		1.87	0.64
D	Alcohols			10.13	11.61
18	2-Methylbutan-1-ol	$C_5H_{12}O$	Cooked, roasted	ND	5.89
19	(E)-Hex-2-en-1-ol	$C6H_{12}O$	Bitter, green	7.34	ND
20	8-Azabicyclo[3.2.1]oct-6-en-3-ol, 8-methyl-	$C_8H_{13}NO$	NF	ND	2.85
21	p-Menth-1-ene-9-ol	$C_{10}H_{18}O$	Fruity, herbal	0.65	ND
22	13-Tetradece-11-yn-1-ol	$C_{14}H_{24}O$	NF	ND	0.63
23	1-Phenylhexan-1-ol	$C_{12}H_{18}O$	NF	ND	1.59
24	α-Santalol	$C_{15}H_{24}O$	Deep sweet sandalwood, woody	ND	0.29
25	Phytol	$C20H_{40}O$	Faint floral	2.14	0.36
E	Aldehydes			22.86	5.3
26	Propanal	C_3H_6O	Green grass, fruity	1.96	ND
27	Pentanal	$C_5H_{10}O$	Fruity nutty	0.58	ND
28	(Z)-Hex-3-enal	$C_6H_{10}O$	Green, grassy	2.09	ND
29	2-Ethylbutanal	$C_6H_{12}O$	Fruity, varnish, bitter, aldehydic	3.68	2.11
30	2-Hexenal	$C_6H_{12}O$	Grassy, herbal	1.16	0.22
31	(E)-Hept-2-enal	$C_7H_{12}O$	Somewhat fatty, green	5.36	1.11
32	1-Ethylpyrrole-2-carbaldehyde	C_7H_9NO	Burnt, roasted, smoky	ND	0.87
33	(E)-non-2-enal	$C_9H_{16}O$	Fatty, green, violet aroma	2.79	ND
34	2-Phenylbut-2-enal	$C_{10}H_{10}O$	Cocoa-like, roasted, woody	ND	0.81

Table 3. *Cont.*

No.	Compound	Molecular Formula	Odour Description *	% Content	
				HKF	RHKF
35	Cyclohex-3-ene-1-carbaldehyde	$C_7H_{10}O$	Fruity, aromatic, sweetish	4.92	ND
36	(Z)-Hexadec-11-enal	$C_{16}H_{30}O$	Waxy	0.32	0.18
F	Ketones			12.17	6.68
37	1-(3,4-Dihydro-2H-pyrrol-5-yl) ethenone	C_6H_9NO	Roasted, popcorn-like, popcorn toasted, grain malty	ND	2.27
38	Octane-2,3-dione	$C_8H_{14}O_2$	Roasted, fruity nutty	ND	1.36
39	6-Methylhept-5-en-2-one	$C_8H_{14}O$	Fatty, green citrus-like odour	ND	0.25
40	Decan-2-one	$C_{10}H_{20}O$	Fatty, peachy	4.67	0.38
41	3-But-3-enylcyclohexan-1-one	$C_{10}H_{16}O$	NF	ND	0.51
42	Dodec-11-en-2-one	$C_{12}H_{22}O$	NF	0.85	ND
43	7-Acetyl-3,3-dimethylbicyclo[4.1.0]heptan-2-one	$C_{11}H_{16}O_2$	NF	ND	0.33
44	Cycloheptadecanone	$C_{17}H_{32}O$	Musky, animal	0.78	ND
45	Pentadecan-2-one	$C_{15}H_{30}O$	Floral, fresh, jasmine, celery	1.39	0.25
46	1-Hydroxy-4-methoxy-3,3-dimethyl-1,3-dihydro-2H-indol-2-one	$C_{11}H_{13}NO_3$	NF	0.19	ND
47	Cyclopentane-1,2-dione	$C_5H_6O_2$	NF	ND	0.22
48	3,4-Dihydro-2H-thiopyran-3-one	C_5H_8OS	Unpleasant	4.23	ND
49	Dodecahydropyrido[1,2-b] isoquinolin-6-one	$C_{13}H_{21}NO$	NF	0.06	ND
50	9-(Oxan-2-yloxy) nonan-2-one	$C_{14}H_{26}O_3$	NF	ND	0.46
51	Vestitenone	$C_{12}H_{18}O$	NF	ND	0.65
G	Esters			27.53	20.36
52	Methyl 2-hydroxyacetate	$C_3H_6O_3$	Sweet fruity	1.16	0.7
53	Methyl heptanoate	$C_8H_{16}O_2$	Fruity, orris	4.12	1.12
54	Methyl 2-norbornanecarboxylate	$C_9H_{14}O_2$	NF	ND	1.59
55	3-Methyl-2-buten-1-yl trichloroacetate	$C_7H_9Cl_3O_2$	NF	ND	0.73
56	Ethyl nonanoate	$C_{11}H_{22}O$	Fruity, fatty	2.25	ND
57	Methyl undec-10-enoate	$C_{12}H_{22}O_2$	Oily	ND	0.84
58	3,7,11,Trimethyl-8,10-dodecedienylacetate	$C_{17}H_{30}O_2$	NF	ND	6.28
59	Decyl butanoate	$C_{14}H_{28}O_2$	Sweet, fruity, waxy slightly rosy	0.7	ND
60	Undec-10-enyl pentanoate	$C_{16}H_{30}O_2$	NF	ND	0.47
61	Ethyl 6,8-difluoro-4-hydroxy-3-quinolinecarboxylate	$C_{12}H_9F_2NO_3$	NF	0.96	ND
62	Methyl hexadecanoate	$C_{17}H_{34}O_2$	Fatty, oily, waxy	1.76	1.96
63	11,13-Dimethyl-12-tetradecen-1-ol acetate	$C_{18}H_{34}O_2$	NF	0.47	ND
64	[(E)-8-Methyltetradec-9-enyl] acetate	$C_{17}H_{32}O_2$	NF	0.83	ND
65	Methyl lineoleate	$C_{19}H_{34}O_2$	Oily, fatty, woody	1.37	2.46
66	Methyl oleate	$C_{19}H_{36}O_2$	Mild fatty	2.74	0.78
67	Methyl stearate	$C_{19}H_{38}O_2$	Oily waxy	1.36	0.33
68	6-{[(2E)-2-Methyl-2-butenoyl] amino} hexyl (2E)-2-methyl-2-butenoate	$C_{16}H_{27}NO_3$	NF	ND	0.88

