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Full Length Research Paper

Analysis of different Namibian traditional oils against commercial sunflower and olive oils

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The current situation in many developing countries is that, vegetable oils are replacing animal fats because of health concerns and cost. The objective of the study was to compare the iodine value, acid value, ester value, peroxide value, saponification number and cholesterol content of some locally produced vegetable oils like refined marula cooking oil, marula traditional cooking oil, marula cosmetic oil, melon oil, ximenia oil viz. olive oil and commercial sunflower oil. The physicochemical analysis helps to justify the usage of these different traditional oils. The analysis showed that marula cooking oil is close to olive oil in the unsaturation level and better than olive oil in ester value, peroxide value and has lower cholesterol content.

Key words: Marula cooking oil, marula traditional oil, marula cosmetic oil, melon oil, olive oil, ximenia oil and sunflower oil.

INTRODUCTION

Food and nutrition problems are particularly severe in developing countries, many of which are located in tropical regions (Mercy et al., 2005). One of the ways of achieving food security is through the exploitation of available local resources, in order to satisfy the needs of the increasing population (Mercy et al., 2005). Lipids are one of the major constituents of foods, and are important in our diet for a number of reasons. They are a major source of energy and provide essential lipid nutrients. Nevertheless, over-consumption of certain lipid components can be detrimental to our health, for example cholesterol (not more than 200 mg/100 mL serum) and saturated fats. Vegetable oils in particular are natural lipids of plant origin consisting of ester mixtures derived from glycerol with chains of fatty acid contain about 14 to 20 carbon atoms with different degrees of unsaturation (Emmanuel and Mudiakeoghene, 2008). Vegetable oil is used as antidote to prevent some oxidative stress related diseases and a complication is advocated for different purposes (Oguntibeju et al., 2010). Vegetable oils play important functional and sensory roles in food products, and they act as carriers of fat-soluble vitamins (A, D, E and K). They also provide essential linoleic and linolenic acids, responsible for growth (Fasina et al., 2006). One

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Abbreviations: TAG, Triacylglycerol; **FA,** fatty acid; **AV,** acid value; **EV,** ester value; **SV,** saponification value.

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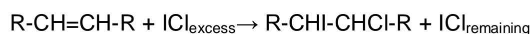
important parameter of different vegetable oils is the amount of unsaturation of the constituent fatty acids (Nikolaos and Theophanis, 2000). It is widely known that the physical and chemical properties of oils are a strong function of the triacylglycerol (TAG) and fatty acid (FA) composition (Abdulkarim et al., 2010).

MATERIALS AND METHODS

Refined marula cooking oil, marula cosmetic oil and melon oil were supplied by Edufano Women's Cooperative oil factory, Ondangwa for the study, marula traditional cooking oil, ximenia oil were bought from an open market in Oshakati town, olive oil and sunflower oil were bought from a supermarket. Experiments in this study were done in triplicate.

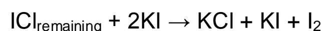
Iodine value

The iodine value is expressed in grams of iodine for the amount of halogens linked with 100 g test sample, and is used as degree of unsaturated bonds of fats and oils. The higher the iodine value, the greater the degree of unsaturation. One of the most commonly used methods for determining the iodine value of lipids is "Wijs method". The lipid to be analyzed is weighed and dissolved in a suitable organic solvent, to which a known excess of iodine chloride is added. Some of the ICl reacts with the double bonds in the unsaturated lipids, while the rest remains:

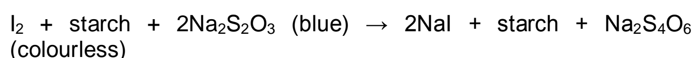


$$R\text{-}CH{=}CH\text{-}R + ICl_{excess} \rightarrow R\text{-}CHI\text{-}CHCl\text{-}R + ICl_{remaining}$$

The amount of ICl that has reacted is determined by measuring the amount of ICl remaining after the reaction has gone to completion ($ICl_{reacted} = ICl_{excess} - ICl_{remaining}$). The amount of ICl remaining is determined by adding excess potassium iodide to the solution to liberate iodine, and then titrating with a sodium thiosulfate ($Na_2S_2O_3$) solution in the presence of starch to determine the concentration of iodine released:



$$ICl_{remaining} + 2KI \rightarrow KCl + KI + I_2$$



$$I_2 + \text{starch} + 2Na_2S_2O_3 \text{ (blue)} \rightarrow 2NaI + \text{starch} + Na_2S_4O_6 \text{ (colourless)}$$

