Sustainable Agriculture Research; Vol. 3, No. 1; 2014
ISSN 1927-050X E-ISSN 1927-0518
Published by Canadian Center of Science and Education

Marketed and Original Shea Butters of Côte d'Ivoire: Physicochemical and Biochemical Characterization and Evaluation of the Potential Utilizations

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Received: December 16, 2013 Accepted: January 15, 2014 Online Published: January 17, 2014

doi:10.5539/sar.v3n1p50 URL: http://dx.doi.org/10.5539/sar.v3n1p50

Abstract

Many standards constitute shea butter trading conditions, but the exploitation of this greasy product is submitted to other industrial exigencies. The aim of this study was to characterize and evaluate the utilization potentiality of the artisanal shea butter produced in Côte d'Ivoire, on the basis of the industrials exigencies. Hence, both beige and yellow artisanal (original and market) shea butters were collected and analyzed. The refractive indexes (1.46 ± 0.00) did not vary while specific gravity at 40 °C (0.86 ± 0.00 - 0.92 ± 0.00), unsaponifiable matter (1.80 ± 0.01 - 3.76 ± 0.02%) and pH values (5.39 - 6.69) showed significant differences from a sample to another. The viscosity was very high at 40 °C (86.78 ± 0.89 - 130.10 ± 0.26 mPas) and decreased with the temperature increasing (40 to 65 °C). The UV-Vis spectrum showed a very weak absorption from 300 to 400 nm (UV-B and UV-A domains) while the near infra-red (NIR) one, revealed peaks at 450 and 700 nm for yellow shea butters only and peaks at 1200, 1400, 1725 and 2150 nm for all the samples. The fatty acids profile highlighted four main fatty acids (palmitic, stearic, oleic and linoleic acids); saturated fatty acids (56.00 ± 0.20 - 63.00 ± 0.20%) were the most important. All these interesting characteristics should arouse attention for using traditional shea butters in food, cosmetic and pharmaceutical industries.

Keywords: artisanal shea butter, quality assessment, biochemical properties, nutritive properties

1. Introduction

Shea butter tree (*Vitellaria paradoxa*, syn. *Butyrospermum parkii*, *B. paradoxa*), represents an important socio-economical agro-resource for the producing countries (Schreckenberg, 2004; Programme des Nations Unies pour le Développement [PNUD], 2010). This importance is linked not only to the nuts and the butter commercialization, but mainly to the wide range of usages (Hall et al., 1996). Indeed, according to these authors, shea butter has long been used in sub-Saharan Africa and elsewhere for medicinal, culinary, and other applications. Nowadays, this oleaginous plant serves as a cocoa butter equivalent in the manufacture of chocolate as well as ingredient in cosmetic and pharmaceutical industries (Pesquet, 1992; Hall et al., 1996; Pontillon, 1996; Nahm, 2011; Aarhus Karlshamn [AAK Global], 2012). About shea butter exploitation in these latest industries, it is worth noting that shea Butter has shown to be a superb moisturizer, with exceptional healing properties for the skin. In fact, shea butter is involved in the treatment of skin allergies, insect bites, sunburns, frostbites, and a number of other conditions of the skin. However, shea butter uses depend on the butter colors and physicochemical properties which also vary as function to the processing (nut pre-treatment and butter extraction) (Womeni et al., 2006; Omujal, 2009). According to the PNUD (2010) and the FAOSTAT (2012), the highest shea producers' countries originated from West Africa (701510 tons) and Côte d'Ivoire represents the fifth producer with average 30000 tons. In the whole producing countries, the shea butter industry depends mainly on the work of women and their own approach of process (Nahm, 2011).

