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Research article

Sterols as a biomarker in tracing niger and sesame seeds oils adulterated with palm oil

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ABSTRACT

Food adulteration is a serious social problem all over the world. The oil obtained from the niger and sesame is known for its quality and has a high market value in Ethiopia. The cost of the oil obtained from these oilseed crops is high unlike other plant oils, thus prone to be mixed with other cheap oils to increase profits. The study aimed to quantify the sterol profile of niger seed and sesame oils thereby trace adulteration of these oils with palm oil. Gas Chromatography coupled to Mass Spectrometry was used to analyze the sterol fractions of oils. A blend of palm oil, at a level of 10%, with niger seed and sesame oil was prepared. In all the studied oils; sitosterol (467.2–2778.96 mg/kg), campesterol (295.9–869.85 mg/kg) and stigmasterol (125.6–920 mg/kg) were the dominant sterols identified. Lupeol, Lanosterol, and Olean-12-en-3-one were only identified in a significant proportion for niger seed oil. Moreover, cholestroltrimethyl silyl ether (19.9 mg/kg) and 24-Nor-22,23- methylenecholest-5-en-3β-ol trimethylsilyl (TMS) ethers (139.14 mg/kg) were only identified in palm oil and used to trace adulteration. An attempt made to trace these compounds by mixing palm oil at a level of 10% with niger seed and sesame oils was successfully detected its presence. Hence, as the physicochemical properties of oils can be arranged to cover adulteration, marker identification provides a reliable identity of the specific oil.

1. Introduction

Food products like butter, honey, edible oils are foods that can be adulterated with lower quality or cheaper price substitutes. Among the commodities prone to adulteration, the maximum proportion is for oil which is 24% (Moore et al., 2012). Edible oils can be mislabelled with the replacement of one constituent by a comparable but low-priced one (Woolfe and Primrose 2004). Oils obtained from different oilseeds such as niger seed and sesame have high commercial value in Ethiopia. At the current market prices, the value for the two oils is roughly US$ 3/liter as compared to palm oil with a market value of US$ 1/ liter. Due to the interest to make more profit illegal producers adulterate these oils with palm oil. In addition to economic benefit, the oil from these oilseeds is also preferred healthy due to their polyunsaturated fatty acid content (Osman, 2020). Dossa et al. (2018) had confirmed that sesame is an imperative commodity in Africa and Asia due to its being nutritious and with high market value.

Worldwide, it's a common experience to adulterate plant oils of high commercial value. The commonly used parameters, for example, melting point, saponification, refractive index, viscosity, etc. are not reliable procedures to trace adulteration. It is possible to maintain the range of these parameters in adulterated oils and fats from plant origin. Phytosterols, tocopherols, etc are constituents of edible oils and fats (Azadmard-Damirchi and Torbati 2015). The composition of certain plant sterols is generally recognized to be a strong marker in adulterated vegetable oils (Moreau et al., 2002). Al-Ismail et al. (2010) indicated that it is possible to detect vegetable oils adulterating olive oil by gas-liquid chromatography (GLC) determination of sterols.

From the study of Zhang et al. (2014), the fatty acid composition of different oils could classify edible oils and hence applied to check the identity of the oil. Studies were conducted to discover the sterol

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composition and factors affecting its content in different oil. For instance, the sterol profile of tomato seed oil and olive oil may vary due to variety differences (Giuffrè and Capocasale 2016; Giuffrè et al., 2012). Another study to use sterols to differentiate sunflower seeds was also conducted (Velasco et al., 2014).

Phytosterols are the minor constituents that contribute the largest portion of non-saponifiable in lipids (Carretero et al., 2007). They are naturally present in all plants including plant oils. They are useful indicators for detecting adulteration or confirming the authenticity of plant oils (European Commission, 2002). Ramadan (2012) also indicated that investigation of sterols is a reliable mechanism in tracing the purity of plant oils that may not be able to use other components like fatty acids. Besides being strong means in detecting oil fraud, it is recognized that sterols exhibit an antioxidant property while interacting with oil surfaces and prevent rancidity (Ramadan and Mörsel, 2004; Ramadan et al., 2003).

A group of steroid alcohols and esters like phytosterols, phytostanols, and their esters are synthesized from triterpenes that occur naturally in plants. The phospholipid bi-layers in plant cell walls are stabilized by triterpenes hence, they are indispensable components of plant membranes (Moreau et al., 2002). In normal diets, vegetable oils are usually recognized as a good source for plant sterols, though certain variances among oils as edible plant sterols are obvious (Normén et al., 2004).