Table 3. *Cont.*

No.	Compound	Molecular Formula	Odour Description *	% Content	
				HKF	RHKF
69	But-3-enyl pentadecyl carbonate	$C_{20}H_{38}O_3$	NF	0.83	0.42
70	methyl icosa-8,11,14,17-tetraenoate	$C_{21}H_{34}O_2$	NF	4.11	1.8
71	Fumaric acid, cyclohex-3-enylmethyl heptadecyl ester	$C_{28}H_{48}O_4$	NF	1.14	ND
72	Didodecyl succinate	$C_{28}H_{54}O_4$	NF	3.73	ND
H	Oxetanes			2.31	1.71
73	2-Ethyloxetane	$C_5H_{10}O$	NF	2.31	1.71
I	Pyrazines			0	14.92
74	2- Methyl-pyrazine	$C_5H_6N_2$	Nutty, cocoa-like	ND	3.62
75	2,3,5-Trimethylpyrazine	$C_7H_{10}N_2$	Roasted nut, baked potato	ND	2.26
76	3-Ethyl-2,5-dimethylpyrazine	$C_8H_{12}N_2$	Roasted potato, cocoa-like, nutty	ND	2.08
77	2-Ethyl-3,5-dimethylpyrazine	$C_8H_{12}O_2$	Roasted, toasted nut, chocolaty, sweet woody	ND	2.18
78	2-Isoamylpyrazine	$C_9H_{14}N_2$	Roasted	ND	1.36
79	2-Methoxy-3-(2-methylpropyl) pyrazine	$C_9H_{14}N_2O$	Green bell pepper, green pea-like	ND	1.75
80	2,5-Dimethyl-3-(2-methylpropyl) pyrazine	$C_{10}H_{16}N_2$	Nutty, roasted	ND	1.67
J	Pyrroles			0	3.81
81	1H-Pyrrole	C_4H_5N	Nutty, sweet	ND	0.48
82	1-Ethylpyrrole	C_6H_9N	Roasted, burnt	ND	1.79
83	2-Methyl-1H-pyrrole	C_5H_7N	Burnt, roasted	ND	1.54
K	Furans			2.02	6.59
84	1-(Furan-2-yl) ethenone	$C_6H_6O_2$	Sweet, almondy, nutty, coffee-like	ND	1.03
85	2-[(E)-Pent-2-enyl] furan	$C_9H_{12}O$	Roasted	ND	1.6
86	2-Heptylfuran	$C_{11}H_{18}O$	Nutty, coffee-like	0.93	2.19
87	2-Decylfuran	$C_{14}H_{24}O$	Spicy, aldehydic, fatty	1.09	1.77
L	Amines			0.84	3.36
88	Piperazine	$C_4H_{10}N_2$	Ammoniacal	ND	3.36
89	Tricyclo[4.3.1.1(3,8)]undecan-1-amine	$C_{11}H_{19}N$	NF	0.53	ND
90	5H-Dibenzo[a,d]cyclohepten-5-amine	$C_{15}H_{13}N$	NF	0.31	ND
M	Imines			0	0.86
91	(2E)-N-(Allyloxy)-4,7,7-trimethylbicyclo [2.2.1] heptan-2-imine	$C_{13}H_{21}NO$	NF	ND	0.86
N	Thiazines			0	0.97
92	3,4-Dimethyl-2-phenylthiomorpholine	$C_{12}H_{17}NS$	NF	ND	0.97
O	Oximes			0	4.99
93	2-Decanone, O-methyloxime	$C_{11}H_{23}NO$	NF	ND	3.73
94	2-Tridecanone, O-methyloxime	$C_{14}H_{29}NO$	NF	ND	1.26
	Sum of the identified compounds			96.21	93.25