Shea butter is generally prepared by producers following traditional processes, in shea production areas (original shea butter) and then forwarded in towns for sale (marketed shea butter). Three colors (beige or white, yellow and grey) of shea butter are sold on markets, but the beige and the yellow ones are well known by the consumers

(Carette, Malotaux, Van Leeuwen, & Tolkamp, 2009; Mégnanou & Diopoh, 2008). If the grey shea butter is considered as a bad product of preparation (Hall et al., 1996; Megnanou, 2008), the beige (abusively considered as "white"), and the yellow shea butter are strictly preferred by consumers (Carette et al., 2009; Mégnanou & Niamke, 2013). Several studies have underlined the difference between the preparation modes of beige and yellow shea butters and the different sensorial characteristics associated (Hall et al., 1996; Mégnanou, 2008). Nevertheless, because of increasing shea butter utilization sectors, additional criteria were defined by industrials. Even if, some of these new criteria were considered by UEMOA shea producing countries (Union Economique et Monétaire Ouest Africaine [UEMOA], 2011), what about the other exigencies such as fatty acids profile, ultra-violet and near infrared spectra, viscosity variation and the pH?. The present study aimed to determine physicochemical and biochemical characteristics of Ivorian traditional shea butter and evaluate its potential utilizations on the basis of the industrials exigencies such as the fatty acids profiles, the viscosity as function to the temperature, the infrared and ultraviolet spectra. Therefore, more than the basic physicochemical characteristics (specific gravity, viscosity, pH, and unsaponifiable matter) other parameters such as fatty acids profiles, viscosity as function to the temperature, infrared and ultraviolet spectra of both beige and yellow artisanal shea butters from markets and producing areas units were investigated.

2. Materials and Methods

2.1 Sampling

For this study, beige and yellow shea butter (*Vitellaria paradoxa*) samples were collected from the market and from the production area. Thirty (30) samples (25 - 30 g, for each sample) of each beige and yellow shea butters, were randomly collected from the markets of Abidjan District (Côte d'Ivoire) on March 2013. In the same period, thirty (30) samples of each beige and yellow shea butters, were also randomly collected from traditional factory in Dabakala (North of Côte d'Ivoire). The collected samples were mixed together in laboratory to constitute two representative samples (beige and yellow) from both market (moisture content 3.36 and 8.36%, respectively) and traditional production (moisture content 0.15 and 0.20%, respectively). These four samples were stored at 4 °C in air tight brown sterile glass bottles until further use for analysis.

2.2 Chemicals

Analytical grade solvents, standards and reagents were used to perform analysis. Solvents (n-hexane, acetic acid, diethyl-ether, ethanol, methanol and n-heptane) were provided from Merck (Germany). Standards such as fatty acids (palmitic acid, stearic acid, oleic acid, and linoleic acid) and erucic acid were purchased from Sigma-Aldrich (Germany). Wijs reagent was from Prolabo (France). All other reagents used were of analytical grade.

2.3 Physicochemical Analysis

In the present experiment, each test for the sample was analyzed in triplicate.

2.3.1 Specific Gravity, Refractive Index and Viscosity

Specific gravity and refractive index of melted butters were determined at 40 °C following the International Union of Pure and Applied Chemistry [IUPAC] (1979) method by using a pycnometer and a refractometer (RM40, Metller Toledo, Switzerland), respectively. Viscosity was determined at different temperatures (40 - 65 °C) by using a viscometer apparatus (SVM 3000, Anton Paar GmbH, Austria) equipped with a syringe filled with 1 mL of melted butter sample. Values of viscosities were automatically recorded after temperature programming.

2.3.2 PH, Colour and Melting Point

pH value of melted butter samples was determined at 25 °C according to Afane et al. (1997) by using a pH-meter Hi 8915 ATC, Hanna, Spain). 2 mL of melted butter sample were dissolved in 15 mL of n-hexane. The pH-meter electrode was standardized with buffer solutions (pH 4.0 and 7.0) and then, immersed into the sample to record pH value.

Colour of melted shea butter (40 °C) and melting point were determined according to the Malaysian Palm Oil Board [MPOB] (2005) methods by using a Lovibond colorimeter (Lico, Labomat, France) and a thermometric system (FP900, Metller Toledo, Switzerland), respectively.

2.3.3 UV-Vis Spectra

UV-Vis spectra of melted butter samples were determined by measuring absorbance of hexanic melted butter solution (1 %) by using a UV-Vis spectrophotometer (T80+, PG Instruments, England) in the range of 200 to 600 nm (Besbes et al., 2004).

2.3.4 NIR Spectrum

Near infrared spectrum (NIR) was determined by reading absorbance of melted butter sample in the range (400-2500 nm) using an infrared spectrophotometer (Foss Liquid Analyzer, Denmark) equipped with a software (NIR Vision Spectral Analysis, Model 6500) for data acquisition.