The concentration of C=C in the original sample can therefore be calculated by measuring the amount of sodium thiosulfate needed to complete the titration (Determination of the iodine number of lipids, 2010). The iodine value was determined by taking 0.2 g of the sample and placing it in a 300 ml conical flask. To dissolve the sample, 10.0 ml of ethanol was added to the sample and placed in an ultrasonic bath. After dissolution, 25.0 ml Hanus solution (0.2 N ICl) added, sealed and shaken for 1 min. The solution was kept sealed and left in a dark room at about 20°C for 30 min. Ten millilitres of 15% KI and 100 ml water were added, solution sealed and shaken for 30 s. The mixture was titrated with 0.1 N $Na_2S_2O_3$ until the solution turned yellow. Five millilitre of 1% starch solution was added, solution turned blue-black colour and again titrated with 0.1 N $Na_2S_2O_3$ until the solution turned clear. The same method was performed on a blank, for the control. Calculation:

Volume of Sodium thiosulphate used = [Blank- Test] ml

$$\text{Iodine No. of fat} = \frac{\text{Equivalent Wt. of Iodine} \times \text{Volume of } Na_2S_2O_3 \text{ used} \times \text{Normality of } Na_2S_2O_3 \times 100 \times 10^{-3}}{\text{Weight of fat sample used for analysis(g)}}$$

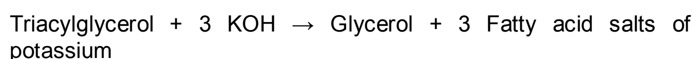
Equivalent weight of Iodine = 127, Normality of sodium thiosulphate ($Na_2S_2O_3$) = 0.1

$$\text{Iodine value} = \frac{(B - S) \times 12.7 \times 100}{\text{Sample weight (g)} \times 1000}$$

Where, B = Blank titration, ml; S = Sample titration, ml

Saponification number

Saponification value (SV) is expressed by potassium hydroxide in mg required to saponify one (1) gram of fat. The *saponification number* is a measure of the average molecular weight of the triacylglycerols in a sample. Saponification value is inversely related to mean molecular mass. Saponification is the process of breaking down a neutral fat into glycerol and fatty acids by treatment with alkali:



Triacylglycerol + 3 KOH → Glycerol + 3 Fatty acid salts of potassium

The lipid is first extracted and then dissolved in an ethanol solution which contains a known excess of KOH. This solution is then heated so that the reaction goes to completion. The unreacted KOH is then determined by adding an indicator and titrating the sample with HCl. The saponification number is then calculated from the knowledge of the weight of sample and the amount of KOH that reacted. The smaller the saponification numbers the larger the average molecular weight of the triacylglycerols presents (Analytical methods to measure the constants of fats and oils, 2011). The saponification value was obtained by placing 2.0 g sample in a 200 ml round bottom flask, and 25.0 ml of 0.5 M ethanolic KOH was added. The mixture was refluxed for at 65°C for 1 h. The flask was occasionally shaken while the heat was adjusted to prevent backflow of the ethanol. After heating at 65°C for 1 h, the mixture was cooled immediately and titrated with 0.5 N HCl before the test liquid solidified. A blank test was performed in triplicate to obtain the mean titre. Calculation:

$$\text{Saponification value} = \frac{(B - S) \times N \times 56.1}{\text{Sample weight (g)}}$$

Where, B = Blank titration, ml; S = Sample titration, ml; N= Normality of HCl

Acid value (AV)

The "acidity" in oil is the result of the degree of breakdown of the triacylglycerols, due to a chemical reaction called hydrolysis or lipolysis, in which free fatty acids are formed. The free fatty acidity is thus a direct measure of the quality of the oil, and reflects the care taken right from blossoming and fruit setting to the eventual sale and consumption of the oil. The acid value (AV) is defined as the mg of KOH necessary to neutralize the fatty acids present in 1 g of lipid. The acid value of oil must not be too high, as this denotes an excessively high content of free fatty acids, which causes the oil to turn sour. The lipids are extracted from the food sample and then dissolved in an ethanol solution containing an indicator. This solution is then titrated with alkali (KOH) until a pinkish colour appears. The rapid screening of acid value of fats and oils should be applied to control the quality of cooking oils. AV is considered a measure of hydrolytic rancidity. In general, it gives an indication about edibility of the lipid (Analytical methods to measure the constants of fats and oils, 2011). Five grams of fat sample were

