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Cosmetic or Dietary Vegetable Oils Sampled in the Cameroonian Market May Not Expose Consumers to Lipid Oxidation Products Generating Oxidative Stress and Inflammation

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ABSTRACT

Vegetable oils are a source of energy, essential fatty acids, antioxidants and fat-soluble vitamins useful for human health care and development. These oils also contribute in organoleptic quality of their products derivatives. However, their chemical and physical properties can be modified by the mode of their extraction, storage and distribution. These modifications might negatively affect the nutritional quality of the oils. The goals of this study were to: sample different vegetable oils for cosmetic or dietary use marketed in Cameroon; verify purity and oxidation states of each oil through determination of its acidity, iodine, peroxide, saponification, refractive indexes and the conformity of the labeling. The caroten content, the level of polar components and specific absorbance were also determined. As the results, six oils namely palm, palm kernel, coconut, black cumin, peanut and shea butter were collected. Apart from labeling, chemicals and physicals parameters analyzed were generally in accordance with the Cameroonian and Codex Alimentarius standard. This study suggests that vegetable oils sampled in the Cameroonian market may not expose consumers to lipid oxidation products generating pathological oxidative stress and inflammation. However, efforts in application of existing standard need to be done as far as labeling are concerned.

Keywords: Vegetable Oils; Quality Control; Labeling Compliance; Lipid Oxidation; Oxidative Pathology

Abbreviations: WHO: World Health Organization; FAME: Fatty Acid Methyl Esters; LA: linoleic Acid; ALA: Alpha-Linolenic Acid; FFA: Free Fatty Acids; USM: Unsaponifiable Matter; SV: Saponification Value; PV: Peroxide Value; RI: Refractive Index; AV: Acidity Value; IV: Iodine Value

Introduction

Vegetable oils derived from oil plants. Oil is extracted from seeds or kernels. These oils are composed of triglycerides, which contain primarily polyunsaturated and monounsaturated fatty acids. In developing countries like Cameroon, the commercial sector is strongly liberalized. There are little or no quality standards, and limited informa-

tion on the quality of locally consumed foods. Oils and fats, employed particularly for cosmetic or alimentation use, are typical examples [1,2]. On the other hand, vegetable oils are oxidized during processing and storage via autoxidation and photosensitized oxidation. Oxidative stability of vegetable oils are particularly related to their unsaturated fatty acids [3]. The oxidative mechanisms are based on complex and

radical reactions that always result in a significant loss of oil quality in both sensorial (rancidity) and nutritional values (loss of polyunsaturated fatty acids and vitamin E). Oxidation is among mechanism of degradation of oil. It is some time associate to polymerization and hydrolysis of the oil's chemical compounds. Lipids oxidation is one of the most important issues related the health effect such as oxidative stress relates to chronic disease, mainly inflammation and cardiovascular disease. However, providing people with healthy, nutritious and affordable oils is important for food security [4]. Moreover, for a healthy diet the World Health Organization (WHO) has established that 30% of energy consumption should originate from vegetable oils and fats [5].

Vegetable oil remains an indispensable ingredient in the human daily life diet. It's a cooking medium (due to its sensory attributes) as supplier of energy to maintain body normal temperature [6]. In this study, we have decide to control the quality of the common consume oils produced in local or imported. Commercially vegetable oils in Cameroun for cosmetic or alimentation include at less: palm oil, palm kernel oil, coconut oil, black cumin oil, peanut oil and shea butter. In this work physical and chemical characteristics of the six oils were analyzed as well as their compliance with the Cameroonian standard NC 04: 2000-20 on the labeling of prepackaged foods. Our main objective was to see if those oils may have a high degree of degradation or oxidation which may expose of humans health to lipid oxidation products. In addition, does the information provided by the labelling comply with the standards.

Materials and Methods

Oils were all available in Cameroon. They were purchased from local market and supermarket, Yaoundé. Both physical and chemical characteristics of oils were determined.

