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Comparative Elucidation of Aroma, Key Odorants, and Fatty Acid Profiles of Ivorian Shea Butter Prepared by Three Different Extraction Methods

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Abstract: In the present study, the volatile compounds, key odorants, and fatty acid profiles of Ivorian shea butter produced by cold press extraction (CPE), solvent extraction (SE) and traditional extraction (TE) methods were investigated for the first time. The aroma compounds of shea butter were extracted by the purge and trap method and analyzed by the gas chromatography–mass spectrometry and olfactometry (GC-MS/O) technique. Totals of 51, 49 and 46 aroma compounds were determined in samples from CPE, SE and TE, respectively. It was observed that the volatile compounds of studied material dominated after CPE, in which alcohols (11) were the most abundant chemical group, followed by aldehydes (10) and acids (7). The application of aroma extract dilution analysis (AEDA) resulted in 22, 20, and 16 key odorants in shea butter from CPE, SE and TE, respectively. 3-Hexanol with flavor dilution (FD) factors (2048 in CPS, 1024 in SE and 64 in TE) was found to be the most active aroma compound in all samples. In the fatty acid fraction obtained using the gas chromatography–flame ionization detector (GC-FID) method, 22, 24 and 19 fatty acids were detected in samples after CPE, SE and TE, respectively. The highest number of fatty acids was determined in shea butter using CPE (89.98%). Stearic and oleic acids were the most dominant fatty acids, and all samples of shea butter were rich sources of saturated fatty acids (SFAs). Moreover, the SE samples showed the highest values of DPPH (238.36 μM TEq/kg) and ABTS (534.96 μM TEq/kg), while the CPE samples had the highest total phenolic content (104.64 mg GAE/kg). Principal component analysis (PCA) clearly indicated that the extraction technique could quantitatively or qualitatively induce changes. Thus, this investigation demonstrated that extraction methods have a considerable impact on the quality and chemical composition of the presented material.

Keywords: shea butter; aroma; extraction process; fatty acids; key odorants

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1. Introduction

A great variety of tropical edible seeds have gained a pervasive demand for their considerable source of lipids, high nutritional value and potential health benefits. Among them, shea butter is a plant-based fat generated from shea tree (*Vitellaria paradoxa*) kernels. *V. paradoxa*, also named *Butyrospermum parkii* L., is the unique species of the *Vitellaria* genus from *Sapotaceae* family. The shea tree is a perennial wild tree widely distributed in the savanna across West and Central Africa [1]. Shea butter is one of the oldest kernel fat products in that territory. It has been used for culinary and traditional medicinal purposes for centuries. The shea butter has a long allocation in tradition, medicine and culture in Ivory Coast. It is locally named "*beurre de karité*" and used to mitigate irritation, insect bites, bruises and rheumatic pains, as well as for newborn skin care. Nowadays, its

industrial applications in cosmetic, pharmaceutical, modern culinary and confectionary industries (as a substituent of cocoa butter in chocolate) make it an attractive product for commercial use [2,3]. Some previous studies reported high contents of several bioactive and nutritive compounds, e.g., unsaponifiable triterpenes, phytosterols, tocopherols and phenolic compounds, in shea butter, which justifies its intensive usage in the cosmetic sector, especially in skin care formulations [4]. Various types of shea butter (white and black) are produced for different needs, especially for culinary and industrial purposes [5]. Shea butter contains a rich source of fatty acids, and its composition could be influenced by extraction processes and climatic conditions [5]. The fat yield of shea seed is up to 50%, whereas the butter has high contents of stearic (25–50%) and oleic (37–62%) acids. Moreover, a fraction of triacylglycerols in shea butter was already described in the literature [6].

Shea butter has a strong characteristic aroma, which is a combination of the interaction and the perception of various chemicals. The number of low molecular weight volatile compounds and in most cases their composition and amount significantly vary. It depends on the food matrix, processing techniques, cultivar, climatic conditions, storage and other internal and external conditions. The majority of oil seeds or kernels are dried or roasted to reduce water content for better preservation or to facilitate oil extraction. During these processes, some volatile substances can be degraded or retained, while some volatile compounds may be generated via several reactions, such as oxidation. The shea butter is very popular, especially in the northern part of Ivory Coast, for its unique strong aroma and taste. Although some limited studies have been focused on the bioactive compounds and physicochemical and nutritional constituents of shea butter, only two detailed works have been published on the volatile components of shea butter so far. Krist et al. [7] investigated the volatiles of black and white shea butters using SPME-GC-MS and detected about 100 volatile substances, mainly composed of volatile fatty acids, carbonyl compounds, terpenes, furans and pyrazines. Bail et al. [5] studied the volatile constituents of shea butter from different regions of Africa and identified 28 to 47 aroma compounds, including mostly volatile acids, aldehydes, furans and pyrroles, in extracts of shea butter.

The aromatic fractions of food matrixes are composed of a large number of groups of volatile substances, but only a small proportion of these fractions provides the specific odors of foods and plants. Therefore, the isolation and identification of these key odorants from the complex matrix of volatile compounds is one of the crucial points of aroma investigations. The gas chromatography–olfactometry (GC-O) technique has been widely used to determine the characteristic aroma-active compounds [8,9].

To the best of our knowledge, the aroma-active compounds responsible for the characteristic odor of shea butter still have not been investigated. Therefore, the topic of the present study is to elucidate the key odorants of shea butter samples by gas chromatography–mass spectrometry and olfactometry (GC-MS-O) for the first time and to ascertain the effects of different extraction methods (CPE, SE and TE) on shea butter aroma, fatty acid profile, total phenolic content and antioxidant capacity.

2. Materials and Methods

2.1. Materials

2.1.1. Plant Material

The fruits (approx. 10 kg) of shea were freshly collected from shea butter production area of Korogho in northern part of Ivory Coast in 2021 harvesting season. At the same time, traditionally processed shea butter was also obtained from the production area and stored in 25 mL brown bottles. The collected fruits were sun-dried at an estimated temperature of 40 °C for 3–4 days up to a moisture content of 7%. After the removal of kernels from the nuts, sun-dried shea kernels were packed in polyethylene humidity-proof bags and brought to Cukurova University (Adana, Turkey), where they were stored at 4 °C until experiments.

2.1.2. Chemicals and Reagents

Distilled water was obtained by double purification using a Millipore-Q system (Millipore, Billerica, MA, USA). Dichloromethane (≥99.8 purity, CAS#: 75-09-2), methanol (≥99.9 purity, CAS#: 67-56-1), sodium carbonate (CAS#: 497-19-8), potassium hydroxide (CAS#: 1310-58-3), n-hexane (≥99.8 purity, CAS#: 110-54-3) and 4-nonanol (CAS#: 5932-79-6) were provided by Merck (Darmstadt, Germany). Folin–Ciocalteu (CAS#: 12111-13-6), gallic acid (CAS#: 149-91-7), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS, CAS#: 28752-68-3), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox, CAS#: 53188-07-1), 2,2-diphenyl-1-picrylhydrazyl (DPPH, CAS#: 1898-66-4) and all aroma and phenolic standards used in this work were acquired from Sigma-Aldrich (St Louis, MO, USA).

2.2. Shea Butter Extraction Process

Shea butter extraction was based on an artisanal and lab-scale extraction technique. Once harvested, the shea nuts were sun-dried, slightly roasted and crushed into a paste (manually or using a mill), from which the lipid fraction was removed through a process called "kneading", consisting of manually mixing and squeezing the oil from the kernel paste with a substitute mixture of hot and cold water. Afterward, the liquid (shea butter and water) was boiled out to remove the water. Then, shea butter was poured through a white filter cloth and left to dry completely. The dried shea butter was directly stored in two brown bottles of 25 mL. This traditional shea butter extraction method (TE) is popular in western Africa and has been well explained by Krist et al. [7] and Bail et al. [5].