2.4 Biochemical and Nutritive Analysis

2.4.1 Unsaponifiable Matter Content

Unsaponifiable matter content of oil was determined following the IUPAC (1979) method. Oil sample (5 g) was saponified with 50 mL of 2 N KOH methanolic solution for 1 h. To the resulted mixture, 50 mL of distilled water was added. The unsaponifiable matter was extracted three times with 50 mL of diethyl-ether. Organic fractions were collected, washed three times with 50 mL of distilled water and then dried with sodium sulfate. Diethyl-ether was removed in a rotary evaporator (Heidolph, Hei-Vap, Germany) to recover the unsaponifiable matter which was then weighed.

2.4.2 Fatty Acid Composition

The fatty acids were converted to their methyl esters (FAMEs) as described by the European Communities (1991) methods. About 0.1 g of oil sample was mixed with 2 mL of n-heptane and 0.2 mL of a methanolic solution of potassium hydroxide (2N). The whole mixture was shaken up for 30 s and allowed to settle for 5 min. The top layer containing the FAMEs was used for gas chromatography (GC) analysis. FAMEs solution (1 µL) containing the internal standard (erucic acid) was injected into a gas chromatograph (Shimadzu, GC-9A, Japan) equipped with a mass spectrometer (MS) and a RTX5 fused silica capillary column (30 m × 0.32 mm i.d. × 0.25 µm film thickness). The carrier gas was helium and the flow rate adjusted to 23 mL/min. Temperatures of detector and injector were 250 °C. The initial column temperature was fixed to 100 °C and programmed to increase by 5 °C per min intervals until 220 °C and, kept for 10 min at this temperature. The fatty acid methyl esters peaks were identified by comparing their retention times with those of standards. After adjusting areas with the internal standard (erucic acid), the yield of each fatty acid was calculated as follow: area of the fatty acid/areas of total fatty acids in the oil sample × 100 (%).

2.5 Statistical Analysis

In the present experiment, each test for the sample was analyzed in triplicate. Data were expressed as means ± standard deviation (SD). Differences between means were analysed by analysis of variance (one way ANOVA) using XLstat 2009 3.1.5 software. Statistical significant difference was stated at $p < 0.05$.

3. Results and Discussion

3.1 Physicochemical Properties

The physicochemical parameters of beige and yellow market and original shea butters are shown in Table 1.

Table 1. Physicochemical properties of beige and yellow market and original shea butters

Parameters	Beige market	Yellow market	Beige original	Yellow original
Specific gravity (40 °C)	0.91 ± 0.00^{ab}	00.92 ± 0.00^{a}	0.89 ± 0.01^{b}	0.88 ± 0.00^{c}
Refractive index (40 °C)	1.464 ± 0.00^{a}	01.464 ± 0.00^{a}	01.464 ± 0.00^{a}	1.464 ± 0.00^{a}
Viscosity (mPas) (40 °C)	86.78 ± 0.39^{d}	91.75 ± 0.26^{c}	130.10 ± 5.02^{a}	110.69 ± 5.21^{b}
Colour (Ly)	18.67 ± 1.15^{d}	63.66 ± 1.15^{b}	23.67 ± 1.15^{c}	68.67 ± 0.58^{a}
pH (25 °C)	05.64 ± 0.01^{c}	05.39 ± 0.01^{d}	05.68 ± 0.01^{b}	06.69 ± 0.01^{a}

Values are expressed as mean±SD. Means in the lines with no common superscript differ significantly ($p < 0.05$).

All the parameters generally showed significant difference ($p < 0.05$) except for refractive index. The value of specific gravity was about 0.90 ± 0.00 while the refractive index was 1.46 ± 0.00. The specific gravity and refractive index of shea butter samples are within the range of those reported for most conventional edible oils (Codex-Alimentarius, 1993). Furthermore, all studied shea butters could be classified as non-drying fats in view to their refractive index value (Rossell, 1991). This property would underline their quality of edible fat and also disqualify them for varnish manufacturing in chemical industry. The viscosity of liquids as vegetable oil is commonly perceived as thickness, or resistance to pouring (Ndangui et al., 2010). Beige and yellow market shea

butters are less viscous (86-92 mPas) than original manufactured ones (105-135 mPas). In addition, these viscosity values are relatively higher than the mean value (75 mPas) of most vegetable oils (Besbes et al., 2004). This physical property linked to the solid state of the studied shea butters could be used in food and cosmetic industry to confer an adequate texture to final fat products (Dubois et al., 2007).