Fatty Acid Methyl Esters (FAME) Analysis

150 μ L of oil in 2 mL of hexane was trans-methylated with 200 μ L of a cold solution of KOH in methanol (2 M), according to the European Standard NF EN ISO 12966 [7]. Fatty acid methyl esters (FAMES) were analyzed in accordance with the European Standard NF EN ISO 5508. Analyses were performed on a Varian Gas Chromatograph CP3800 equipped with the flame ionization detector (GC-FID) ($T = 250^{\circ}\text{C}$), using a capillary column using a DB-FastFAME 30 m \times 0.25 mm, 0.25 μ m. The carrier gas was hydrogen (column flow 30 cm/s at 40 cm/s) and the split ratio was 1:100. The oven temperature was programmed as follows: 2 min at 120°C , increased from 120°C to 240°C at $4^{\circ}\text{C}/\text{min}$, held for 7 min. FAMES were identified by comparing the retention times with the standard solution of Supelco 37 Component FAME Mix (Sigma-Aldrich, St. Louis, MO, USA).

Refractive Index

Refractive index of vegetable oils was measured at 40°C using «Abbat 200» Refractometer with a precision of $\pm 0.000\text{nD}$ at a wavelength of 589 nm, according to the methods described in the ISO 6320 (4th Edn.), (2000).

Quality and Oxidation Index

Acidity was measured and expressed as the quantity (in mg) of potassium hydroxide used to neutralised free fatty acids (FFA) present in 1g of oil. We had followed the analytical methods described in NF EN ISO 660. Peroxide value (PV) was stated as milliequivalents of active oxygen per kilogram of oil ($\text{meq O}_2 \text{ kg}^{-1}$). It is determined by titrating iodine liberated from potassium iodide with sodium thio-sulphate solution, as described in NF EN ISO 3960. Hydroxyl value is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one mg of the sample. The analytical methods described in NF T60-213 were followed. UV absorbance (UV) K232 and K270 extinction coefficients were calculated from absorption at the exact λ wavelengths in nm, following the analytical methods described in NF EN ISO 3656.

Saponification Index

This parameter is defined as the weight of potassium hydroxide, in milligrams, needed to saponify one gram of oil and was evaluated following the analytical methods described in ISO 3657.

Unsaponifiable Matter

The amount of the unsaponifiable matter is calculated according to the NF EN ISO 18609.

Contain of Caroten

Analysis of carotenoids was determined at 446nm and 269nm, following EN ISO 17932 protocol.

Level of Polar Components

The content of total polar compounds in oil sample was determined based on the methods of NF EN ISO 8420.

Briefly, a glass column (35 cm in length and 2.1 cm in diameter) was used for chromatography. The oil sample (2.5 g) was loaded into the packed column and the non-polar fraction was eluted. The content of total polar compounds (%) was calculated as the mass fraction of the total polar compounds in the oil sample in percentage.

Conformity of the Labeling

Samples analyzed complied with the Cameroonian standard NC 04: 2000-20 on the labeling of prepackaged foods.

Results and Discussion

Fatty Acid Methyl Esters (FAME)

For each oil, the main analyzed saturated or unsaturated fatty acids are show in (Table 1). In this figure we find higher amount of arachidic acid in practical values (Norm value) compare to theoretical one (Sample value). Oleic, palmitic, and linoleic acids are presented in all oils as well as the polyunsaturated linoleic, that play a very important role on oil stability [8]. There are two major families of essential fatty acids. The first one, omega 6 polyunsaturated fatty acids, its precursor and major representative is essential linoleic acid (LA). Its majority derivative is arachidonic acid, conditionally essential. The second

group is omega 3 polyunsaturated fatty acids. Its essential precursor is alpha-linolenic acid (ALA). Omega 6 has many properties like Omega 3. They are just as essential for reproduction and immune defenses, and also allow us to preserve our cardiovascular system. Clearly, a good balance between these two types of Omega is clearly necessary

for our body. In Cameroon, palm kernel oil is sometimes used in cooking because its lower cost than other oils and remains stable at high cooking temperatures. This oil can also be stored longer than other vegetable oils [9]. This choice of palm kernel oil is live-saving for the preservation of health (Table 2).

Table 1: Oils Composition of Fatty Acid Methyl Esther (FAME).