For the other two extraction methods, the dried kernels of shea (approximately 8 kg) were finely ground using a lab-scale grinder (Waring 8011; Torrington, CT, USA). The obtained powder was divided into two batches for lab-scale extraction techniques. The first batch was subjected to a solvent extraction (SE method) using the method of Folch with some modifications [10]. Briefly, 10 g of finely ground shea kernel samples was placed into a 100 mL flask, in which 50 mL of n-hexane was added. The solution was left at room temperature overnight. Then, the solvent was evaporated (rotary evaporator, CCA-1100, EYELA, Tokio, Japan) at 50 °C, oven-dried (50 °C) and afterwards dried under nitrogen gas flow for an hour. The analysis was conducted in three repetitions and the fat yield was computed in percentage (%). A second batch was subjected to a cold press extraction (CPE method) using a Karaerler (NF-80) cold press machine (Mamak, Ankara, Turkey) at room temperature. Therefore, we obtained samples of shea butter that were stored into 25 mL closed brown bottles prior to analysis.

2.3. Color Measurement

The color profiles of shea butter samples were determined using a calibrated color measurement instrument (Minolta, CR 400, Osaka, Japan) using CIE Lab scale (L*, a* and b*). Before analysis, shea butter samples in solid form were slightly heated in water bath at 50 °C. The obtained liquid samples of shea butter were placed into sample cells (6 cm diameter; 2 cm deep) and measured, and the revealed data were recorded to the software. All measurements were performed at room temperature (22 ± 2 °C) in triplicates.

2.4. Total Phenolic Content (TPC) Analysis

The TPC of shea butter extracts was assessed by the Folin–Ciocalteu method [11,12]. The absorbance was recorded at 765 nm using a UV spectrophotometer (Shimadzu UV1201, Tokyo, Japan). The TPC amount was computed using gallic acid as reference for the calibration curve (r = 0.999) and expressed as milligrams of gallic acid equivalents per kilogram of sample (mg GAE/kg). The TPC of each shea butter sample was conducted in three replications.

2.5. Analyses of Antioxidant Capacity

ABTS (2,2′-azino-bis (3-ethylbenzothiazoline)-6-sulphonic acid) and DPPH (2,2-diphenyl-1-picrylhydrazyl) assays were carried out according to the method described by Kesen et al. [13] and Kelebek and Selli [14].

In the ABTS assay, the absorbance at 734 nm was read by a UV spectrophotometer (Shimadzu UV1201, Tokyo, Japan) and the ABTS radical scavenging activity of each shea butter extract was evaluated from the calibration curve of Trolox (R^2 = 0.999). The ABTS results were given in µmoL TEq/kg [13].

For the DPPH assay, the absorbance was measured at 515 nm and the DPPH potential was calculated as µmoL TEq/kg using Trolox by a calibration curve (R^2 = 0.997). All antioxidant analyses were performed in three repetitions [14].

2.6. Fatty Acid Analyses

The fatty acids of shea butter samples were firstly transformed into fatty acid methyl esters (FAMEs) by cold transmethylation using methanolic KOH solution [15]. Briefly, 0.1 g of each sample was put in different screw-top test tubes and 2 mL of heptane was added. The tubes were slightly shaken and 0.2 mL of methanolic KOH solution was added. Afterwards, tubes were vigorously shaken for a minute and the clear proportion of methylated phase of each assay was passed through a 0.45 membrane filter and transferred into a vial for GC-FID analysis.

Fatty acids were identified by a gas chromatography (Agilent 6890 N gas chromatography, Wilmington, DE, USA) system coupled with a flame ionization detector (FID). Each individual fatty acid was fragmented on a DB23 capillary column (60 m × 0.25 mm inner diameter) from Agilent Technologies, Inc. (Santa Clara, CA, USA). The carrier gas used in the analysis was hydrogen and the temperatures of the injector and detector were set at 250 °C and 300 °C, respectively. An aliquot volume of 1 µL was injected into GC-FID with an initial oven temperature adjusted to 130 °C, maintained for a minute and increased from 130 to 170 °C with a rate of 6.5 °C/min. The temperature was then raised to 215 °C with an increase of 2.75 °C/min and kept for 12 min and finally increased to 230 °C by an increase of 40 °C/min for 3 min. FID consists of a hydrogen (H_2)/air flame and a collector plate to carry out the ionization. The individual fatty acids were detected by matching their retention times to those of known fatty acid standards and the concentration of fatty acids was expressed in percentage (%, *w*/*w*).

2.7. Extraction of Shea Butter Volatile Compounds by Purge and Trap Technique

Volatile components of shea butter samples were extracted using purge and trap extraction (PTE) technique, which was composed of a flowmeter to control the nitrogen gas flow and a splitter system splitting the gas into different channels to purge several samples simultaneously. Lichrolut EN tubes were filled with 200 mg of resins which were provided as suitable absorbent material regarding earlier studies [16,17]. A total of 6 g of each shea butter sample was placed into 20 mL vials and 5 µL of 4-nonanol (41.5 µg/L) was used as an internal standard. The vials were sealed and preheated at 60 °C for 10 min regarding the purging procedure optimization. Afterwards, the process was conducted at the same temperature for 120 min under a constant nitrogen gas flow rate of 50 mL/min. The volatiles grabbed in the cartridges were desorbed with 6 mL dichloromethane after the purge. Eluted volatiles were dried with anhydrous sodium sulphate and condensed by evaporation to 5 mL in a Kuderna Danish concentrator coupled with a Snyder column at 40 °C and were used to concentrate the aromatic extracts. Subsequently, the extract volume was reduced to 0.5 mL with a nitrogen gas stream. The final extract volume was transferred into an inert glass vial and kept at −20 °C until GC-FID/MS analysis. The quantification of volatile components was assessed by the internal standard method, as previously mentioned in detail by Sevindik et al. [18]. The extraction of each sample was performed in triplicates.

2.8. GC-MS Analyses of Shea Butter

A GC device composed of an Agilent 6890 chromatograph coupled to a flame ionization detector (FID) (DE, USA) and an Agilent 5973 N mass selective detector (MSD) (DE, USA) were utilized in the characterization of volatile constituents. GC effluent was divided into three channels as 1:1:1 between the FID, MS and sniffing port by a Deans switch. Volatile substances were split up on DB-Wax (30 m × 0.25 mm, 0.5 thickness, J W Scientific, Folsom, CA) column. An amount of 3 µL of each volatile extract was injected in pulsed splitless (40 psi, 0.5 min) mode. The FID and injector were adjusted at 270 °C and 280 °C, respectively. The carrier gas (helium) was set at 1.5 mL/min. The GC oven was operated from 40 to 130 °C at 5 °C/min and then to 240 at 8 °C/min. The MS parameters were programmed according to our previous well-documented studies [15,19]. The volatile components were scanned by comparing their mass spectra with those of mass spectra data libraries (Wiley 11, Flavor 2 L, NIST). Standards of some identified volatile compounds were injected to GC-MS for a double-check, while the retention indices of individual compounds were computed using the retention data of a linear n-alkane (C_5–C_{30}) series. The internal standard method was conducted to quantify the volatiles. 4-nonanol was used as internal standard in the extractions because it fulfilled all necessary criteria as internal standards [20,21] and behaved similarly with the main groups of analytes in studied samples. A quantitative method based on a combination of experimental calibration by internal standards and FID response factors was employed.

2.9. Aroma Extract Dilution Analysis (AEDA)

The key odorants of shea butter were determined by using a GC-MS system equipped with a Gerstel ODP-2 (Baltimore, MD, USA). Briefly, the original extracts (200 µL) of each shea butter were serially diluted by using dichloromethane from 1:1 to 1:2, to 1:16 and to 1:2048 until no odor stimulation could be perceived at the sniffing port regarding AEDA method. Consequently, flavor dilution (FD) factors were calculated for individually identified aroma-active compounds (FD $\geq$ 4). The procedure was successfully conducted and well explained in our previous studies [22,23].