* Odour description found in the PubChem database of the National Institutes of Health (NIH) (https://pubchem.ncbi.nlm.nih.gov/) and The Good Scents Company Information System (TGSC) (http://www.thegoodscentscompany.com). NF: no odour description information was found in the sources. ND: not detected; HKF: raw Hass kernel flour; RHKF: roasted Hass kernel flour.

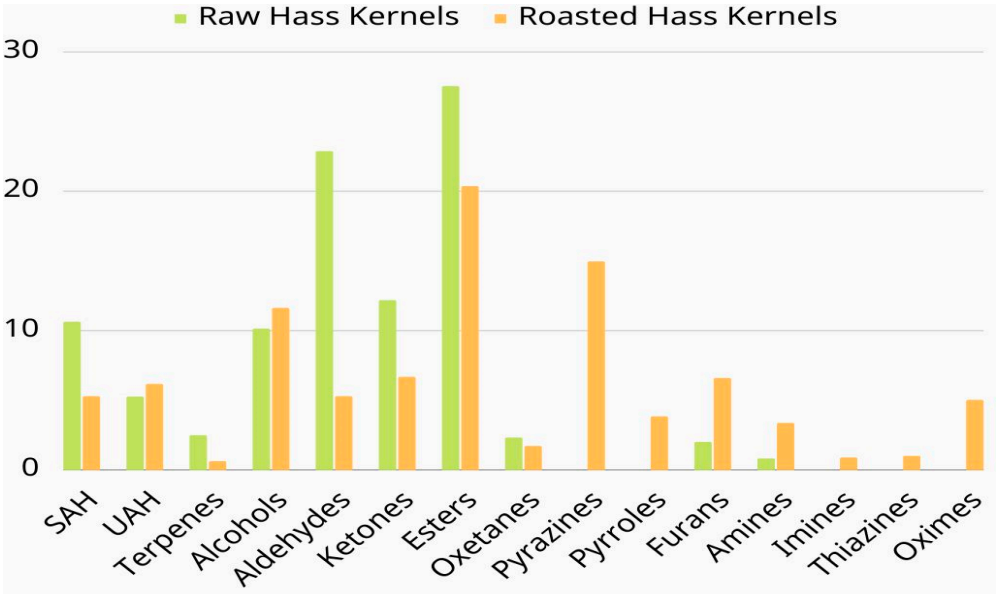

Figure 3. The total percentages of the chemical classes found in the GC-MS profile of raw and roasted avocado kernels.