Fame Oils	Octanoate		Laurate		Myristate		Palmitate		Stearate		Oleate		Linoleate		Arachidate	
	Percentage (%)															
	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S
Palm	0	0	0.2	1.6	1	1.38	40-42	41.21	3-5	4.83	40-43	40.44	8-10	8.49	0.4	0
Palm Kernel	0	0.99	40-50	1.27	16-20	1.39	6-8	40.74	0	3.59	5-8	35.08	1-3	7.89	0	0
Coconut		3.82	41.21	46.47	23.9	17.24	16.5	7.47	3.14	3.52	9.47	5.37	1.61	3.94		0
Black cumin	0	0	0	3.75	0	1.13	10-15	20.9	3-4	16.87	18-29	9.78	50-60	6.09	0	3.14
Shea butter	0	0	0	0	0	0	2-9	1.59	20-50	36.07	40-60	50.45	<1	0.52	<1	0.75
Peanut	0	0	0	0	0	0	8-10	10.60	2-4	2.08	43-55	45.04	30-32	29.24	1-2	1.05

Note: N: Norm value and S: Sample value.

Table 2: Chemical and physical characteristics of vegetable oils.

Oils	AV		IV		RI		PV		SV		Unsaponifiable Matter	
	N	S	N	S	N	S	N	S	N	S	N	S
Palm	10	10.1 +/-0.01	44-58	50.7+/-0.008			2,2-10.3	9.4 +/-0.002	195-205	204 +/-0.2	0.5-1,2%	0.5% +/-0.007
Palm Kernel	0.3-0.6	0.5 +/-0.01	16-19	18.4+/-0.001	1.449-1.452	1.456	15-21	17.3 +/-0.015	242-254	253 +/-0.7	0.2-0,8%	0.3% +/-0.011
Coconut	0,6	0.54 +/-0.01	10-Jul	8.7+/-0.001	1.448-1.450	1.455	11-Jul	8.9 +/- 0.004	250-262	259 +/- 0.5	0.15-0,60%	0.2% +/- 0.009
Black Cumin	24	24.1 +/-0.02	126	127+/-0.060	1.470-1.480	1.474	≤ 15	15.1 +/- 0.008	195	195 +/-0.7	0.5-2%	0.8% +/- 0.043
Shea Butter	2	2.0 +/-0.02	64-72	69+/-0.024			14-Dec	13.9 +/- 0.005	160-195	189 +/- 0.5	2-15%	14.5% +/- 0.308
Peanut	0.08-0.6	0.2 +/-0.01	84-102	92+/-0.034	1.468-1.472	1.468	≤ 5	4.2 +/- 0.003	188-195	195 +/- 0.4	0.6-1%	0.8% +/- 0.028

Note: N: Norm value and S: Sample value.

Iodine Value (IV)

The IV is the mass of iodine in grams that is consumed by 100g of oil. The IV provides an overall status of unsaturation of the oils. Iodine value increases with increasing of unsaturation of oil. Our values are in accordance with those suggested by ISO 3961 norm. This accordance could be related to absence of degradation or oxidation of oil or fat.

Acidity Value (AV)

The acid index is expressed as the amount of potassium hydroxide (KOH), in mg, needed to neutralize 1 g of oil or fat. It's a measure of the free fatty acids (FFA) present in the fat or oil. An increment in the amount of FFA in a sample of oil or fat indicates hydrolysis of triglycerides. Such reaction occurs by the action of lipase enzyme and it is an indicator of inadequate processing and storage conditions (i.e., high temperature and relative humidity, tissue damage). As far as our results are concerned, they are in agreement with NF EN ISO 660 norm.

Refractive Index (RI)

Most processors to measure the change in unsaturation as the fat use refractive index or oil is hydrogenated. The refractive index of oils depends on their molecular weight, fatty acid chain length, degree of unsaturation, and degree of conjugation [10]. Both IV and RI indexes are important characteristics, which determine the degree of saturation or unsaturation of fats and oils. It appears that our results of RI are in accordance with those suggested by ISO 6320 4th edition (2000) norm.

Peroxide Value (PV)

The PV of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. This parameter expresses the oxidation in its early stages. Values were in agreement with NF EN ISO 3960 norm. So, the oils tested were not engage in their early stages of oxidation. Also, we found no evidence of rancidity.