2.10. Sensory Analysis of Shea Butter

Descriptive sensory evaluation was conducted to determine the sensory markers of shea butter samples. For this purpose, nine trained panelists (four females and five males, aged between 25 and 55 years) were selected among trained panelists of Food Engineering Department of Cukurova University. Eleven descriptors, including fatty, smoky, rancid, pungent, fruity, nutty, floral and earthy scents, overall aroma, color and general acceptability were selected to ascertain sensory profiles of shea butter. Expert panelists assessed the sensory properties corresponding to the above-mentioned attributes of the given samples on a scale of 10 cm, where 0 was extremely low or no perception and 10 symbolized intense perception. The average score of sensory marks collected from the panelists (each repeated three times) on a scale of 10 cm was computed in centimeters and given as a spider graph.

2.11. Statistical Analysis

All the numerical data obtained from the experiment were treated in the SPSS software program (SPSS Inc., Chicago, IL, USA). The analysis was carried out in triplicates and the results were given as mean ± standard deviation. One-way analysis of variance (ANOVA) with 95% confidence level and multiple range test (Duncan's test) were conducted on the aroma components characterized to the difference between different extraction methods of shea butter. In addition, principal component analysis (PCA) was performed using XL-Stat software 2020.1 (Addinsoft, New York, NY, USA) to elucidate the discrimination of volatiles based on shea butter extraction processes.

3. Results and Discussions

3.1. Color Properties and Lipid Contents

The variation in the color parameters of shea butter is shown in Table 1. It was observed that the extraction method of shea butter significantly induced color change. The L* values of TE, SE and CPE were measured as 66.18, 55.23 and 37.18, respectively. According to these results, it may be stated that the CPE extraction process caused a considerable decrease in L* values, which is a consequence of this darker color developed in CPE extraction. However, the TE butter sample had an increase in L* values corresponding to lighter colors. Moreover, an increment in a* values was observed in the CPE and SE samples (Table 1). Similarly, a significant increase in b* values was recorded in the samples: 19.42, 28.06 and 39.10 for TE, SE and CPE samples, respectively. These findings show that there existed a degradation in the yellow color of shea butter during the traditional extraction process. In addition, it was found that CPE caused a significant color alteration ($p < 0.05$) when compared to SE and TE samples.

Table 1. Physicochemical composition of shea butter.

Parameters †	CPE	SE	TE
	Mean (SD)		
Phenolic content (mg GAE/kg)	104.64 (0.61) [a]	88.52 (0.13) [b]	56.58 (0.64) [c]
ABTS (μM TEq/kg)	226.50 (19.44) [b]	534.96 (17.07) [a]	128.29 (12.02) [c]
DPPH (μM TEq/kg)	132.84 (25.09) [b]	238.36 (21.41) [a]	96.29 (21.41) [c]
Oil content (%, *w*/*w*)	48.73 (2.52) [b]	57.23 (1.60) [a]	-
Acid value (mg KOH/kg)	2.06 (0.65) [c]	2.94 (0.45) [b]	4.66 (1.54) [a]
Peroxide value (mEq/kg)	2.28 (0.44) [b]	1.88 (0.42) [c]	2.94 (0.88) [a]
Iodine value (I_2 g/100 g)	28.74 (2.41) [c]	32.36 (1.06) [b]	44.52 (4.86) [a]
L *	37.18 (1.98) [c]	55.23 (1.43) [b]	66.18 (2.19) [a]
a *	12.35 (0.11) [a]	9.83 (0.34) [b]	5.68 (0.46) [c]
b *	39.10 (0.64) [a]	28.06 (0.85) [b]	19.42 (1.85) [c]

† Values are means and standard deviations (mean (SD)) of ten measurements for color analysis and three replications for other experiments. Different lowercase letters on the numbers in the same line represent significant differences ($p < 0.05$). CPE: cold press extraction; SE: solvent extraction; TE: traditional extraction methods.

3.2. Total Phenolic Content and Antioxidant Potential

The total phenolic content of shea butters obtained from the three different extraction processes are given in Table 1. It was found that the TPC of the CPE shea butter sample (104.64 mg GAE/kg) was higher than that of the SE (88.52 mg GAE/kg) and TE (56.58 mg GAE/kg) samples. According to the revealed data, a significant loss was determined in the TPC level of the TE sample. The alteration of TPCs among the samples was statistically significant ($p < 0.05$). Maranz et al. [24] investigated the TPC of shea butter samples extracted from different shea kernels. The authors determined that the TPCs of the shea butter samples were in the range of 62–135 μg/g with an average value of 97 μg/g. It was also reported that about 90% of phenolics were lost during the butter extraction. Similarly, in our study, TPC changed significantly according to the extraction process and CPE was found to preserve the phenolics better that the other methods.

As the antioxidant activity assays are based on different specific mechanisms, it is crucial to apply more than one method to determine activity and account for various mechanisms. The antioxidant potentials of shea butter determined with the application of DPPH and ABTS techniques are grouped in Table 1. Based on the data, ABTS values were recorded to be significantly higher than DPPH values in all samples. These differences may be explained by the fact that ABTS can be utilized in lipophilic and hydrophilic mediums, while DPPH is more attractive in lipophilic medium [25]. Similarly, Sinan et al. [26] reported higher antioxidant activity in the ABTS procedure than the DPPH method applied to shea leaves and stem barks. In our study, the lowest value of DPPH was measured in TE

(96.29 μM TEq/kg), while the highest value was observed in SE (238.36 μM TEq/kg). In regard to ABTS results, the highest value was calculated in SE (534.96 μM TEq/kg), which was statistically higher than that of CPE and TE.

3.3. Fatty Acid Composition

The fatty acid profiles of shea butter samples were calculated in terms of percentage. The revealed data are composed of saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs) and polyunsaturated fatty acids (PUFAs). A total of 24 different fatty acids with a chain length from C14 to C24 was identified in shea butters obtained from CPE, SE and TE (Table 2). The profiles of fatty acids were quite similar in all shea butter samples from CPE and SE, while arachidic acid (C20:0), *y*-linolenic acid (C18:3 n6), arachidonic acid (C20:4), eicosapentaenoic acid (C20:5), lignoceric acid (C24:0), and nervonic acid (C24:1) were not detected in the TE sample. The total fatty acid content was higher in the CPE (89.98%) sample than in the TE (80.70%) and SE (68.55%) samples. Interestingly, SFAs were the major fatty acids in the CPE and SE shea butter samples, in which the stearic acid (C18:0) was quantitatively the prominent SFA in the CPE (46.8%) and SE (38.6%) samples, respectively. Okullo et al. [27] analyzed the composition of fatty acids in shea butter, and they found that the stearic acid level was 30.9%. Similarly, according to the study of Ugese et al. [28], stearic acid was found to be the dominant fatty acid in shea butter. These results are compatible with the data revealed in the present study. Monounsaturated fatty acids were found to be the second most abundant fatty acid in CPE (37.12%), SE (26.80%) and TE (41.86%), respectively. MUFAs were the highest fatty acid group found in shea butters obtained from the traditional extraction process. In all shea butter samples, transoleic acid (C18:1T) was identified as the prevailing MUFA (Table 2). This value was quite similar to that determined by Hartman et al. [29]. Low amounts of PUFAs were found and dominated by α-linolenic acid (C18:3 n3) (CPE: 0.26%, SE: 0.28% and TE: 1.24%). It can be stated from the results that shea butter contains a significant amount of saturated fatty acids. The compositions of MUFAs and SFAs in shea butter were similar to those of coconut oil and different to those of sunflower, rapeseed, maize and palm oils, according to the research of Mitrea et al. [30]. It is a well-known fact that these fatty acids are resistant to some adverse conditions, mainly light, temperature and oxygen through oxidation [31]. Some other fatty acids were present in trace amounts in shea butter samples.