placed in a conical flask to which 25 ml absolute ethanol was added and 3 drops of phenolphthalein. The mixture was heated in a warm bath (65°C) and occasionally shaken for 10 min after which it was cooled and titrated with 0.1 N KOH until a faint pink colour appeared. The test was done in triplicate for each sample. Calculation:

$$\text{Acid value (mg KOH/g fat)} = \frac{\text{ml KOH used for titration} \times \text{N} \times 56.1}{\text{Sample mass (g)}}$$

Where, N = Normality of KOH, % Free Fatty Acids = AV × 0.503

Ester value

Ester value (EV) is defined as the milligrams of KOH required to react with glycerine after saponification of 1 g of lipid. It is calculated from the saponification value (SV) and acid value (AV) (Analytical methods to measure the constants of fats and oils, 2011). Calculation:

EV = SV –AV

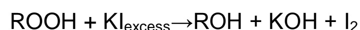
% glycerine = EV × 0.054664

Peroxide value

Peroxides (R-OOH) are primary reaction products formed in the initial stages of oxidation, and therefore give an indication of the progress of lipid oxidation. Lipid oxidation is an extremely complex process involving numerous reactions that give rise to a variety of chemical and physical changes in lipids:

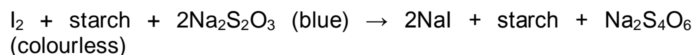
Reactants → primary products → secondary products (unsaturated lipids and O_2) → (peroxides and conjugated dienes) → (ketones, aldehydes, alcohols, hydrocarbons)

One of the most commonly used methods to determine peroxide value utilizes the ability of peroxides to liberate iodine from potassium iodide. The lipid is dissolved in a suitable organic solvent and an excess of KI is added:



$ROOH + KI_{excess} \rightarrow ROH + KOH + I_2$

Once the reaction has gone to completion, the amount of ROOH that has reacted can be determined by measuring the amount of iodine formed. This is done by titration with sodium thiosulfate and a starch indicator:



$I_2 + starch + 2Na_2S_2O_3$ (blue) → $2NaI + starch + Na_2S_4O_6$ (colourless)

The amount of sodium thiosulfate required to titrate the reaction is related to the concentration of peroxides in the original sample (Determination of peroxide value, 2011). To obtain the peroxide value, 1 g of the sample was weighed and transferred to a 300 mL flask. To this 1 g of KI and 20 ml of solvent mixture (2 volumes of glacial acetic acid and 1 volume chloroform) was added and placed in a boiling water bath for 30 s. To this mixture 20 mL of 5% KI, 50 ml distilled water and 0.5 ml 1% starch solution was added. This mixture was titrated with N/500 $Na_2S_2O_3$ until solution became clear. A blank test was performed to serve as the control.

Cholesterol content

Cholesterol is a waxy steroid of fat that is produced in the liver or intestines. It is used to produce hormones and cell membranes and is transported in the blood plasma of all mammals. It is an essential structural component of mammalian cell membranes and is required to establish proper membrane permeability and fluidity. In addition, cholesterol is an important component for the manufacture of bile acids, steroid hormones, and vitamin D. Cholesterol is the principal sterol synthesized by animals. Although, cholesterol is important and necessary for mammals, high levels of cholesterol in the blood (higher than 200 mg/100 ml serum in humans) can damage arteries and are potentially linked to diseases such as those associated with the cardiovascular system (heart disease) (Okpuzar et al., 2009; Whitney and Rolfes, 2011).

Method 1: Acid ferric chloride reagent method

Standard cholesterol of 1 mg/ml was prepared in chloroform. The standard cholesterol was placed in test tubes which contained 0.1 ml of the test sample. To this 1 ml of chloroform was added. Three millilitres of acetic acid and 3 ml of acidic ferric chloride reagent were added. The mixture was left in the dark for 30 min and the absorbance was read at 560 nm. A blank test was also done which served as the control. Calculation:

Cholesterol (mg/ml) = AB/AS × CS

Where, AB = Absorbance of oil, AS = Absorbance of standard cholesterol, CS = Concentration of standard cholesterol.