The effect of temperature on viscosity of the whole shea butter samples is depicted in Figure 1. For all of the samples, the value of viscosity decreases (130.10 to 36.29 mPas) continuously when the temperature increases from 40 to 65 °C and would confirm the Arrhenius law (Nzikou et al., 2007) which indicates that the viscosity of fats decreases exponentially with increasing of temperature. It is worth noting here that the appearance of linear relationship between viscosity and temperature would be due to the relative small interval of temperature (40 to 65 °C); the figures might represent a portion of hyperboles. It was also observed a relative similitude in the evolution of the viscosity for all the samples. This situation could also suggest similarity in fatty acids composition, for both marketed and original shea butters. However, such rheological property (viscosity/temperature) of the studied shea butters could be exploited in cosmetic industries for emulsions making (Lefur & Arnaud, 2004).

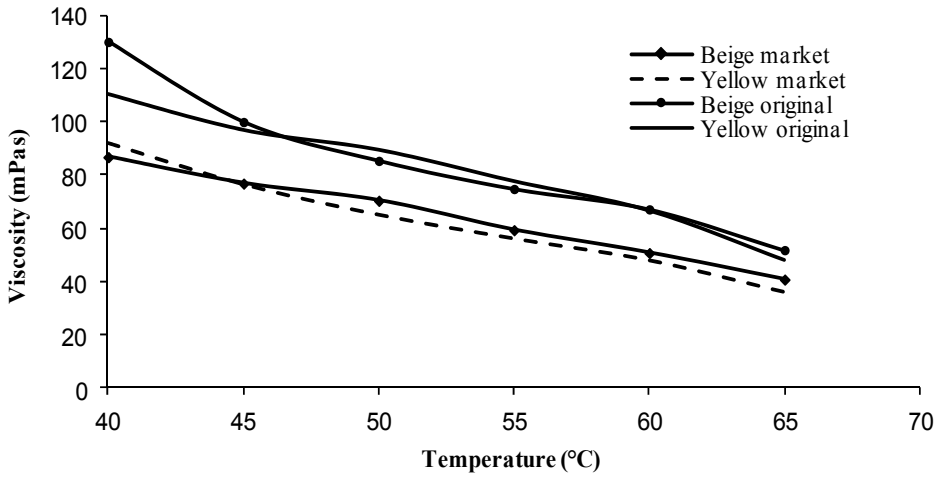

Figure 1. Effect of temperature on market and original manufactured shea butters viscosity

The Lovibond colour in yellow light (Ly) of yellow market and original shea butters were 63.66 ± 1.15 and 68.67 ± 0.58, respectively. This parameter, generally related to carotenoids content and bleachability index of oil sample, is higher than that (47.7) of crude palm kernel oil (MPOB, 2005). Consequently, yellow market and original shea butters could be exploited in cosmetic industries in view to the antioxidant activity and the protective skin effect of carotenoids (Platon, 1997). As concern the Lovibond colour values registered by the beige shea butter, it was relatively weak compared to the yellow shea butter and would be due to the presence of residual pigment of shea almond (Sanou, 2002; Kitamura et al., 2003). Concerning the yellow shea butter strong coloration, it should result from the adjunction of natural yellow pigment extracted from the roots of *Cochlospermum tinctorium* (Hall et al., 1996; Jansen, 2005). Nevertheless, a similar yellow colour could also result from some synthetic pigments producers add to their butter, or from the presence of fungal secondary metabolite (Mégnanou, 2008). However other analyses were performed and provided clearer precision.

The UV-Visible spectrum of beige and yellow market and original shea butters is shown in Figure 2.