Table 2. Fatty acids composition.

No.	Fatty Acids	Denotation	Shea Butter Samples [%, *w*/*w*]		
			CPE	SE	TE
			Mean (SD)		
1	Myristic acid	C14:0	0.02 (0.00) ^{b}	0.01 (0.00) ^{b}	0.04 (0.01) ^{a}
2	*cis*-10-Pentadecanoic acid	C15:1	6.12 (1.21) ^{a}	3.12 (0.04) ^{b}	Trace
3	Palmitoleic acid	C16:1	0.70 (0.01) ^{a}	Trace	0.02 (0.00) ^{b}
4	Margaric acid	C17:0	0.08 (0.02) ^{b}	0.02 (0.00) ^{c}	1.36 (0.05) ^{a}
5	Margoleic acid	C17:1	0.02 (0.00) ^{c}	0.03 (0.01) ^{b}	4.56 (0.08) ^{a}
6	Stearic acid	C18:0	46.8 (2.70) ^{a}	38.6 (1.56) ^{b}	32.9 (0.9) ^{c}
7	*trans* Oleic acid	C18:1 *T*	29.37 (1.2) ^{b}	22.58 (0.8) ^{c}	36.86 (1.4) ^{a}
8	*cis* Oleic acid	C18:1 *is*	0.81 (0.03) ^{a}	0.52 (0.01) ^{b}	0.34 (0.02) ^{c}
9	*trans* Linoleic acid	C18:2 *T*	0.23 (0.01) ^{a}	0.25 (0.01) ^{a}	0.09 (0.00) ^{b}
10	Linoleic acid	C18:2	0.06 (0.00) ^{a}	0.05 (0.00) ^{a}	Trace
11	Arachidic acid	C20:0	5.22 (0.81) ^{a}	1.39 (0.08) ^{b}	ND
12	*y*-Linolenic acid (GLA)	C18:3 *n*6	trace	0.22 (0.00)	ND
13	Gadoleic acid	C20:1	0.05 (0.01) ^{b}	0.5 (0.02) ^{a}	0.02 (0.00) ^{c}
14	*α*-Linolenic acid (ALA)	C18:3 *n*3	0.26 (0.02) ^{b}	0.28 (0.03) ^{b}	1.24 (0.9) ^{a}
15	Heneicosylic acid	C21:0	Trace	Trace	0.08 (0.01)
16	*Cis*-11,14-Eicosadienoic acid	C20:2	ND	0.05 (0.00) ^{b}	0.73 (0.10) ^{a}
17	Dihomo *Y*-linolenic acid (DGLA)	C20:3 *n*6	0.10 (0.03) ^{a}	0.12 (0.02) ^{a}	0.04 (0.00) ^{b}

Table 2. *Cont.*

No.	Fatty Acids	Denotation	Shea Butter Samples [%, *w*/*w*]		
			CPE	SE	TE
			Mean (SD)		
18	Behenic acid	C22:0	0.05 (0.00) ^{c}	0.39 (0.00) ^{b}	0.85 (0.04) ^{a}
19	Arachidonic acid	C20:4	0.02 (0.00) ^{b}	0.1 (0.02) ^{a}	ND
20	Erucic acid	C22:1	ND	0.02 (0.00) ^{b}	0.06 (0.00) ^{a}
21	Tricosanoic acid	C23:0	0.01 (0.00) ^{b}	0.02 (0.00) ^{b}	1.56 (0.05) ^{a}
22	Eicosapentaenoic acid	C20:5	0.06 (0.00) ^{a}	0.09 (0.00) ^{a}	ND
23	Lignoceric acid	C24:0	0.06 (0.00) ^{b}	0.1 (0.02) ^{a}	ND
24	Nervonic acid	C24:1	0.05 (0.00) ^{a}	0.03 (0.00) ^{a}	ND
	ΣSFA		52.25	40.6	36.78
	Σ MUFA		37.12	26.8	41.86
	Σ PUFA		0.61	1.15	2.06
	ΣFA		89.98	68.55	80.7

Values are means and standard deviations (mean (SD)) of three replications. Different lowercase letters on numbers in the same line represent significant difference ($p < 0.05$). CPE: cold press extraction; SE: solvent extraction; TE: traditional extraction methods.

3.4. Sensory Assessment of Shea Butter

Similarity and intensity. The selection of a suitable extraction technique in aroma analysis is based on the similarity and intensity of extracts to that of the essayed sample before GC-MS-O analysis. According to results obtained by the selected panelists, the mean similarity (69.2 mm on 100 mm scale) and intensity scores (78.5 mm on 100 mm scale) of aromatic extracts were found to be acceptable. These results are in accordance with previous studies conducted on different food matrixes such as orange wine, edible red algae and *Hibiscus sabdariffa* [19,20,31]. Hence, the purge and trap extraction technique was found as the most appropriate method for detailed shea butter aroma analysis.

Sensory profiles. The results of the sensory evaluation of shea butter samples obtained from the panelists are designed as a spider graph (Figure 1) using eleven attributes (fatty, smoky, rancid, nutty, pungent, floral, earthy and fruity notes, overall aroma, color and general acceptability). The sensory results collected from each panelist were transformed in numerical data and computed by analysis of variance using a confidence level of 95%. Regarding the sensory analysis, the strongest nutty note was observed in CPE (8.2), while its score was found to be 6.4 and 4.6 in the SE and TE samples. The aroma dominancy was mostly attributed to CPE (7.8) and the lowest aroma value was obtained in the TE sample (4.9). As it can be indicated in Figure 1, the color and fruity and fatty notes values were mostly assigned a shea sample from cold press extraction process. Considering the general acceptability values, CPE possessed the highest values of the samples. In regard to rancid notes, TE (8.2) demonstrated the highest value, followed by the CPE (5.4) and SE (4.7) samples.

3.5. Volatile Composition of Shea Butter (Vitellaria Paradoxa) Samples

Table 3 shows the GC-MS results of the aroma compounds of shea butter samples obtained from CPE, SE and TE using the purge and trap technique, the identification parameters, the concentration (mg/kg) of the detected compounds and the standard deviations. The aroma profiles of the shea butter samples were observed to be greatly influenced by extraction conditions. As shown in Table 3, totals of 51, 49 and 46 compounds were found in CPE, SE and TE processes, including aldehydes (10), alcohols (11), acids (7), pyrazines (2), ketones (5), furans (4), ester (3), terpenes (6) lactones (2), volatile phenols (3), hydrocarbons (2) and a pyrrole. It was observed that the CPE and SE samples provided quite similar aroma profiles, while a great difference was seen in TE sample. This difference showed the significant role played by the extraction process on the number of identified aroma compounds. The prevalent aroma group in all samples was alcohols, followed by aldehydes and acids. Nonetheless, other volatile groups such as furans and terpenes were quantitatively reported in all shea butter samples. The majority of these compounds have

been indicated in many varieties of seed oils, as mentioned in earlier studies [16,32]. The total amount of volatile compounds in the CPE (229.28 mg/kg) sample was higher than in the SE (210.92 mg/kg) and TE (174.38 mg/kg) samples. According to the revealed data, the traditional extraction process caused some aroma loss both quantitatively and qualitatively. It is well understood that drying (temperature and time) and extraction conditions together with many other factors significantly influence chemical composition, particularly the volatile compounds of food-based nuts or seeds [33].