4. Discussion

Roasting led to the loss of some substances in the form of water vapour and volatile compounds, and the decomposition of simple sugars, polysaccharides, amino acids, and chlorogenic acids, resulting in the formation of caramel and condensation products. On the other hand, there was an increase in some substances, especially organic acids and mineral elements. Here, we highlight the changes that occurred in the components of avocado kernels after roasting, considering the paucity of scientific research. Roasting was associated with a reduction in moisture resulting from the loss of water vapour, followed by an increase in the dry matter. The reduction in the protein content of RHKF may be attributed to the breakdown of protein into the peptides and amino acids that can participate in Maillard reactions [26,27]. The reaction between the carbonyl group of reducing sugars and the amino group of amino acids at roasting heat produces melanoidins, which are insoluble brown polymers [28]. These compounds contribute to the aroma generated by roasting, which is discussed later. Our finding is in harmony with Hosseini Bai et al., [27], who found that the protein content decreased in Canarium indicum kernels after roasting. The findings also agreed with Oboh [28] about the reduction in protein after roasting, which was 8.45% and 7.85% in raw and roasted yellow maize, respectively. Oboh [28] studied the effect of roasting yellow corn on the chemical composition and found that the crude fat, crude fibre, ash, and carbohydrate in yellow maize changed from 6.21%, 1.46%, 1.98%, and 68.23% to 7.34%, 1.26%, 1.85%, and 71.77%, respectively. This is in line with our current results. An increase in the crude fibre and ash content was reported in roasted samh (*Mesembryanthemum forsskalei* Hochst) seeds grown in Saudi Arabia [29]. Higher fibre intake is linked to a decreased risk of high cholesterol and chronic heart disease. Perhaps the increase in oil extract was caused by the breaking of the bonds between the fat and the matrix, protein denaturation, and cell membrane damage, which led to improved fat extraction [28,30]. Another conclusion was made clear by Vasconcelos et al., who reported that there was no change in the protein levels, a minor drop in the amount of ash, and a slight rise in the amount of oil extracts after roasting coffee beans [31]. Regarding the carbohydrate content of plant foods calculated by the difference after roasting, the 47% decrease in the moisture content of avocado kernels after roasting (180 °C for 30 min) ultimately affects the assessment of the carbohydrate content and the glycaemic index of roasted avocado kernel. Similar findings demonstrated that roasting skinless peanut kernels at 160 °C for 50 min increased the quantity of total phenolic compounds from 94 mg GAE/100 g raw peanut

kernels to 204 mg GAE/100 g in roasted peanut kernels [32]. The total phenol levels of raw and roasted chia seed were 3.07 and 3.43 mg GAE/g, respectively [33], which is consistent with our findings. The phenolic content in roasted avocado seed at 180 °C for 25 min and found was 179.07 ± 4.09 mg GAE/100 g [34]. These differences from our results may be caused by the different roasting times. Phenolic compounds are a class of organic molecules that have antioxidant characteristics because of their capacity to capture free radicals [35]. The increase in phenolic compounds might be caused by rupturing of the cell walls during roasting and the release of the associated phenolic compounds. Similarly, other studies have investigated the effects of roasting seeds and have suggested that roasting increases antioxidant activity through the release of phenolic fractions through the Maillard reaction during heat treatment, forming new components with antioxidant activity [12,36]. The breakdown of flavonoids during roasting may be the cause of decreases. These findings were consistent with El Anany, who found that the roasting reduced the flavonoid content of guava seeds [37], and contrasting with other researchers [29], who found that roasting samh (*Mesembryanthemum forsskalei* Hochst) seeds improved the concentration of most flavonoid compounds. There were discrepancies between the current results and those found in the literature regarding antioxidants. Another study discovered that the antioxidant activity value of chia seed extracts was 4.24 µmol TE/g for raw chia seeds, which decreased to 3.31 µmol TE/g in roasted chia seeds [33]. The variations can be related to differences in the raw materials and the roasting method.

Minerals are important in the human diet, playing a vital role as a cofactor in many reactions as well as maintaining many balances within the human body, including acid–base balance and blood pressure [38]. The higher mineral content after roasting may be a result of the increase in dry matter caused by water volatilization. The Ca, Na, Mg, and Zn content of roasted maize kernels increased significantly ($p < 0.05$) in a previous study [28]. Conversely, a significant decrease ($p < 0.05$) was observed in the Fe and K content. Another study agrees with the direction of our study. An increase was found in the content of minerals, except for iron, which decreased slightly after roasting nongerminated peanut kernels in an oven [39]. Several studies confirmed our results regarding the high content of minerals after roasting, except for iron [28,39] and potassium [28]. In 2020, Ahmed et al., reported that roasting samh (*Mesembryanthemum forsskalei* Hochst) seeds enhanced the content of major minerals (potassium and calcium), though minor minerals were reduced [29]. The results of the current study are consistent with previous studies on the effect of the roasting process on the content of minerals, although the proportions differed due to the difference in the type of seeds and the applied roasting conditions.