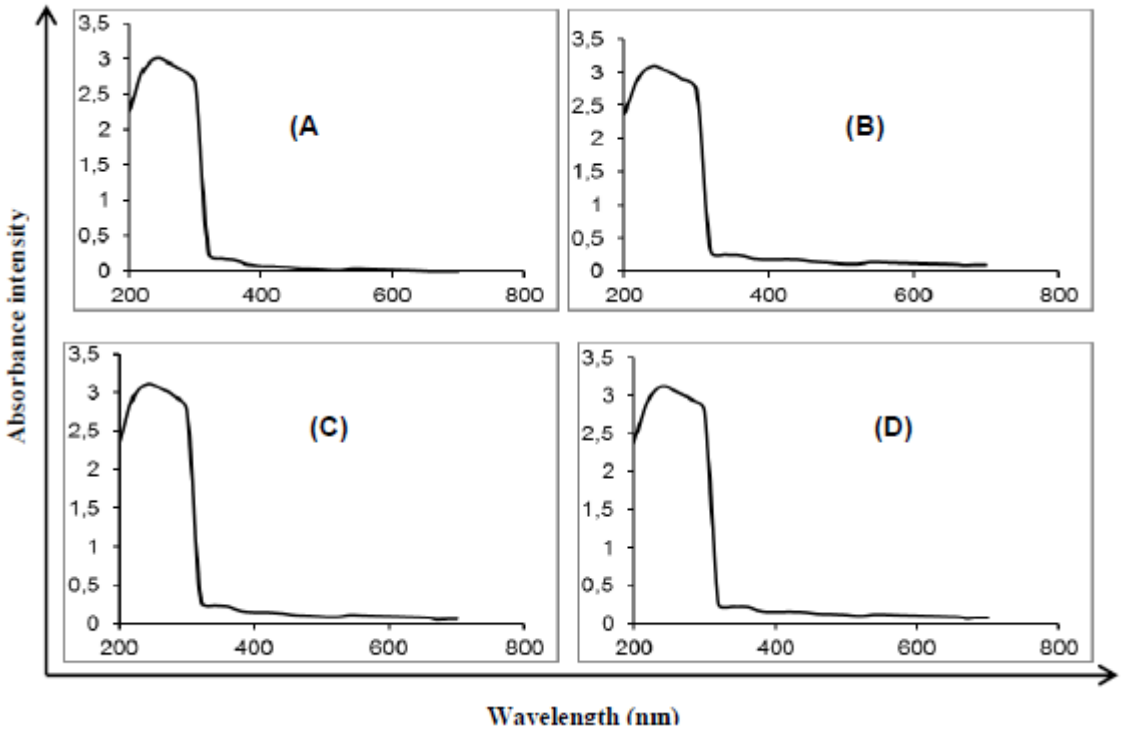

Figure 2. UV-Visible spectrum of market and original manufactured shea butters. (A): beige market; (B): yellow market; (C): beige original; (D): yellow original

All the spectra presented the same profile with a wide peak from 200 to 300 nm and then a rapid decrease of absorbance in the interval of 300 to 500 nm (Figure 2). The wide peak appeared between 200 and 300 nm would suggest the presence of either ethylenic bonds with conjugation or carbonyl compounds (Yadav, Chudasama, & Jasra, 2004). The strong decrease of absorbance as for it would presume the presence of UV-filter compounds in shea butter samples (Besbes et al., 2004). This would justify the great interest of cosmetic and pharmaceutical industries for shea butter, and would then constitute an advantage for using the studied shea butters in cosmetics formulations as UV protectors against carcinogenic UV (B and A). The similitude between market and original samples spectra could not only suppose the use of the same shea variety but also the same manufacturing process. The UV spectra could then be considered as a distinctive (specific) characteristic allowing any shea butter traceability (as function to the variety and/or the manufacturing process).

The visible and near infrared spectrum shea butters samples is shown in Figure 3. The visible domain of this spectrum showed maximum absorbance at 450 nm for yellow marketed and original shea butters, and a relatively weak peak at 700 nm for market yellow shea butter (Figure 3C). If the absorbance at 450 nm would suggest the presence of carotenoids compounds in both samples (Psomiadou & Tsimidou, 2001), the peak at 700 nm as for it would suggest the presence of chlorophyll. These observations would confirm yellow shea butters high Lovibond colour value in yellow light. Very slight absorbance was also observed for beige shea butters at 450-500 and would then suppose the presence of carotenoid in weak amount. As for the near infrared domain of the spectrum, it showed four main peaks at 1200, 1400, 1725 and 2150 nm. About the peaks observed at 1200, 1400, 1725 and 2150 nm, they would be related to C-H stretching 2nd overtone (oil), C-H stretching 1st overtone (oil), CO stretching 1st overtone (oil), and C-H bending 2nd overtone (oil), respectively (Kim, Park, Choung, & Jang, 2005). The peaks at 1200 and 1400 would indicate the presence of hydrocarbon, when fatty acids (FFA) would be characterized by the peak at 1725 nm (CO stretching 1st overtone). As for the peak (vibration of C–H *cis*-unsaturation bonds) observed at 2150 nm, it would suppose the presence of unsaturated compound such as unsaturated fatty acids (Man & Moh, 1998). These previous information (UV and IR spectra) would suggest the presence of hydrocarbon, unsaturated compound, fatty acids and compounds protecting against damages sun rays could cause (allergy and cancer).