Saponification Value (SV)

SV indicates how much potassium hydroxide is needed to saponify 1g oil or fat. It's an indicator of the average molecular weight and hence chain length. The greater the number of saponification, the more short- and medium-chain fatty acids the fat or contains. Values found in this study are in accordance with those suggested by ISO 3657 norm. This could suggest that oils or fat tested have not been submitted to degradation.

UV Absorbance (UV)

Black seed oil and shea butter were highly concentrated. Even in high level of dilution they showed absorbance that exceeded 0.8. The specific extinction at 232 and 270 nm of the five left samples (palm oil, palm kernel oil, coconut oil and peanut oil) are shown in Figure 1.

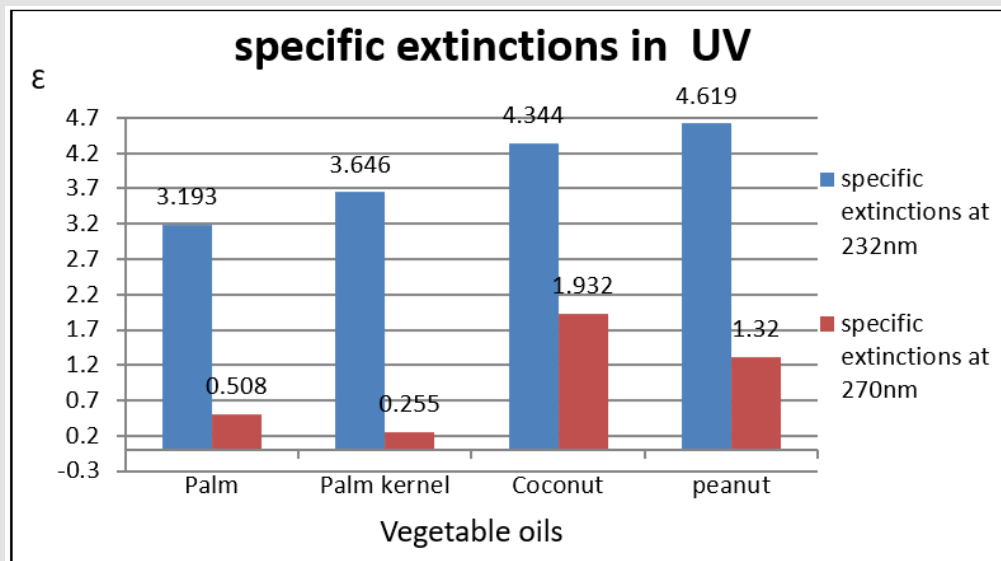


Figure 1: Specific extinction of oils samples at 232 and 270nm.

Unsaponifiable Matter

Unsaponifiable matter (USM) is known to contain hydrocarbons, terpene alcohols, sterols, tocopherols and other phenolic compounds, which may act as oxidation inhibitors. Vegetable oils typically contain

0.5-2.5 percent of USM while some others have higher amounts. The obtained values are in accordance with those suggested by the NF EN ISO 18609 norm. Obtained data are also in agreement with those of L. PULP and al. [11] (Figure 2).

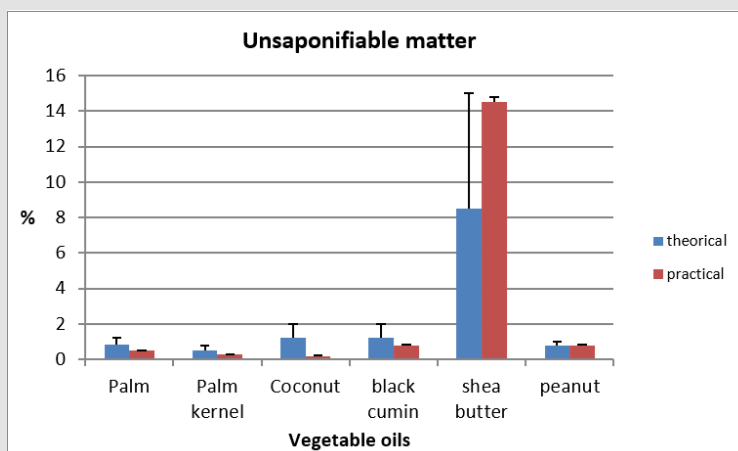


Figure 2: Unsaponifiable matters content of studied oils.