The distribution of phytosterols in plant tissue varies among four common forms: free sterols (FSs), steryl fatty acid esters (SE), steryl glycosides (SG), and acylated sterylglycosides (ASG). Unlike free sterols, the latter (steryl fatty acid esters (SE), steryl glycosides (SG), and acylated sterylglycosides (ASG)) are commonly termed "phytosterol conjugates". The free sterols have a free OH group on the A-ring of the sterol nucleus while the OH group of sterol conjugates are ester-linked to fatty acids or hydroycinnamic acid (HSE) or ether linked to hexose saccharides (Moreau et al., 2002; Moreau et al., 2005).

The amount of methyl groups present on the fourth carbon (i.e. two, one, or nil) is the most important distinguishing characteristic among phytosterols. Based on this structural characteristic, a catalog of phytosterols is grouped as, 4-dimethysterols, 4-monomethylsterols, and 4-desmethylsterols. The most common 4-dimethylsterol is cycloartanol; for instance, gramisterol is a 4-monomethysterol (Moreau et al., 2002). 4-desmethylsterols can have 27-carbon, 28-carbon, or 29- carbons. Most 4-desmethylsterols are Δ5-phytosterols in which multiple bond exists between 5^{th} and 6^{th} carbons in the ring. An example is β-sitosterol, one of the most abundant phytosterols in plants and vegetable oils. Another family having a multiple bond between 7^{th} and 8^{th} carbon is referred to as Δ7-phytosterols.

The composition and content of desmethylsterols can serve in checking the identity of plant oils irrespective of being minor constituents. Therefore, assessment of oil purity usually done using phytosterols and other unsaponifiable compounds as a marker (Remaud et al., 1997). To our knowledge, there is no work that is related to setting a marker for the identification of oil obtained from niger seed and sesame. The objective of this study was to use sterols as a marker for the detection of niger seed and sesame oil adulterated with palm oil.

2. Materials and method

2.1. Materials

Niger seed oil sample was extracted from oilseed donated from Holeta Agricultural Research Centre (Holeta Genet, Ethiopia) and sesame seed was donated from Melka Werer Research Centre. The seeds were thoroughly cleaned manually to remove dust, chaffs, broken seeds, and other foreign materials. Thirty-five grams of niger seed and sesame were extracted by hexane for 5 h using the soxhlet method. A temperature of -20 °C was used to store the oil samples until chemical analysis. Palm oil used for adulteration was bought from the local grocery (Addis Ababa, Ethiopia), and a blend of 10% was prepared. Three replicates were performed for each oil sample. 5α-cholestane (Newport, RI. USA) was used as an internal standard. Stock internal standard (1 mg/mL (w/v) was prepared by dissolving 5α-cholestane in ethyl acetate (Sigma-Aldrich, St. Louis, Missouri, USA). Two other independent standards of cholesterol and stigmastanol were purchased from SteraloidsInc (Newport, RI. USA) and dissolved in ethyl acetate (1 mg/mL) standard solution. One plant sterol mixture of 25 mg/mL, containing 13% brassicasterol, 26% campesterol, 7% stigmasterol, and 53% β-sitosterol, was obtained from Matreya Inc. (Pleasant Gap, PA, USA). It was diluted to 1 mg/mL in a 25 mL volumetric flask. The derivatizing reagent, Tri-Sil reagent (99% pure) was purchased from Pierce Chemical Co., Rockford, IL, USA. The remaining reagents were obtained from Fisher Scientific (Waltham, Massachusetts, USA). Solid-phase extraction (SPE) Strata 37Si-1 Silica (55 μm, 70 A) 1g/6mL from Phenomenex (CA, USA) were used in this study.

2.2. Sample preparation

Each oil sample ca. 0.30 g was weighed into a brown glass screw-top tube then the solution of 5α-cholestane internal standard (IS) 0.2 mL was added for final quantitation. After the addition of the IS, the sample was mixed with 7 mL of 2M KOH in 99% ethanol and shaken thoroughly. The tube was heated in a heating block at 80 °C for one hour. Once the tubes containing the samples were cooled using tap water, 10 mL distilled water has been added then the samples were transferred into a separatory funnel for further isolation of the unsaponifiable matter. The solution was extracted (three times) with 10 mL diethyl ether and the ether extract washed (once with 0.5 M KOH in ethanol) and again with 10 mL distilled water. The collected diethyl ether layer was passed through anhydrous sodium sulfate and the extract was evaporated to dryness in a rotary vacuum evaporator at 30 °C. The dry unsaponifiable matter was dissolved in 5 mL n-hexane for the SPE column enrichment step (Azadmard-Damirchi et al., 2010; Zhou 2012).