Avocado kernels contain some inherent antinutrients, limiting their nutritional value by interfering with the absorption or use of the minerals in the kernels [40]. Several studies have shown that the levels of tannins, saponin, phytates, alkaloids, trypsin inhibitor, and oligosaccharides was greatly reduced after heat treatment [34]. The negative effects of saponins include haemolytic action, bitterness, weakened foaming stability, and enzyme inhibition. Oxalate binds with calcium to form calcium-oxalate crystals, which are excreted in the form of urinary calcium (stones) and are linked to renal tubule obstruction. Phytic acid also prevents the absorption of Ca, Fe, Mg, and Zn through its capacity to chelate divalent cations [41]. The significant decrease in the level of antinutrients after roasting can be attributed to heat hydrolysis and/or the formation of insoluble or poorly extracted complexes [42,43]. This result confirms previous findings that plant foods' phytate content is decreased by typical food processing methods such heat treatment [44]. Ibhaze observed that after 60 min of heat treatment, avocado kernels had 10.83, 1.6, 1.44, 10.34, 6.16, and 0.02 mg/100 g of saponins, alkaloids, oxalates, phytates, flavonoids, and tannins, respectively [45]. Accordingly, the various treatments, cultivars, harvesting times, seed types (immature or ripe), extraction processes, and estimation methods may all be responsible for the high level of antinutrients.

Visible colour is an important aspect of overall quality for maintaining the level of consumer acceptance, and colour characteristics can be used as quality control indicators

in roasted food [23]. The colour parameters were described using a Konica Minolta CR-410 Chroma meter (Konica Minolta, Sensing, Inc., Japan), which include lightness (L*), redness/greenness (a*), and yellowness/blueness (b*); moreover, the browning index was used to describe the colour differences between treatments. A brown pigment created by nonenzymatic browning reactions may be the cause of the overall drop in the L* value. The heat may also have broken down some of the pigments responsible for the yellow colour. Different results were observed after roasting soybean kernels, the *L** value reported a decline from 80.62 to 49.30 and increases in the a*, b*, and browning index from 3.18 to 12.43, 24.11 to 29.49, and 38.46 to 93.82, respectively [46]. The Maillard reaction, oxidative polymerization, and the degradation of phenolic compounds are the primary processes during roasting that lead to the development of colour compounds [9]. These reactions result in molecules that are brown in colour and have a familiar caramel and roasty fragrance, depending on the type of sugar and the reaction temperatures. The amount of sugar, the presence of reducing sugars, and their interaction with protein are among the main factors for the degree of change in colour parameters, in addition to lipids, roasting time, temperature, and roasting methods. One of the elements that is frequently used to assess the impact of roasting is colour evolution.

Typically, avocados are harvested from trees when they are physiologically mature but unripe, which means that the phytochemical composition of each part, including the kernels, may change as the fruit ripens for various times [47]. Looking at the results (Table 3), we can notice that esters and aldehydes together account for 50.39% which is more than half of the relative content of the GC-MS profile of raw avocado kernels. Some of the most significant compounds responsible for the characteristic odour are esters, which are especially responsible for the fruity smell in many plants. Esters represent 27.53% of the total content of the compounds that have been identified in raw avocado kernels, with a total of 15 compounds. These compounds are characterized by various odours. Methyl heptanoate was the most abundant, with 4.12%; this compound is characterized by a fruity smell. Moreover, other compounds described as having a fruity odour have been identified in different proportions, namely ethyl nonanoate (2.25%), methyl 2-hydroxyacetate (1.16%), and decyl butanoate (0.7%). Some esters with an oily smell have been identified, such as methyl oleate (2.74%), methyl hexadecanoate (1.76%), methyl lineoleate (1.37%), methyl stearate (1.36%), and methyl undec-10-enoate (0.84%). Aldehydes are important compounds with a variety of fragrance notes. Under the conditions of our present study, 11 aldehyde compounds were identified from the GC-MS profile, making up 22.86% of the relative content of the GC-MS profile of raw avocado kernels. Some of these compounds are expressed in the scientific literature as having a green grassy odour, such as (E)-hept-2-enal (5.36%), (Z)-hex-3-enal (2.09%), and propanal (1.96), or a fruity odour, such as cyclohex-3-ene-1-carbaldehyde (4.92%) and 2-ethylbutanal (3.68%).