Alcohols. Alcohols were the principal aroma group in terms of total number and concentration in all samples. The formation of these compounds is related to the oxidation of USFAs or the degradation of aldehydes [34]. The total amount of alcohols was 110.09 mg/kg (48.01% of overall aroma), 75.92 mg/kg (35.99% of overall aroma) and 49.60 mg/kg (28.44% of overall aroma) in the CPE, SE and TE samples, respectively. Among the samples, CPE exhibited the highest number of volatile alcohols. Moreover, 3-hexanol was the prevailing aroma constituent in CPE (27.77 mg/kg), SE (58.91 mg/kg) and TE (41.99 mg/kg) samples, respectively. The straight chain alcohols such as 3-hexanol could be generated from the oxidative degradation of their corresponding aldehydes (hexanal) and other aldehydes. 3-Octanol was the second most abundant alcohol in all the samples, especially in the CPE sample (19.64 mg/kg). Thus, alcohol compounds were similar in number, while *(E)*-2-hexanol and phenylethyl alcohol were not found in the TE sample. Alcohols are known to be special compounds arisen from lipid oxidation by lipoxygenase enzyme activities and *β*-oxidation [3]. Most of the alcohols identified in this study were previously characterized in shea butter [7].

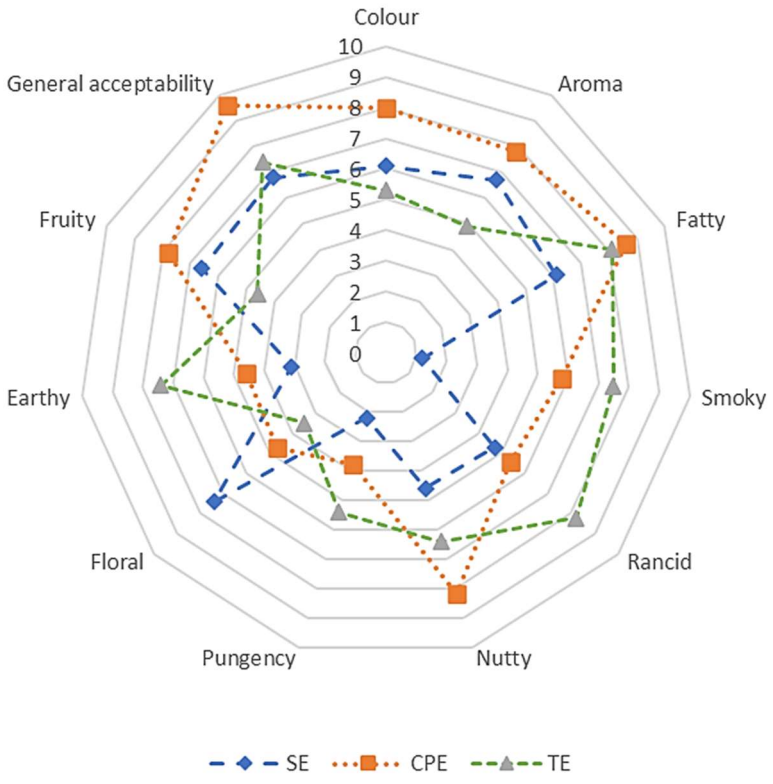

Figure 1. Sensory profiles of shea butters.

Table 3. Volatile compounds of shea butter extracted with CPE, SE and TE methods.

No	Compounds	LRI	Concentrations (mg/kg)			Identification *
			CPE	SE	TE	
			Mean (SD)			
Aldehydes						
1	*β*-Methylbutanal	912	1.4 (0.2) ^{c}	6.86 (0.9) ^{a}	3.52 (1.5) ^{b}	LRI and MS, std
2	3-Methylbutanal	916	12.74 (3.5) ^{a}	7.21 (2.4) ^{c}	9.65 (1.2) ^{b}	LRI and MS, std
3	*(Z)*-2-Hexenal	1193	0.25 (0.1) ^{b}	2.32 (0.7) ^{a}	<LOD	LRI and MS, std
4	*(E)*-2-Hexenal	1207	3.31 (0.0) ^{b}	5.63 (0.7) ^{a}	<LOD	LRI and MS, std
5	*(E)*-2-Heptenal	1334	0.55 (0.1) ^{c}	6.10 (1.0) ^{a}	4.40 (0.8) ^{b}	LRI and MS, std
6	*(Z)*-6-Nonenal	1453	0.54 (0.1) ^{b}	4.76 (1.6) ^{a}	<LOD	LRI and MS, std
7	Benzaldehyde	1508	4.04 (0.4) ^{b}	1.75 (0.1) ^{c}	5.77 (0.3) ^{a}	LRI and MS, std
8	*(E, E)*-2,4-Nonadienal	1702	13.25 (2.5) ^{a}	8.54 (1.0) ^{b}	3.65 (0.9) ^{c}	LRI and MS, std
9	*(E, E)* 2,4-Decadienal	1805	4.16 (0.65) ^{b}	12.00 (4.6) ^{a}	<LOD	LRI and MS, std
10	4-Methoxy-benzaldehyde	2011	4.86 (0.7) ^{b}	6.30 (0.8) ^{a}	<LOD	LRI and MS, std
Subtotal Alcohols			**45.10**	**61.47**	**26.99**	
11	1-Penten-3-ol	1165	11.19 (2.8) ^{b}	18.67 (5.5) ^{a}	3.93 (0.8) ^{c}	LRI and MS, std
12	3-Hexanol	1190	58.98 (8.5) ^{a}	11.37 (4.8) ^{c}	17.96 (3.1) ^{b}	LRI and MS, std
13	1-Hexanol	1226	1.39 (0.0) ^{b}	1.64 (0.4) ^{b}	4.33 (1.2) ^{a}	LRI and MS, std
14	2-Methyl-2-butenol	1326	5.17 (0.8) ^{b}	9.5 (2.3) ^{a}	1.90 (0.0) ^{c}	LRI and MS, std
15	2-Heptanol	1335	0.45 (0.1) ^{c}	1.02 (0.0) ^{b}	3.14 (0.8) ^{a}	LRI and MS, std
16	*(E)*-2-Hexenol	1388	3.48 (0.6) ^{a}	1.5 (0.1) ^{b}	<LOD	LRI and MS, std
17	3-Octanol	1400	19.64 (5.3) ^{a}	8.24 (2.5) ^{c}	15.30 (2.8) ^{b}	LRI and MS, std
18	2,3-Butanediol	1545	2.02 (0.3) ^{b}	7.54 (1.0) ^{a}	0.39 (0.0) ^{c}	LRI and MS, std
19	Benzyl alcohol	1861	1.86 (0.0) ^{b}	3.74 (0.5) ^{a}	0.89 (0.1) ^{c}	LRI and MS, std
20	Phenylethyl alcohol	1871	4.75 (0.7) ^{b}	8.46 (1.9) ^{a}	1.76 (0.40) ^{c}	LRI and MS, std
21	3-Methoxy-2-butanol	1910	1.16 (0.1) ^{b}	4.24 (0.4) ^{a}	<LOD	LRI and MS, std
Subtotal Ketones			**110.09**	**75.92**	**49.60**	
22	4-Methyl-3-penten-2-one	1131	0.27 (0.1) ^{b}	0.61 (0.1) ^{a}	<LOD	LRI and MS, std
23	2-Heptanone	1184	<LOD	0.87 (0.1) ^{b}	1.20 (0.2) ^{a}	LRI and MS, std
24	3-Hydroxy-2-butanone	1287	1.33 (0.1) ^{c}	4.67 (0.5) ^{b}	5.32 (0.7) ^{a}	LRI and MS, std
25	Acetophenone	1645	<LOD	3.53 (0.3) ^{a}	2.24 (0.1) ^{c}	LRI and MS, std
26	1-Phenylethanone	1652	0.48 (0.1) ^{b}	3.21 (0.5) ^{a}	<LOD	LRI and MS, tent
Subtotal Esters			**2.08**	**12.89**	**8.76**	
27	Ethylacetate	891	0.2 (0.1) ^{b}	<LOD	2.8 (0.2) ^{a}	LRI and MS, std
28	Butylacetate	1078	3.8 (0.6) ^{a}	<LOD	4.11 (0.9) ^{a}	LRI and MS, std
29	Phenylacetate	1660	<LOD	4.25 (0.8) ^{a}	1.71 (0.1) ^{b}	LRI and MS, std
Subtotal Acids			**4.00**	**4.25**	**8.62**	
30	Acetic acid	1461	5.63 (0.7) ^{a}	6.57 (1.4) ^{a}	1.87 (0.4) ^{b}	LRI and MS, std
31	Propanoic acid	1528	0.57 (0.1) ^{b}	1.98 (0.1) ^{a}	1.59 (0.1) ^{a}	LRI and MS, std
32	Butyric acid	1637	0.84 (0.1) ^{b}	5.28 (1.4) ^{a}	0.99 (0.1) ^{b}	LRI and MS, std
33	Valeric acid	1744	0.86 (0.1) ^{b}	0.90 (0.1) ^{b}	4.32 (0.2) ^{a}	LRI and MS, std
34	Hexanoic acid	1849	3.92 (0.8) ^{a}	0.66 (0.0) ^{c}	1.72 (0.1) ^{b}	LRI and MS, std
35	Heptanoic acid	1960	6.46 (1.4) ^{a}	2.64 (0.6) ^{b}	0.20 (0.0) ^{c}	LRI and MS, std
37	Nonanoic acid	2174	9.37 (2.6) ^{a}	4.29 (0.7) ^{b}	1.67 (0.1) ^{c}	LRI and MS, std