2.3. Sterol enrichment by SPE column

SPE cartridge was conditioned with 5 mL n-hexane. Unsaponifiables re-dissolved in 5 mL n-hexane were loaded onto the SPE column. Washing out non-sterol compounds using 10 mL n-hexane: diethyl ether (v/v, 95:5) solvent which was then discarded. Eluting phytosterol fraction with 7 mL n-hexane-diethyl ether (v/v, 60:40) and the solvent collected. The eluates were evaporated to dryness using a beam of N_2 before they were derivatized to trimethylsilyl (TMS) ethers (Figure 1).

2.4. Preparation of TMS ether derivatives of sterols

Unsaponifiables were derivatized to TMS ethers by adding 100 μL of Tri-Sil reagent (Pierce Chemical Co., Rockford, IL, USA) and incubating the tubes at 60 °C for 45 min. A stream of nitrogen was used to evaporate the solvent, and the TMS ether derivatives were dissolved in 1 mL n-hexane. The tubes were sonicated in an ultrasonic bath for 1 min and centrifuged for 3 min. The hexane layer was transferred to another tube, avoiding any solid particles, evaporated to dryness, and dissolved in 0.2 mL hexane, for further analyses by GC-MS (Zhou 2012; Azadmard-Damirchi et al., 2010; Savage et al., 1997).

2.5. Gas chromatography and mass spectrometry

The Gas Chromatography and Mass Spectrometry evaluation was done on a GC8000 Top Series GC (Thermo Quest Italia S.P.A., Rodano, Italy) equipped with a fused-silica capillary column DB-5MS (J &W Scientific, Folsom, CA, USA, length = 30 m, i.d. = 0.25 mm, film thickness = 0.50 μm) and coupled to a Voyager mass spectrometer with Mass Lab data system version 1.4V (Finnigan, Manchester, United Kingdom). The GC conditions were: (i) injector 260 °C, (ii) oven 60 °C for 1 min, rate 40 °C/min, final temperature 310 °C for 27 min, (iii) helium as a carrier gas

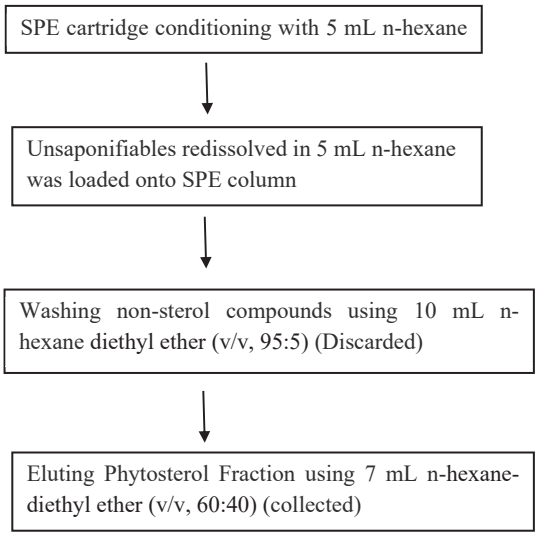

Figure 1. Clean-up steps of SPE method for purification of phytosterol fraction (Azadmard-Damirchi and Dutta 2006; Mariani et al., 2006; Azadmard-Damirchi et al., 2010; Zhou, 2012).

and nitrogen as a makeup gas at a flow rate of 30 mL/min, (iv) detector 310 °C. Auto injection of 1μL of the solution of sterol was done in the split mode. The mass spectra were recorded at electron energy of 70 eV, and the ion source temperature was set at 200 °C. The spectra were scanned in the range of *m/z* 20–500. The sterols were identified by comparing the mass spectra with pure samples of cholesterol, stigmastanol, brassicasterol, campesterol, stigmasterol, and sitosterol. The other sterols were identified by comparing the mass spectra with published values (Dutta et al., 1994; Damirchi et al., 2005; Moreau et al., 2002; Zhou 2012). Each injection was repeated three times in the same operating conditions to verify the reproducibility of the results. The quantity of individual sterol was computed as mg/kg of oil.

2.6. Statistical analysis

The triplicate data was obtained for phytosterols content of the three oils of niger seed, sesame, and palm. Mean separation was done by SPSS version 20 program. The significance at $P < 0.05$ level among means was determined by one-way ANOVA to evaluate the influence of the difference of oils on the phytosterol profiles. Moreover, further variation between the oils was evaluated using principal component analysis using the software XLSTAT version 2015.5.01.22537 and Heatmap analysis.