Method 2: Liebermann-Buchard method

Standard cholesterol solution

Dissolve 10 mg of cholesterol in 10 ml chloroform, shake well.

Liebermann- Burchard reagent

Dissolve 0.5 mL of sulfuric acid in 10 ml of acetic anhydride. Cover and keep in ice bucket.

Sample preparation

One gram of sample was dissolved in 10 ml chloroform and further diluted to 10 times to give 10 000 ppm mixture. Three millilitres of diluted sample solution was placed in a test to which 2 ml of Liebermann-Burchard reagent and 2 ml chloroform was added. The tubes were covered with black carbon paper and kept in an ice-bucket in a dark place for 15 min. The Liebermann-Burchard reagent reacted with the sterol to produce the characteristic green colour. The absorbance was determined on a UV spectrophotometer (Helios Gamma – spectronic unicam) at 640 nm.

Working standard cholesterol solutions preparation

From the standard cholesterol solution different aliquots were pipetted (0.5, 1.0, 1.5, 2.0, 2.5 ml) into five test tubes and tube 6 was kept blank. The tubes were marked S_1, S_2, S_3, S_4, S_5 and S_6, respectively. Two millilitres Liebermann-Burchard reagent was added to all six tubes and the final volume was made up to 5 mL by adding chloroform. The tubes were covered with black carbon paper and kept in an ice-bucket in a dark place for 15 min. The Liebermann-Burchard reagent reacted with the sterol to produce the characteristic green colour. The base line was taken on the spectrophotometer with the blank (S_6) at 640 nm. The absorbance

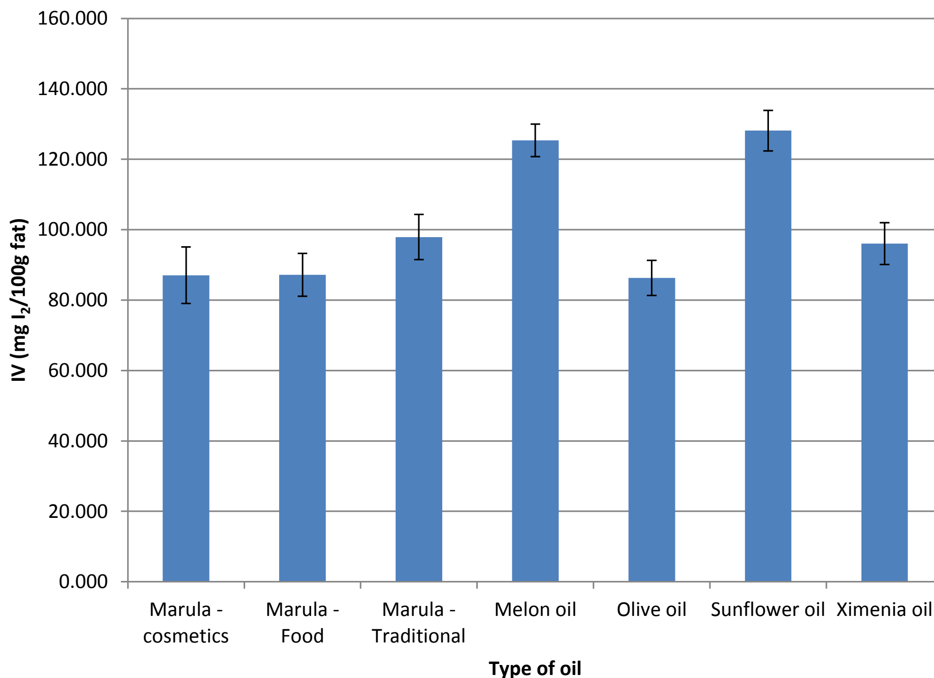


Figure 1. Iodine value of different local oils against commercial sunflower and olive oils.