Table 3. *Cont.*

No	Compounds	LRI	Concentrations (mg/kg)			Identification *
			CPE	SE	TE	
			Mean (SD)			
Subtotal Furans			**27.65**	**22.32**	**12.36**	
38	2-Methylfuran	876	7.32 (1.5) ^{b}	<LOD	15.74 (3.8) ^{a}	LRI and MS, std
39	Furfural	1466	2.10 (0.6) ^{b}	2.50 (0.4) ^{b}	3.45 (0.7) ^{a}	LRI and MS, std
40	2-Acetylfuran	1501	1.46 (0.1) ^{a}	<LOD	0.58 (0.1) ^{b}	LRI and MS, std
41	2-Hydroxymethylfuran	1669	1.99 (0.1) ^{b}	<LOD	3.20 (0.3) ^{a}	LRI and MS, tent
Subtotal Terpenes			**12.87**	**2.50**	**22.97**	
42	α-Pinene	1015	1.35 (0.1) ^{c}	4.11 (0.8) ^{b}	8.75 (2.6) ^{a}	LRI and MS, std
43	Sabinene	1113	0.31 (0.0) ^{c}	2.59 (0.4) ^{a}	0.83 (0.1) ^{b}	LRI and MS, std
44	α-Terpinene	1172	1.88 (0.2) ^{a}	2.02 (0.1) ^{a}	0.67 (0.1) ^{b}	LRI and MS, std
45	*dl*-Limonene	1192	4.94 (1.6) ^{b}	12.29 (3.8) ^{a}	3.32 (1.0) ^{c}	LRI and MS, std
46	*p*-Cymene	1267	0.38 (0.1) ^{c}	1.93 (0.4) ^{a}	0.69 (0.3) ^{b}	LRI and MS, std
47	*β*-Myrcene	1664	1.51 (0.4) ^{a}	0.51 (0.1) ^{b}	<LOD	LRI and MS, std
Subtotal Volatiles Phenols			**10.37**	**23.45**	**14.26**	
48	Guaiacol	1862	<LOD	<LOD	3.71 (0.6)	LRI and MS, std
49	Phenol	2008	0.29 (0.0) ^{c}	2.34 (0.2) ^{a}	0.54 (0.0) ^{b}	LRI and MS, std
50	*p*-Cresol	2078	0.52 (0.1) ^{b}	<LOD	2.48 (0.8) ^{a}	LRI and MS, std
Subtotal Hydrocarbons			**0.81**	**2.34**	**6.73**	
51	*o*-Xylene	1185	1.73 (0.8) ^{a}	0.68 (0.2) ^{c}	2.03 (0.7) ^{b}	LRI and MS, std
52	Styrene	1254	7.45 (1.2) ^{b}	0.82 (0.1) ^{c}	4.76 (1.9) ^{a}	LRI and MS, std
Subtotal Lactones and Pyrroles			**9.19**	**1.50**	**6.79**	
53	γ-Valerolactone	1600	<LOD	0.77 (0.1) ^{b}	2.48 (0.4) ^{a}	LRI and MS, std
54	γ-Butyrolactone	1626	0.27 (0.0) ^{c}	0.73 (0.0) ^{a}	0.50 (0.0) ^{b}	LRI and MS, std
55	2-Acetylpyrrole	1971	3.58 (0.8) ^{a}	0.88 (0.1) ^{c}	1.85 (0.6) ^{b}	LRI and MS, std
Subtotal Pyrazines			**3.85**	**2.38**	**4.83**	
56	2-Ethylpyrazine	1344	2.90 (0.6) ^{b}	1.69 (0.3) ^{c}	8.24 (2.8) ^{a}	LRI and MS, std
57	2-Acetyl-3-methylpyrazine	1629	0.37 (0.0) ^{b}	0.21 (0.0) ^{c}	4.23 (0.6) ^{a}	LRI and MS, tent
Subtotal			**3.27**	**1.9**	**12.47**	
Total			**229.28**	**210.92**	**174.38**	

* LOD: limit of detection; LRI: linear retention index computed on DB-WAX capillary column; std: chemical standard; MS tent (tentatively identified by MS): when MS or LRI is used for the identification of a constituent, it must be stated as an attempt of identification. The data are given as means and standard deviations (mean (SD)) of three replications. Different lowercase letters on numbers in the same line represent significant difference ($p < 0.05$). CPE: cold press extraction; SE: solvent extraction; TE: traditional extraction methods.

Aldehydes. Aldehydes were the second most condensed aroma group in all samples. These compounds are generally synthesized from the oxidation of USFAs, particularly linoleic, oleic, linolenic and arachidonic acids [35]. Shea butter from CPE and SE possessed the same number of aldehyde compounds (10), while only five aldehydes were determined in the TE samples. *β*-Methylbutanal, 3-methylbutanal, *(E)*-2-heptenal, benzaldehyde and (*E, E*)-2,4-nonadienal were present in all samples, whereas *(Z)*-2-hexenal, *(E)*-2-hexenal, *(Z)*-6-nonenal, *(E, E)*-2,4-decadienal and 4-methoxy-benzaldehyde were only in the CPE and SE samples. The total amounts of aldehydes were 45.10 mg/kg, 61.47 mg/kg, and 26.99 mg/kg in the CPE, SE and TE samples. Among all aldehydes quantified, 3-methylbutanal was

found to be the most prominent aldehyde in the CPE (12.74 mg/kg), SE (7.21 mg/kg) and TE (9.65 mg/kg) samples. The second most abundant aldehyde in all samples was *(E, E)*-2,4-nonadienal, with the highest concentration in the CPE sample. All the straight chain aldehydes detected in this study could be probably synthesized from the oxidation of unsaturated fatty acids [36] and microbial β-oxidation [34]. As shea butter is also rich in monounsaturated fatty acids, the high amount of aldehyde compounds confirms the lipid oxidation process in shea butter samples. The majority of the aldehydes recorded in the present work were characterized in some oil seeds such as sesame [37], shea butter [7], roasted peanuts [38] and raw and roasted pistachios [16].