3. Result and discussion

3.1. The composition of sterols in the three oils

Phytosterols contribute a considerable fraction of the unsaponifiable in oils and are characteristic of different vegetable oils (Vichi et al., 2001). Giuffrè and Capocasale (2016) had investigated the influence of variety on the sterol content of tomato seed oil and from which they concluded the composition of sterols was highly affected by variety difference. Moreover, the sterol composition of olive cultivars was studied and the result revealed that the sterol composition is highly influenced by cultivar difference (Giuffrè et al., 2012). Another study to use sterols to differentiate sunflower seeds was also conducted (Velasco et al., 2014). Table 1 presents the major sterol fractions of the oils under the study identified by gas chromatography coupled with mass spectrometry. Each sterol was assured comparing with commercially available standards and the GC-MS library. The analysis revealed that the content of the major sterol for niger seed was β-Sitosterol with a composition of 2778.96 mg/kg. Campesterol and Stigmasterol were identified constituting 869.85 and 920.46 mg/kg respectively. The same trend was observed with the study conducted by Ramadan and Mörsel (2003), for the magnitude of the three major sterol fractions. In addition to the major sterols identified, there were also others not previously known for niger seed oil. Additional sterols identified for niger seed oil in this study include Lupeol, Olean-12-en-3-one, Fucosterol, Elasterol, Lanosterol, Cycloartenol, Cycloartanol, Obtusifoliol, and β-Amyron with the contribution of 587.5, 535.63, 509.62, 215.47, 189.01, 131.03, 139.56,123.66 and 46.8 mg/kg in that order. Figure 2 and Table 2, respectively present the GC-MS chromatogram and fragmentation for sterols identified in niger seed oil.

The result of this finding was in line with the work described by (Ramadan and Morsel, 2002) in that the three sterols are the dominant ones. The result of this finding showed that niger seed oil contains a considerable amount of phytosterols. Marini et al. (2003) and Dutta et al. (1994) were described the dominance of the three sterols in niger seed oil in the range of 40–44 % for sitosterol, 11–14% for campesterol, and stigmasterol. Generally, the sterol fractions β-Sitosterol, Campesterol, Stigmasterol, Lupeol, Fucosterol, and Olean-12-en-3-one were identified to contribute as large as 85% of the sterols in niger seed oil.

The sterol fractions of sesame oil were also identified using GC-MS. Vegetable oils are known to contain unsaponifiable with sesame exhibiting greater in its unsaponifiable content. The composition of unsaponifiable are tocopherols, triterpenes sterols, sesame lignins, and triterpene alcohols. Despite the dominance of free sterols and sterol esters, plant oils contain different forms of sterols like sterol glucosides, free or sterol esters, and esterified steryl glucoside. Desmethylated sterol

Table 1. Mass spectrometric data for derivatives of phytosterols identified by GC-MS.

Peak no	R.time	Sterols identified	Main fragmentation ions
1	10.576	Cholestan	41,55,67,81,95,149,217,357
2	13.939	Campesterol	41,43,57,81,95,119,133,145,213,315,382
3	14.234	Stigmasterol	41,55,69,83,95,107,133,159,255
4	14.817	Obtusifoliol	41,55,69,81,95,109,245,411
5	15.091	γ-Sitosterol, β-Sitosterol	41,43,57,81,95,119,154,161,213
6	15.298	Fucosterol	41,55,69,81,95,107,119,145,213,229,281,299,314
7	15.591	Lupeol	41,43,68,81,95,109,121,189,207,218
8	15.723	Lanosterol	55,69,81,95,121,147,393,411
9	16.021	Olean-12-en-3-one	41,55,69,81,95,109,135,203,218
10	16.241	Elasterol	55,69,81,95,147,255,271,314
11	16.433	Cycloartenol	41,55,69,81,95,121,147,161,286,393
12	16.837	β-Amyron	41,55,69,81,95,122,189,203,218
13	17.061	Simiarenol	55,69,81,95,109,121,134,152,205,260,274
14	17.437	Cycloartanol	41,55,69,81,95,107,121,135,147,161,175,379,407,422