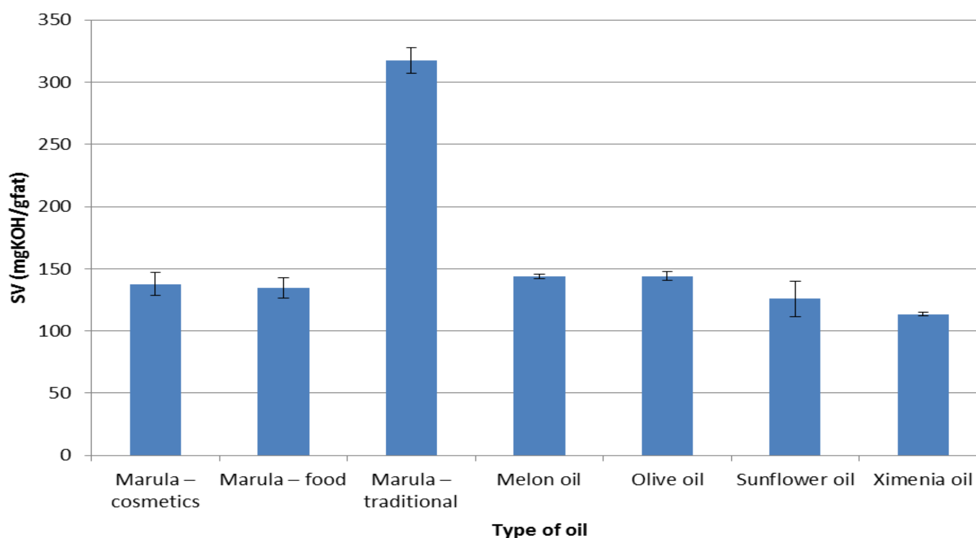


Figure 2. Saponification value of different local oils against commercial sunflower and olive oils.

of all the six tubes was determined on a UV spectrophotometer (Helios Gamma – spectronic unicam) at 640 nm and a standard graph was plotted. The absorbance of all standards (six tubes) was determined on spectrophotometer and standard graph was plotted.

RESULTS

Iodine value

In Figure 1, the highest iodine value (degree of unsaturation) was that of the sunflower oil (128.122 mg I_2/100 g oil), followed by melon oil (125.37 mg I_2/100 g oil), olive oil (86.3 mg I_2/100 g oil) and marula cooking oil was (87.2 mg I_2/100 g oil).

Saponification value

As shown in Figure 2, the highest saponification value (lowest molecular mass) was that of the marula traditional oil (317.2 mg KOH/ g oil) followed by olive oil (144 mg KOH/ g oil), marula cooking oil (134.4 mg KOH/ g oil),

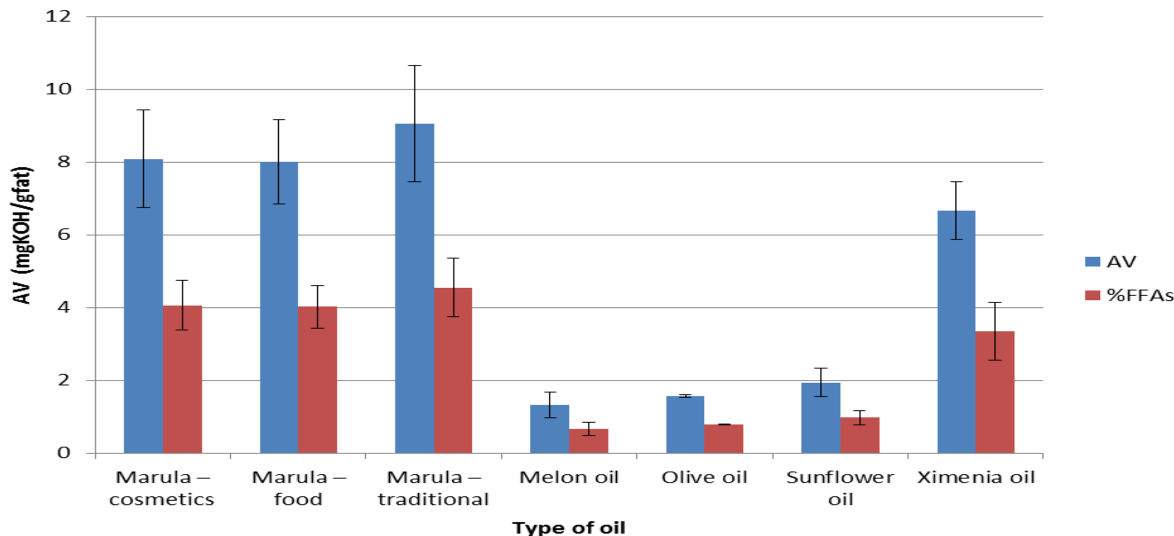


Figure 3. Acid value and free fatty acids of different local oils against commercial sunflower and olive oils.