Carotene Content

The carotene content of different vegetable oils (palm, palm kernel, coconut and peanut) is shown in Figure 3. Palm kernel shown the lowest value. Analysis of carotenoids was determined at 446nm and 269nm, following EN ISO 17932 protocol. Carotene is present in our six vegetable oils. Beta carotene is the most available and therefore important source of pro-vitamin A in the diet of most people living in

developing countries, providing about 66% of vitamin A in their diets. The carotenoids (e.g. beta-carotene and lycopene) are micronutrient antioxidants that have integral role in regulating vital metabolic reactions in the body [12]. Carotenoids play an important potential role by acting as biological antioxidants protecting cells and tissues from the damaging effects of free radicals. The later could cause many diseases such as cancer [13]. Carotenoids also enhance immune function by a variety of mechanisms and improve cardiovascular health [14].

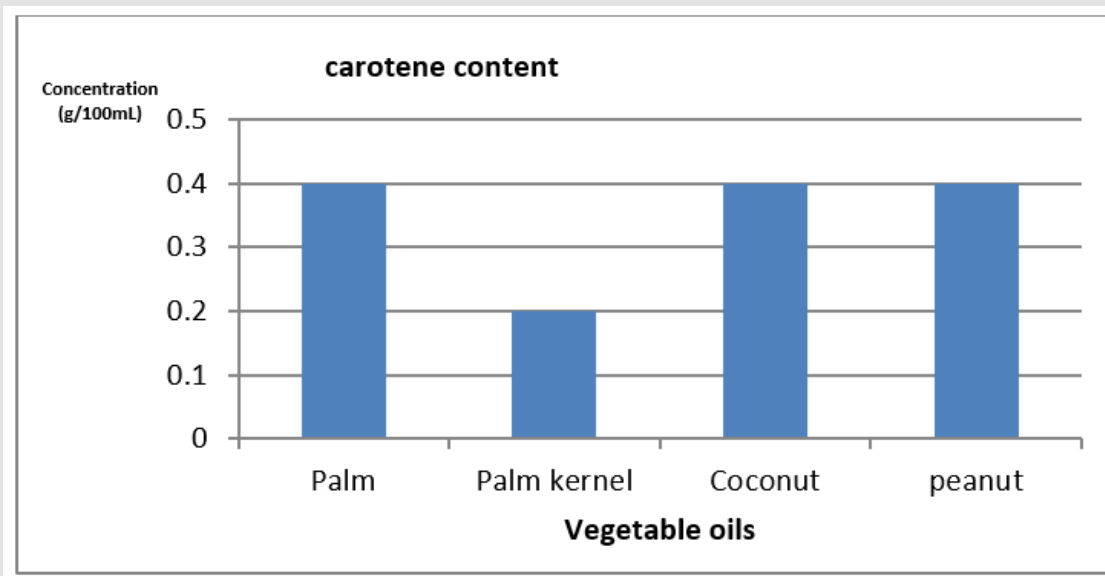


Figure 3: Caroten content of studied oils.

Level of Polar Components

Since oils polar components are the result of oil degradation, all oils exceeding 25% of polar compound are unfit for consumption.

In fact, they are potentially carcinogenic. In Figure 4, black seed oil should not be used as food oil. It is worthy to notice that it was manufactured more than three year ago.