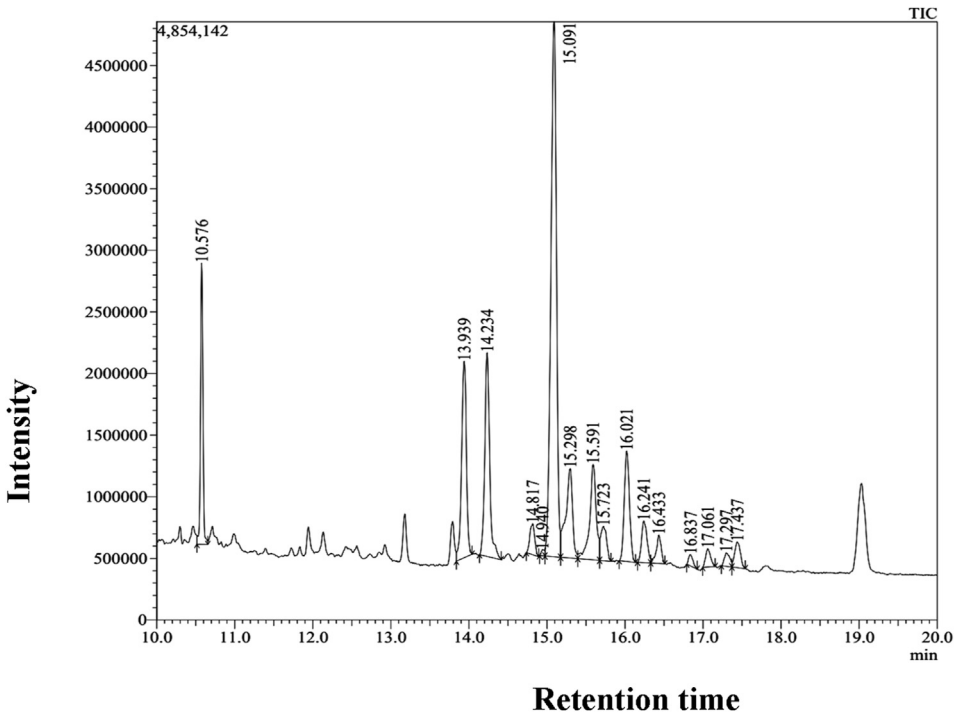

Figure 2. GC-MS Chromatogram of the trimethylsilyl derivatives of main phytosterols in niger seed oil.

Table 2. Sterol fractions of niger seed, sesame, and palm oils mg/kg (%).

Sterol fractions	Oil type		
	Niger seed oil	Sesame oil	Palm oil
Cholesterol	nd	nd	19.9[a] (1.71)
Campesterol	869.85[a] (12.12)*	351.23[d](17.61)	295.9[e] (26.9)
Stigmasterol	920.46[a] (11.75)	125.73[d] (6.19)	125.6[d] (11.6)
β-Sitosterol	2778.96[a] (40.58)	927.42[b] (51.6)	467.2[c] (41.5)
Obtusifoliol	123.66[a] (2.13)	53.88[b] (2.8)	15.38[c] (1.38)
Fucosterol	509.62[a](6.41)	273.89[b] (15.1)	nd
Lupeol	587.5[a] (6.91)	nd	nd
Lanosterol	189.01[a] (2.61)	nd	nd
Olean-12-en-3-one	535.63[a] (7.38)	nd	nd
Elasterol	215.47[a] (2.98)		nd
33-Norgorgosta-5,24(28)-dien-3-ol, (3β)	nd	10.9[a] (0.55)	nd
Simiarenol	82.42[a] (1.14)	nd	nd
Cycloartenol	131.03[a] (1.92)	26.42[b] (1.22)	nd
24-Nor-22,23-methylenecholest-5-en-3β-ol TMS ether	nd	nd	139.14[a] (12.49)
Cycloartanol	139.56[a] (1.93)	11.74[b] (0.68)	4.96[b] (0.43)
β-Amyron	46.8[a] (0.65)	nd	nd

Means having similar superscript in the same row are not statistically different ($p < 0.05$).
* Percent contribution.

is dominant with the contribution of 85–89% of the total sterol. The others monomethylated and dimethylated sterols in sesame oil contribute 9–11% and 24 % respectively (Kamal-Eldin and Appelqvist, 1994). The dominant sterol fractions identified in this study include sitosterol, campesterol, fucosterol, and stigmasterol. From the Codex Standard, the sesame oil exhibited the amount of total sterol accounted for 1.9% confirming it to be an important source of plant sterol (World Health Organization, 2001).

The sterol fractions identified for sesame seed oil were presented in Table 2. Like in the case of the niger seed oil, sitosterol was found to be the principal sterol and constitute 927.42 mg/kg followed by campesterol and stigmasterol comprising 351.23 and 125.73 mg/kg, respectively. Unlike that of niger seed oil, the three sterol fractions (sitosterol, campesterol, and stigmasterol) were found to constitute more than 85% of the sterol content of sesame oil. In addition to the major sterols, others were also identified for sesame oil (Figure 3). Obtusifoliol, Fucosterol, 33-Norgorgosta-5,24(28)-dien-3-ol, (3β), Cycloartenol, Cycloartanol were additional sterols identified with the composition of 53.88, 273.89, 5.14, 26.42 and 11.74 mg/kg, respectively. As it is depicted in Table 2 and Figure 3, the result of this finding was in line with Itoh and Matsumoto (1973) in that no cholesterol was identified for sesame oil in both cases.