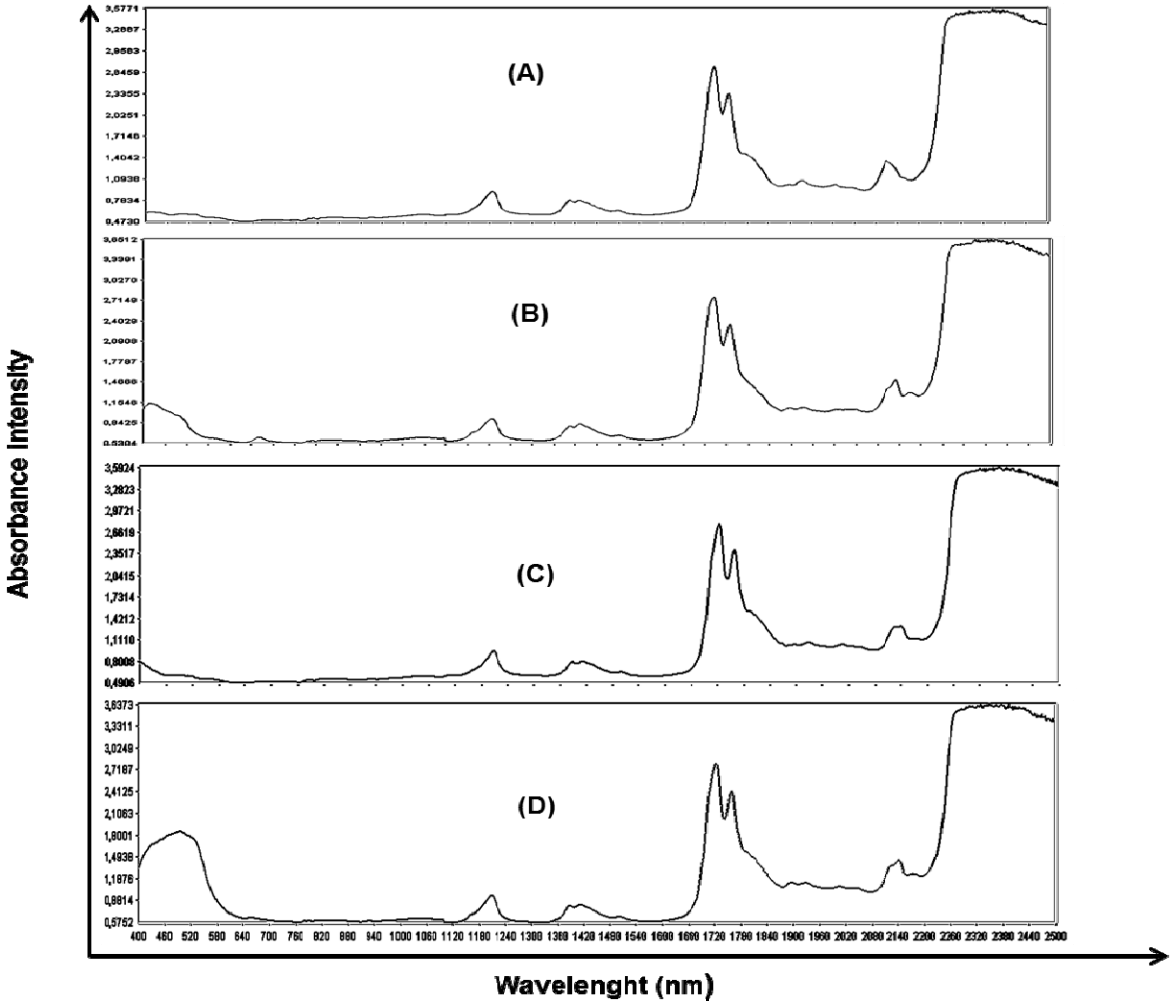

Figure 3. Near infrared (NIR) spectrum of market and original manufactured shea butters. (A): beige market; (B): yellow market; (C): beige original; (D): yellow original

3.2 Biochemical and Nutritive Properties

Biochemical parameters showed significant statistical difference ($p < 0.05$) for the samples analyzed (Table 2).