Regarding the GC-MS profile of raw avocado kernels, the findings of our research differ somewhat from those of Younis et al., who found that Egyptian Hass avocado had 30.4% total esters, 18.83% unsaturated aliphatic hydrocarbons, 13.34% saturated aliphatic hydrocarbons, 6.55% total alcohols, 4% total oxygenated sesquiterpenes, and 0.6% total aldehydes or ketones. In general, these results differed significantly from those for Moroccan and Lebanese Hass avocados, as well as the Reed, Pinkerton, and Gwen cultivars grown in Egypt, South Africa, and Kenya. The difference in the results of the current research and the results of [48] can be explained by the different varieties, the geographical areas from which the samples were taken, the age of the fruits, the duration of seed storage, and the method of analysis.

Roasting significantly reduced the content of aldehydes by 76.82%, that of terpenes by 74.19%, that of saturated aliphatic hydrocarbons by 50.19%, that of ketones by 45.11%, and that of esters by 26.04%. This decrease was favour of the emergence of chemical classes that were not present in HKF, namely pyrazines, pyrroles, imines, thiazines, and oximes.

Generally, pyrazine produces a roasted aroma and is formed by the Maillard reaction to produce glycosylamine, which undergoes the Amadori rearrangement process. Various

derivatives are formed through degradation, dehydration, condensation, and polymerization reactions [49]. The content of pyrazines formed depends on several factors, including the ratio between amino acids and sugars, the roasting temperature, and its duration.

In our current study, seven pyrazines were formed by roasting at 180 °C for 30 min: 2-methyl-pyrazine (nutty, cocoa-like odour), 2,3,5-trimethylpyrazine (roasted nut, baked potato odour), 3-ethyl-2,5-dimethylpyrazine (roasted potato, cocoa-like, nutty), 2-ethyl-3,5-dimethylpyrazine (roasted, toasted nut, chocolaty, sweet woody odour), 2-isoamylpyrazine (roasted odour), 2-methoxy-3-(2-methylpropyl) pyrazine (green bell pepper, green pea-like), and 2,5-dimethyl-3-(2-methylpropyl) pyrazine (nutty, roasted). High-temperature roasting causes the formation of furan through several pathways, and it is suggested that carbohydrates, sugars, amino acids, and ascorbic acid are the most important precursors for furan's formation [50]. One of these pathways is the degradation of carbohydrates through the Amadori rearrangement, which is likely to be the main pathway for the formation of furans in a relatively low-temperature roasting treatment [51]. Here, 1-(furan-2-yl) ethenone (sweet, almondy, nutty, coffee-like odour) and 2-[(E)-pent-2-enyl] furan appeared in the roasted Hass avocado kernels and were not present in the raw Hass kernels; moreover, the quantity of 2-heptylfuran (nutty, coffee-like odour) and 2-decylfuran (spicy, aldehydic, fatty), increased in the roasted avocado kernels, despite their presence in the raw kernels.

Pyrroles can be formed by the thermal degradation of amino acids [52]. Three pyrroles appeared in the roasted Hass kernels, namely 1H-pyrrole (nutty, sweet odour), 1-ethylpyrrole (roasted, burnt odour), and 2-methyl-1H-pyrrole (roasted, burnt odour).

5. Conclusions

The utilization of agricultural waste is a global challenge. The roasting process is characterized by a low cost, and it has a positive impact on the sustainability of environmental systems. The nutritional data revealed a significant increase ($p < 0.05$) in the oil extract, crude fibre, total phenolic compounds, Ca, K, P, Na, Zn, browning index, and redness/greenness after roasting the Hass kernels. In total, 94 volatile compounds were identified in the raw and roasted Hass avocado kernels flour. Esters were the most common chemical compound classes present in both raw and roasted Hass kernel extract, with 15 and 14 compounds identified, respectively. From the results of analysing the chemical composition and antinutritional properties, in addition to the properties revealed by the GC-MS profile, RHKF can be used in different food applications, including pastries and beverages, and especially coffee. The authors recommend further studies on the effect of enrichment with RHKF on the rheological properties and colloidal traits of foods.

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