The sterol composition identified for palm oil is presented in Table 2 and Figure 4. Sitosterol, campesterol, 24-Nor-22,23-

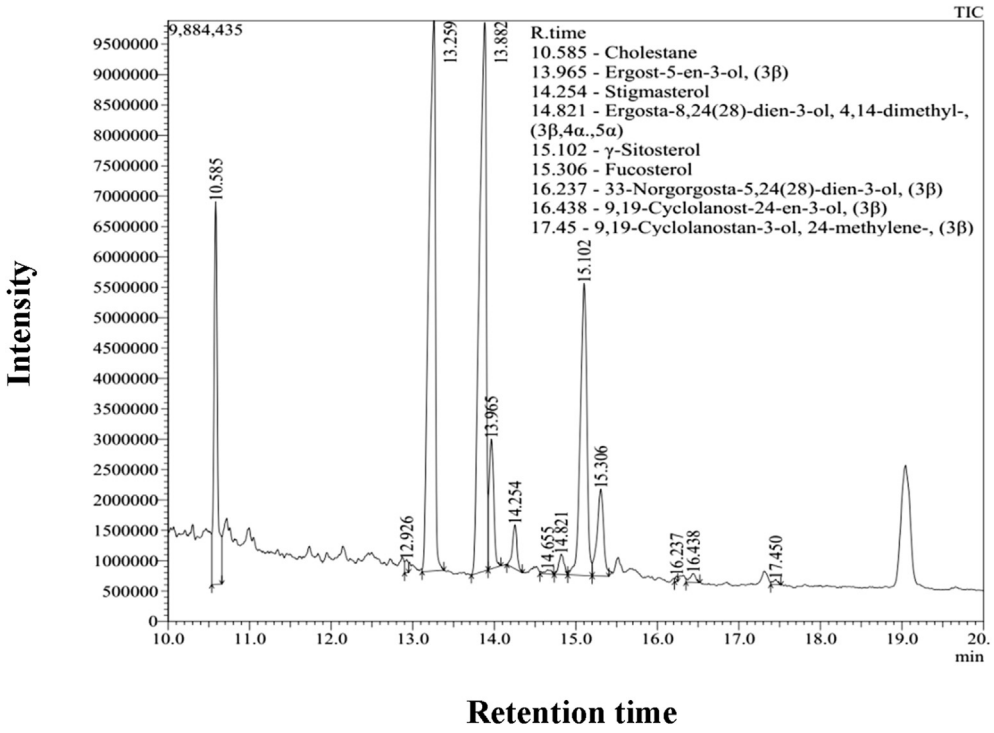

Figure 3. GC-MS Chromatogram of the trimethylsilyl derivatives of main phytosterols in sesame seed oil.

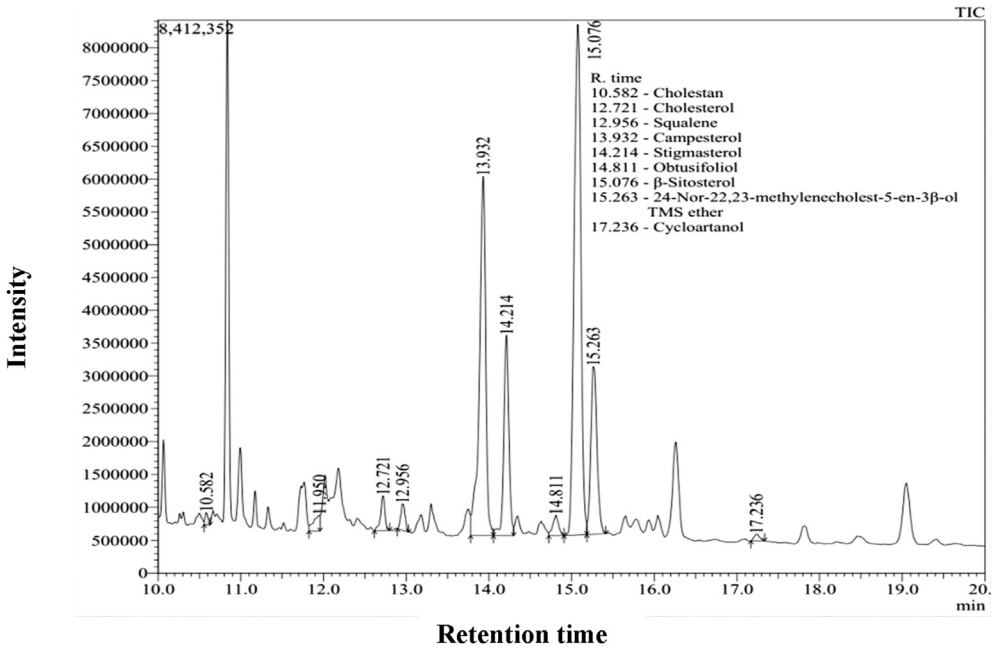

Figure 4. GC-MS chromatogram of the trimethylsilyl derivatives of main sterols in palm oil.

methylenecholest-5-en-3β-ol TMS ether and stigmasterol were the main sterols identified constituting 467.2, 295.9, 139.14 and 125.6 mg/kg, respectively. The four identified sterols accounted for more than 90% of the profile (Table 2). Unlike the niger seed and sesame oils, cholesterol and 24-Nor-22,23-methylenecholest-5-en-3β-ol TMS ether were only found in palm oil.