Table 2. Biochemical properties of beige and yellow market and original shea butters

Parameters	Beige market	Yellow market	Beige original	Yellow original
Unsaponifiable matter (%)	03.18 ± 0.01^{b}	01.80 ± 0.01^{d}	03.76 ± 0.02^{a}	02.20 ± 0.05^{c}
Palmitic acid (%)	23.00 ± 0.10^{b}	18.00 ± 0.10^{d}	24.00 ± 0.01^{a}	22.00 ± 0.10^{c}
Stearic acid (%)	40.00 ± 0.10^{a}	38.00 ± 0.10^{c}	39.00 ± 0.01^{b}	40.00 ± 0.10^{a}
Oleic acid (%)	32.00 ± 0.10^{c}	39.00 ± 0.10^{a}	32.00 ± 0.01^{c}	34.00 ± 0.10^{b}
Linoleic acid (%)	05.00 ± 0.01^{a}	05.00 ± 0.01^{a}	05.00 ± 0.01^{a}	04.00 ± 0.01^{b}
SFA (%)	63.00 ± 0.20^{a}	56.00 ± 0.20^{c}	63.00 ± 0.20^{a}	62.00 ± 0.20^{b}
UFA (%)	37.00 ± 0.10^{c}	44.00 ± 0.10^{a}	37.00 ± 0.10^{c}	38.00 ± 0.10^{b}

Values are expressed as mean ± SD. Means in the lines with no common superscript differ significantly ($p < 0.05$).

Intrinsic biochemical parameter such as unsaponifiable matter varies from 1.78 to 3.79% and are higher than those reported for other high value solid fats such as coconut kernel (0.2 - 0.4%), palm kernel (0.3 - 0.5%) and cocoa (0.5 - 1%) (Karleskind, 1992). Therefore beige and yellow market and original shea butters could be used as a good source of stabilizers in cosmetic and food industry (Pesquet, 1992; Hall et al., 1996; Gunstone, 1999; AAK, 2012).

Chromatographic profiles of fatty acids composition of the samples are given in Figure 4. Fatty acid proportions of the studied shea butters highlighted the presence of four main compounds which are palmitic (17.99 - 24.01%), stearic (38.99 - 40.1%), oleic (31.99 - 39.1%) and linoleic (3.99 - 4.01%) acids (Table 2). It is worth précising here that shea butter contains other fatty acids but the main in content are the previous cited. These other fatty acids were materialized on the spectrum by peak with very slight intensity. However, unsaturated fatty acids (UFA) of the studied shea butters were essentially made up of oleic and linoleic acids. The saturated fatty acids (SFA) as for them consisted in palmitic and stearic acids. It was remarked that the proportion of oleic acid in all the shea butter samples, was more important than in the literature. If for markets shea butter, this situation could be justify by the adulteration (other fat adding), about original samples, it would be difficultly justify. However, the proportions of UFA and SFA were 36.9 – 44.1% and 55.8 – 63.2%, respectively. This amount of SFA (> 50%) would justify the solid state of the studied shea butters at ambient temperature (Alais & Linden, 1997). Indeed, the presence saturated fatty increases the melting point of fats and oils (Salas, Bootello, Martínez-Force, & Garcés, 2009) because of their melting points (62.7 - 69.6%) which are at far higher than (-6.5 - 13.0%) of unsaturated ones (Kandji, 2001). In view of the fatty acids profiles, beige and yellow market and original shea butters could be categorized as stearic-oleic fats such as cocoa butter and mango kernel oil (Dubois et al., 2007). Therefore, the studied shea butters could be used in food industries for frying due to the thermal stability of oleic acid and for margarine making due to the melting point of stearic acid (Gunstone, 1999; Ramadan & Moersel, 2004). Moreover, the important oleic acid content (31.99 - 39.1%) could be advantageous for "oléine de karité" production. This product consists in shea butter liquid fraction and is widely exploited and traded in Burkina Faso. Furthermore, the presence of linoleic acid could be useful in cosmetic industries to decrease trans-epidermal water loss and to eliminate scaly lesions common in patients with essential fatty acid deficiency (Aburjai & Natsheh, 2003). The presence of both oleic and linoleic acids which are essential fatty acids, would also suggest a potential beneficial use as edible fat.