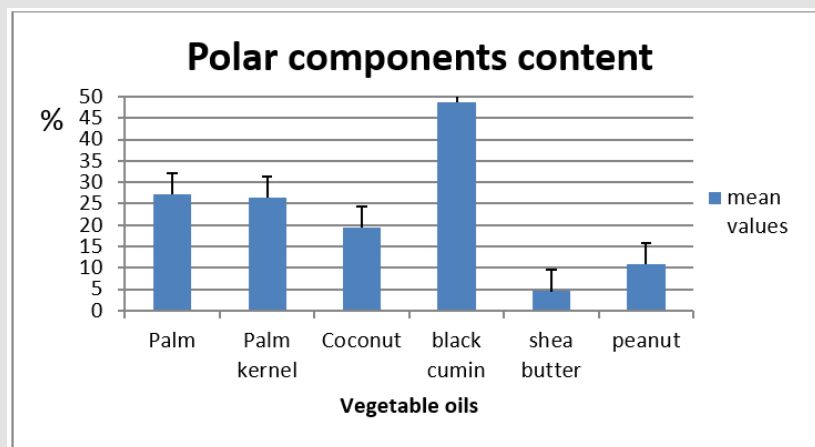


Figure 4: Polar components content of oils.

Conformity of Labelling

Labelling must not cause confusion in the mind of the purchaser or the consumer. In particular, specify NC 04/ 2000-20 norm (Camerounian standard) no confusion on the characteristics of the food and

in particular on the nature, identity, composition, quantity, durability, origin or provenance, method of manufacture or manufacture (Figure 5). As shown in figure 5 efforts must be done on: storage, conservation, how to use, dating, list of ingredients and batch number.

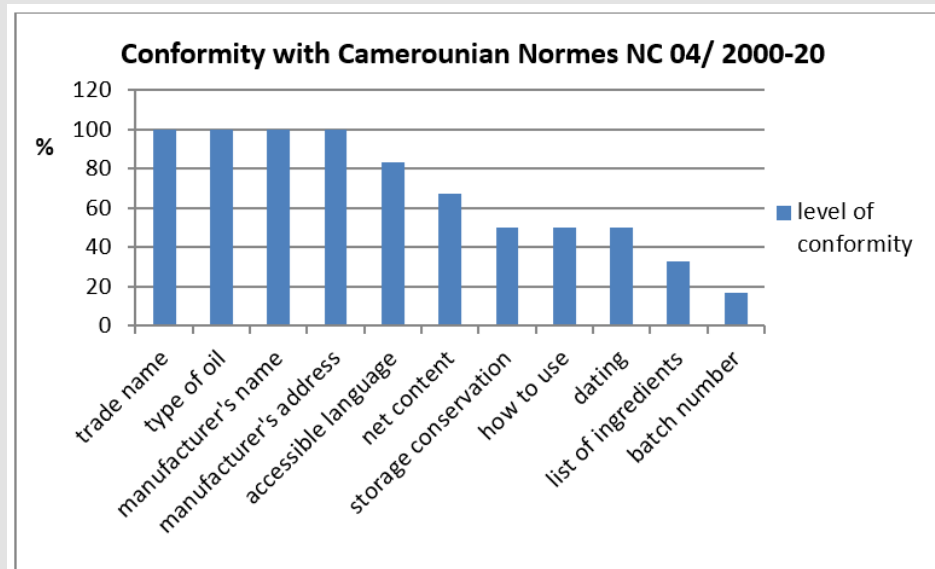


Figure 5: Samples analyzed in regard to Cameroon standard NC 04: 2000-20 on the labeling of prepackaged foods.

Conclusion

In one side, vegetable oils represent a major component of the food system, an important source of energy and an important economic commodity for producers. On the other side, the public is increasingly concerned with the health benefits and nutritional properties of vegetable oils. This study carryout the chemical analysis and health-promoting benefits of the six collected oils. Those oils are rich in components with an important potential role by acting as biological antioxidants (carotene, unsaponifiable matter, polyunsaturated linoleic), source of vitamin A (carotene), essential for reproduction, immune defenses, protection of cardiovascular system (the polyunsaturated linoleic). Also, absence of degradation or oxidation is suggested by the values of iodine, acidity, peroxide, saponification and polar components whose are in accordance with the Cameroonian and Codex Alimentarius standard. Results showed that vegetable oils sampled in the Cameroonian market exhibited levels of oxidation and degradation in accordance with the standards. Those oils may not expose consumers to lipid oxidation products generating pathological oxidative stress and inflammation. However, efforts in application of existing standard need to be done as far as labeling is concerned on three main points: ingredients list, batch number must be present and dating.

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