3.2. Principal component analysis (PCA)

Sterol fractions of the three oils were analyzed using the Principal Component Analysis. Eigenvalues with the magnitude of 13.53(84.57%) and 2.45(15.43%) were obtained. Observing the isolation among the oils, two distinct groups were separated, according to the first two axes. Figure 5 shows the three oils, niger seed oil, sesame seed oil, and palm oil are denoted on three different sides of the plane for all the sterol fractions explaining a substantial variation within the studied oils. On the other hand, Figure 6 depicts the significant contributing factors for the variation among the oils. The plot described PC1 explained 84.57% of the variability and PC2 explained 15.43%. Moreover, the PCA biplot indicated the existence of three important data structures, namely niger seed oil on the upper left quadrant, palm oil and sesame oils on the bottom left and right,

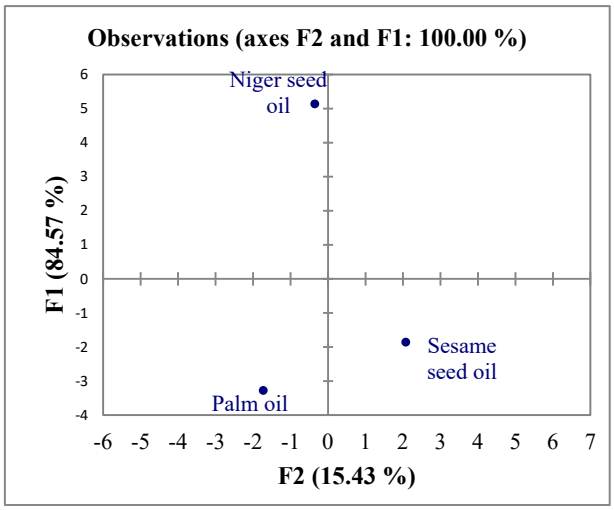

Figure 5. Score plot of the PC1 – PC2 for the sterol profile of the three oils.

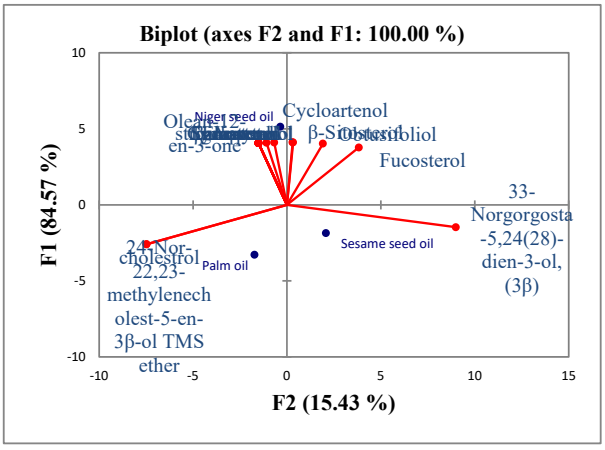

Figure 6. Loading plot of the PC1 – PC2 for the sterol composition of the three oils.

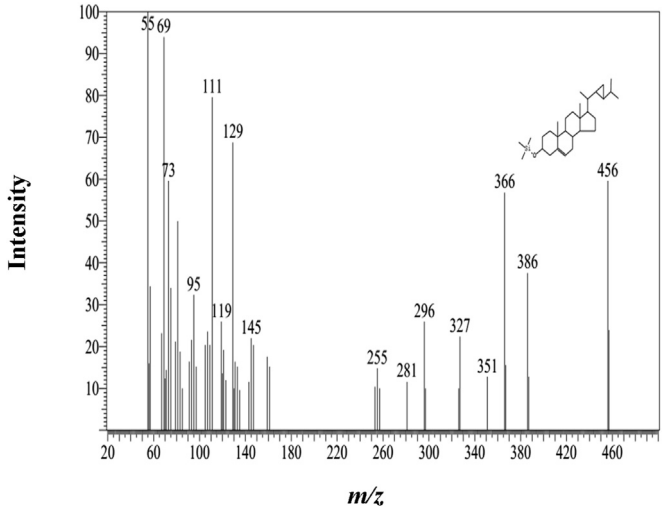

Figure 8. Full scan mass spectra of 24-Nor-22,23-methylenecholest-5-en-3β-ol TMS ether.

respectively, quadrants of the plot. Similarly, the heatmap analysis also dipected the variation in the sterol composition of the three oils using Green- Yellow – Red color Scale (supplementary material 1).