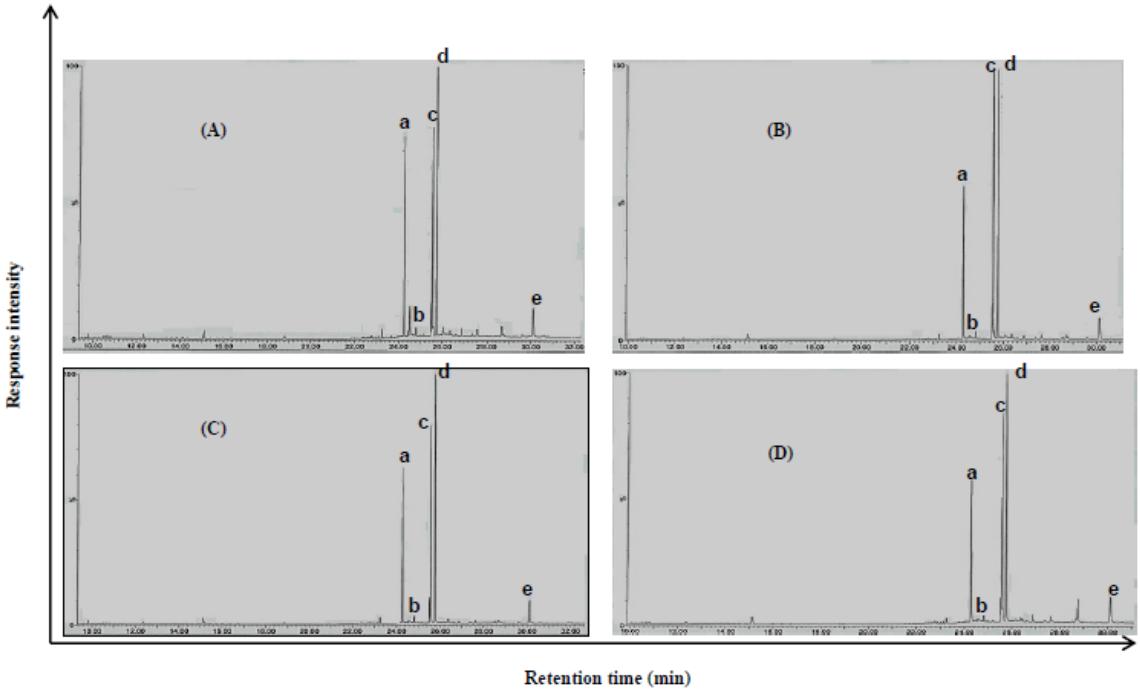

Figure 4. Gas chromatographic profiles of market and original manufactured shea butters fatty acids

Legend: (A): beige market; (B): yellow market; (C): beige original; (D): yellow original; (a): palmitic acid; (b): linoleic acid; (c): oleic acid; (d): stearic acid; (e): erucic acid (internal standard).

4. Conclusion

The main difference between beige and yellow shea butters resides in the presence of carotenoid and chlorophyll which could confer to the yellow one, a higher resistance to oxidation. However, the values of specific gravity and viscosity confer to both beige and yellow shea butters, good characteristics for edible vegetable fat. Moreover, their essential fatty acid (linoleic acid) content would profile a benefic exploitation in human nutrition, and then in food industry. Cosmetic and pharmaceutical industries interest in the studied shea butters would be linked to the pH value in conformity with the human body one, the relatively high unsaponfiable content, the melting point, the very slight absorption of UV-A and UV-B and the presence of hydrocarbon such as karitene. Above all, the similitude between the spectra ultra-violet and infrared of the whole studied samples would suggest the spectra to be essential parameters for shea butter traceability.

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