Furans. According to the data, four furan compounds, including 2-methylfuran, furfural, 2-acetylfuran and 2-hydroxymethylfuran, were identified in all samples. Moreover, furfural was the only furan detected in shea butter from the SE process. Furfural contributes to sweet caramel-like flavors in heat-treated foods and also acts as one of the most crucial intermediate precursors for other heterocyclic compounds and furan derivatives [39]. This class of compounds generally results from the degradation or restructuration of carbohydrates and ascorbic acid molecules. The thermal process leads to the reaction between the sugars and amino acid molecules through the Maillard reaction, which causes an alteration in color and the release of furans, acrylamides and other heterocyclic volatile compounds. Furans had total concentrations of 12.87 mg/kg, 2.50 mg/kg and 22.97 mg/kg in the CPE, SE and TE samples. The highest concentration of furan compounds was detected in the TE sample. This was probably due to the thermal processes applied to the shea grain during the extraction. Among all compounds, 2-methylfuran was found to be quantitatively the dominant furan, followed by furfural. Some of these detected furans have been revealed in different raw and roasted nuts and oils such as tropical almond nuts and pistachios [40].

Pyrazines. Pyrazines have been linked to the aromas of various roasted foods including peanuts starting from the 1960s. They are heterocyclic nitrogen-containing compounds similar to pyrroles, oxalines, pyridines, thiazoles and oxazoles and formed by the condensation of two amino-carbonyls via Strecker degradation. Their formation depends on various factors such as temperature, time, pH, the types and quantities of sugar and amino acid and the ratio of amino acid to sugar [41]. Two pyrazines, 2-ethylpyrazine and 2-acetyl-3-methylpyrazine, were determined in all shea butter samples in the present study. Pyrazines, similarly to furans, in most cases are released during heating processes in nuts, which are rich in lipid content [40]. It was observed that the total amount of pyrazines was higher in the TE sample (12.47 mg/kg) than in the CPE (3.27 mg/kg) and SE (1.90 mg/kg) samples, which could be due to longer exposure to thermal conditions. The detected pyrazines were similar in all samples. 2-Ethylpyrazine was quantified as the most substantial pyrazine compound in all samples. All the pyrazines determined in this study were formerly recorded in several roasted nuts and oils [7,42].

Ketones. Five ketones, comprising 2-heptanone, 4-methyl-3-penten-2-one, 1-phenyleth anone, 3-hydroxy-2-butanone and acetophenone, were identified in shea butter from SE, while three and two ketones were only detected in the TE and CPE samples, respectively. The concentration of ketones was found to be higher in the SE (12.89 mg/kg) sample. 3-Hydroxy-2-butanone was quantified in SE as the most abundant ketone. These group of volatiles are expected to be formed via lipid auto-oxidation. Most of them have been already quantified in some other oil seeds [7,40].

Pyrroles and lactones. As given in Table 3, a pyrrole (2-acetylpyrrole) and two lactones (γ-valerolactone and γ-butyrolactone) were detected in shea butter samples. γ-Valerolactone was only characterized in the SE and TE samples. The total concentrations of these compounds were 3.85, 2.38 and 4.83 mg/kg in the CPE, SE and TE samples, respectively. Noticeably, the lowest amount of pyrrole (0.88 mg/kg) in the SE sample is explainable since they result from the Maillard reaction, and the increase can be associated with the increase in temperature and time. This reaction is known to be an enhancer of the aroma, taste

and specific color, which play a tremendous role in the sensory characteristics of heated foods [43].

Terpenes. A total of six terpenes, including sabinene, *dl*-limonene, *p*-cymene, *α*-pinene, *α*-terpinene and *β*-myrcene, were determined in shea butter. Terpenes are important in citrus, fragrant herbs, essential oils, spices and nuts, which are considered to be the products of the isoprenoids cycle. According to the data, all identified terpenes were present in all samples, except *β*-myrcene, which was only detected in shea butter from CPE and SE. The total amount of terpenes was more condensed in shea butter from SE (23.45 mg/kg) than in CPE (10.37 mg/kg) and TE (14.26 mg/kg) samples. It was observed that solvent extraction increased the total concentration of terpenes. *dl*-limonene, which belongs to the monoterpene family, was found to be the most predominant terpene, covering 4.52, 13.44 and 6.76% of overall aroma in shea butter from CPE, SE and TE, respectively. The increased amount of *dl*-limonene in the SE sample could be allocated to the release of geraniol and geranyl pyrophosphate from isopentenyl pyrophosphate during shea nut maturation. *dl*-limonene is an isoprenoid-synthesized monoterpene commonly found in peanuts and some fruits and vegetables. Guclu et al. [21] reported that terpene derivatives may have a role in the defense mechanism of plants and they are degraded by heat treatment.

Esters. Ethylacetate, butylacetate and phenylacetate were recorded as the ester compounds of shea butter samples. However, ethylacetate and butylacetate were only detected in the CPE sample, while phenylacetate was the only detected ester in the SE sample. The total concentrations of esters calculated in shea butter from the CPE, SE and TE processes were 4.00, 4.25 and 8.62 mg/kg, respectively. Among esters, butylacetate had the highest concentration in all samples.

Volatile acids. Volatile acids are formed from the degradation of triglycerides resulting from the enzymatic activities of microbial lipolytic flora [44]. Seven volatile acids, including acetic, propanoic, butyric, valeric, hexanoic, heptanoic and nonanoic acid, were identified in all shea butter samples. These few numbers of volatile acids could be probably related to their conversion into alcohols, aldehydes, ketones and lactones in shea nut or butter oxidation. Among them, nonanoic acid was recorded as the prevailing compound, followed by acetic acid, in all samples (Table 3). The overall concentrations of volatile acids were quantified as 27.65, 22.32 and 12.36 mg/kg for the CPE, SE and TE samples. The lowest amount of volatile acid was found in shea butter from the traditional extraction process, which is thought to be another consequence of oxidation. The majority of these compounds were previously reported in shea nut, shea butter and other seed oils [7,16,36].

Volatile phenols and hydrocarbons. Three volatile phenols (guaiacol, phenol and *p*-cresol) and two hydrocarbons (*o*-xylene and styrene) were determined in shea butter samples. Shea butter from the TE process showed the highest amount (6.73 mg/kg) of volatile phenol, followed by that from the solvent extraction (2.34 mg/kg) process. Among volatile phenols, guaiacol was calculated as the dominant aroma in shea butter from TE, while phenol was recorded as the predominant aroma in the SE sample. Hydrocarbons were more concentrated in shea butter obtained from the cold press extraction process (9.19 mg/kg), in which styrene (7.46 mg/kg) showed the highest concentration.

Principal component analysis (PCA) was conducted to design a model for the visualization and discrimination of the aroma compounds regarding the different processes applied in shea butter extraction. Two principal components based on a total of 43 variables were utilized for the PCA and the explained total variance was 100% (F1: 78.09; F2: 21.91), as indicated in Figure 2. The aroma constituents of shea butter based on the extraction process were categorized into three parts, as can be seen in the biplot graph. Shea butter from the cold press extraction (CPE) process was differentiated by 3-hexanol, *(Z)*-2-hexenal, acetic acid, sabinene, heptanoic acid, nonanoic acid, 2-acetylfuran, 3-octanol, 3-methylbutanal and *(E)*-2-hexenol. On the other hand, shea butter from solvent extraction (SE) was characterized with *β*-methylbutanal, *(E)*-2-hexenal, 2,3-butanediol, butyric acid, 3-hydroxy-2-butanone, *(E, E)*-2,4-Decadienal and 1-phenylethanone, while shea butter

from traditional extraction (TE) was mostly elucidated by 2-heptanol, 1-hexanol, *α*-pinene, ethylacetate, valeric acid and *(E, E)*-2,4-nonadienal.