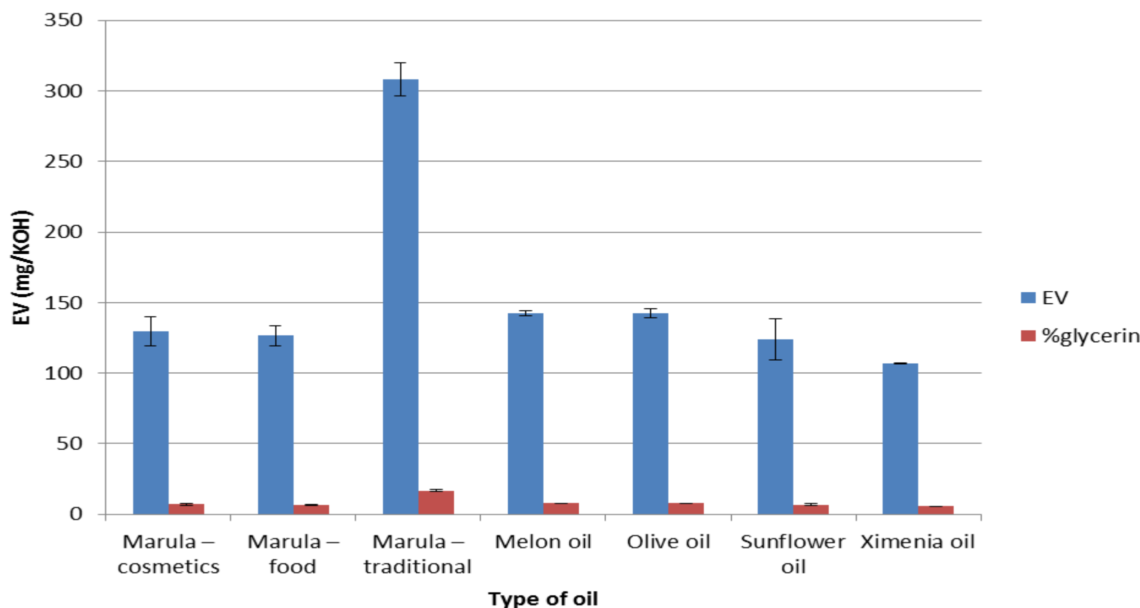


Figure 4. Ester value of different local oils against commercial sunflower and olive oils.

sunflower oil (126 mg KOH/g oil) and the lowest is the ximenia oil (113.6 mg KOH/ g oil).

Acid value and %free fatty acids

In Figure 3, the highest acid value (and free fatty acids, respectively) is marula traditional oil (9.05 mg KOH/ g of lipid), followed by marula cosmetics oil (8.08 mg KOH/ g of lipid), marula cooking oil (7.997 mg KOH/ g of lipid), sunflower oil (1.941 mg KOH/ g of lipid), olive oil (1.571 mg KOH/ g of lipid). The lowest acid values were that of melon oil (1.318 mg KOH/ g of lipid).

Ester value

In Figure 4, the highest ester value was marula traditional oil (308.16 mg KOH/ g of lipid), followed by olive oil (142.5 mg KOH/ g of lipid), melon oil (142.4 mg KOH/ g of lipid), marula cooking oil (126.44 mg KOH/ g of lipid), melon oil (142.4 mg KOH/ g of lipid), sunflower oil (124