3.3. Detection of Niger seed and sesame oil adulterated with palm oil

The sterol profile-based detection of adulteration of the named oils was studied. From the analysis of the sterol profile of the three oils, cholesterol trimethylsilyl ether and 24-Nor-22,23-methyl-enecholest-5-en-3β-ol TMS ether were found only in palm oil. The sterols only identified in palm oil were used as marker compounds to identify whether it was mixed with niger seed and sesame seed

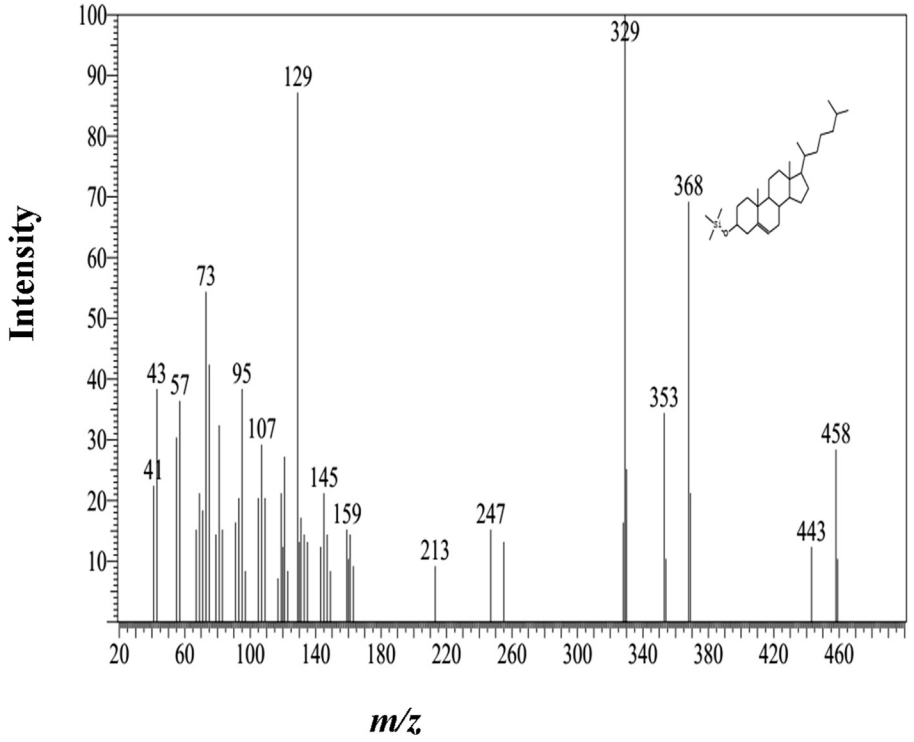

Figure 7. Full scan mass spectra of cholesterol trimethylsilyl ether.

oil. The sterol composition of the mixed oils at a level of 10% was profiled using GC-MS to assure that compounds found only in palm oil would also appear in the mixture at the specified proportion. The analysis revealed the two compounds were also found in the profile of the mixture of palm oil with niger seed and sesame oil. It was possible to distinguish the addition of palm oil at a level of 10% in niger seed and sesame oil by GC-MS. Figures 7 and 8 present the full scan mass spectra of cholesterol trimethylsilyl ether and 24-Nor-22,23-methylenecholest-5-en-3β-ol TMS ether, respectively.

4. Conclusion

The sterol profile of niger seed, sesame, and palm oil was studied using GC-MS. The PCA identified one oil from the other based on the sterol fractions. In niger seed and sesame oils; sitosterol, campesterol, and stigmasterol were the dominant sterols identified. 24-Nor-22,23-methylenecholest-5-en-3β-ol TMS ether was found dominant in palm oil in addition to the three sterols. In all the oils studied, the content of sterols differed significantly ensuring the specificity of sterol composition for different oils. Cholestroltrimethyl silyl ether and 24-Nor-22,23- methylenecholest-5-en-3β-ol TMS ether the sterols only found in palm oil were used to trace adulteration. An attempt made to trace these compounds by mixing palm oil at a level of 10% with niger seed and sesame oils was successfully detected its presence. Hence, it's necessary to devise a means to overcome the challenge of adulteration. As the physicochemical properties of oils can be arranged to cover adulteration, marker identification provides a reliable identity of specific oils.

Declarations

Author contribution statement

Tesfaye Deme: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Gulelat D. Haki, Nigussie Retta, Ashagrie Woldegiorgis, Mulatu Geleta: Analyzed and interpreted the data.

Hinsta Mateos, Paul A. Lewandowski: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data will be made available on request.

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The authors declare no conflict of interest.

Additional information

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