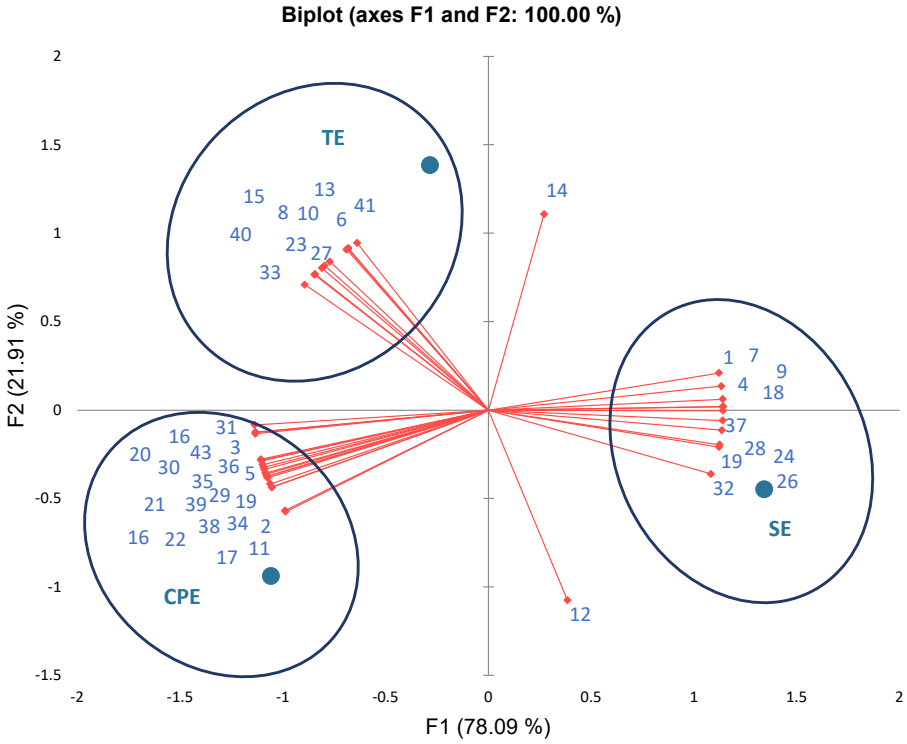

Figure 2. PCA biplot of shea butter.

3.6. Key Odorants of Shea Butter

The GC-MS/O analysis and AEDA results of the shea butter samples are shown in Table 4. AEDA allowed us to identify 22 key odorants in CPE, while 20 and 17 were found in the SE and TE samples, respectively. The number of aroma-active compounds increased with the cold press extraction method (CPE). All perceived aroma-active compounds were almost common in the CPE and SE samples, except pyrazines and furans, which were mostly revealed in shea butter from the TE process. Interestingly, three unknown odorants were perceived by the human nose but could not be detected by GC-MS in this study. Significant variations in FD values and total identified aroma-active compounds were observed in shea butter samples, which could be explained by the impact of nuts treatment and butter extraction processes. Aldehydes were detected as the principal aroma-active compounds in all shea butter samples, followed by alcohols and terpenes (Table 4).

Alcohol compounds were found to be the important key odorant group in the samples. 1-Penten-3-ol, 3-hexanol, 3-methyl-2-butenol and 1-hexanol were determined as aroma-active alcohol compounds (Table 4). Among these, 3-hexanol was found to be the most powerful key odorant in the samples. Alcohols are known to be special compounds arisen from lipid oxidation by lipoxygenase enzyme activities and *β*-oxidation [35]. The straight chain alcohols such as 3-hexanol could be generated from the oxidative degradation of their corresponding aldehydes (hexanal) and other aldehydes. This compound was detected with a higher FD value in the CPE sample (FD: 2048). This is probably related to the cold extraction process, which preserved the volatiles better. Following 3-hexanol, 1-penten-3-ol was also found to be effective on the odor of shea butter. This compound was detected with higher FD values in the CPE (FD: 256) and SE (FD: 64) samples.

Table 4. Aroma-active compounds of shea butter (FD ≥ 4).

No	Compounds	LRI	Odor Description	FD Factors		
				CPE	SE	TE
1	3-Methylbutanal	916	Chocolate	64	4	16
2	α-Pinene	1015	Herbal and fresh	8	8	4
3	Sabinene	1119	Herbal and spicy	4	64	16
4	1-Penten-3-ol	1165	Herbal and oily	256	64	8
5	3-Hexanol	1190	Tropical fruit and floral	2048	1024	64
6	*dl*-Limonene	1192	Citrusy	16	64	4
7	Unknown I	1235	Peanut and fatty	64	128	ND
8	3-Methyl-2-butenol	1326	Fruity and fresh	4	16	ND
9	3-Hydroxy-2-butanone	1287	Cheesy and creamy	8	64	4
10	*(E)*-2-Heptenal	1334	Peanut and oily	8	64	8
11	1-Hexanol	1339	Herb and fresh	4	32	64
12	2-Ethylpyrazine	1344	Roasted nut	8	ND	64
13	Furfural	1365	Burnt and caramel	4	ND	8
14	Unknown II	1372	Spicy and fatty	32	256	64
15	*(E)*-6-Nonenal	1453	Green and grassy	8	64	ND
16	Acetic acid	1461	Vinegar	4	8	ND
17	Benzaldehyde	1501	Almond and nutty	16	8	ND
18	2-Acetylpyrazine	1638	Peanut and roasted	8	4	64
19	*(E, E)*-2,4-Nonadienal	1706	Green and oily	32	8	8
20	Unknown III	1753	Pleasant and floral	64	16	ND
21	Hexanoic acid	1807	Cheesy and rancid	16	4	4
22	2-Acetylpyrrole	1971	Green and fresh	16	4	64

ND: not determined; LRI: linear retention index computed on DB-WAX capillary column; FD factor is the highest dilution of shea butter extract at which odor is perceptible.

Aldehydes are another major group that impact the overall flavors of the shea butter samples. Six aldehydes were detected as aroma-active compounds: 3-Methylbutanal, *(E)*-2-heptenal, furfural, *(E)*-6-nonenal, benzaldehyde and (*E, E*)-2,4-nonadienal. 3-ethylbutanal, providing chocolate odor, had the highest FD (64 in the CPE sample), as reported similarly in sweet cream butter [45]. Similarly, benzaldehyde (almond-nutty odors), which is a product of the Strecker degradation of aromatic amino acids, had a higher FD factor in the CPE sample than in the SE sample, while this compound was not detected in the TE sample (Table 4).

A total of three terpenes (α-pinene, sabinene and *dl*-limonene) influenced the overall aroma of the shea butter with varying FD factor from 4 to 64. In the current study, shea butter obtained the SE method presented very much higher FD values for sabinene (FD: 64) and *dl*-limonene (FD: 64) than the values in the CPE and TE samples. Among terpene compounds, α-pinene and *dl*-limonene were detected in butter using the purge and trap technique [46].

Two powerful aroma-active pyrazines, including 2-ethylpyrazine (roasted nut odor) and 2-acetylpyrazine (peanut-roasted odor), were detected in all samples. The detected pyrazines derive from the heating process and have already been analyzed in shea butter samples made under different production methods in African countries [7]. 2-Acetylpyrazine was also identified in a Chinese butter hotpot seasoning sample and detected as the powerful odorant that gives the roast note to the sample [47].

The other aroma-active compounds identified in shea butter samples were a ketone (3-hydroxy-2-butanone), two acids (acetic acid and hexanoic acid), a pyrrole (2-acetylpyrrole) and three unknown compounds (LRIs: 1235, 1372 and 1753).

4. Conclusions

This study was conducted to provide more details on the aroma compounds, key odorants and fatty acids composition of shea butter obtained from three extraction processes. Aroma compounds were fractionated using the purge and trap technique and elucidated

by GC-MS for the first time, while fatty acid profiles were analyzed using the GC-FID method. The highest concentration of volatiles was observed in shea butter from CPE. The aroma-active compounds were determined for the first time using AEDA coupled to GC-MS/O. The cold-press-extracted (CPE) sample had more key odorants than the other samples. Aldehydes and alcohols were found to be the dominant aroma-active compounds of shea butter samples. It was revealed that saturated and monounsaturated acids were found in higher concentrations among the fatty acids present in shea butter. Stearic and transoleic acids were the most abundant fatty acids in all studied samples of shea butter.

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