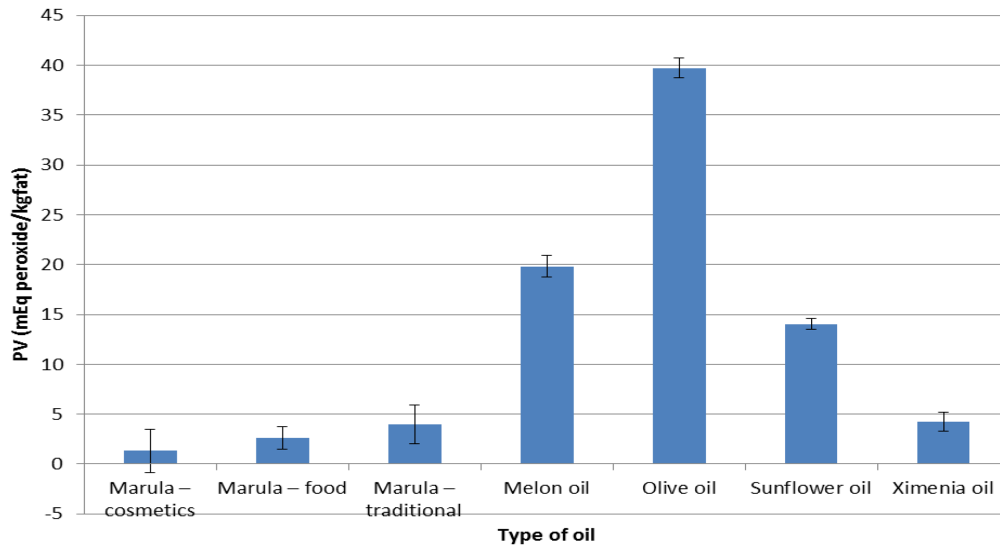


Figure 5. Peroxide value of different local oils against commercial sunflower and olive oils.

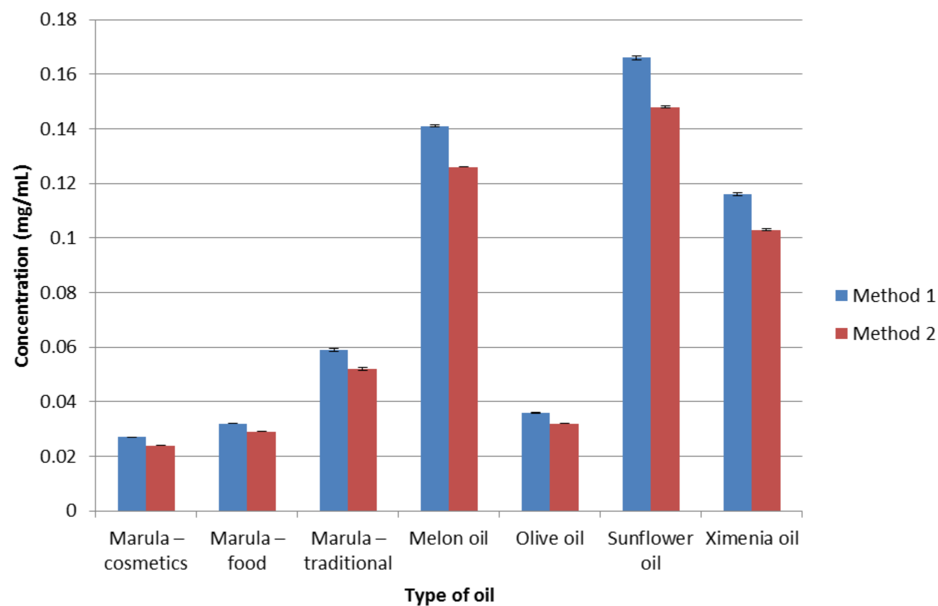


Figure 6. Cholesterol content of different local oils against commercial sunflower and olive oils.

mg KOH/ g of lipid) and the lowest was ximenia oil (106.93 mg KOH/ g of lipid).

Peroxide value

In Figure 5, the highest peroxide value was that of olive oil (39.7 mEq peroxide/Kg fat), followed by melon oil (19.8 mEq peroxide/Kg fat), sunflower oil (14.038 mEq peroxide/Kg fat), ximenia oil (4.287 mEq peroxide/Kg fat), marula cooking oil (2.657 mEq peroxide/Kg fat) and the lowest was marula cosmetics oil (1.329 mEq peroxide/Kg fat).

Cholesterol

As shown in Figure 6, the highest cholesterol content was in sunflower oil (0.166 mg/ml oil), followed by melon oil (0.141 mg/ml oil), ximenia oil (0.116 mg/ml oil), olive oil (0.036 mg/ml oil), marula cooking oil (0.032 mg/ml oil) and lowest was marula cosmetics oil (0.027 mg/ml oil).

DISCUSSION

The degree of unsaturation is measured by the iodine value. According to Whitney and Rolfes, saturated fat is considered the most detrimental to health, because it raises LDL cholesterol which leads to heart disease. The highest iodine value was that of sunflower oil (128.122 mg I_2/100 g oil), followed by melon oil (125.37 mg I_2/100 g oil), traditional marula oil (99 mg I_2/100 g oil), Ximenia oil (96 mg I_2/100 g oil), marula cooking oil was (87.2 mg I_2/100 g oil) and olive oil was the lowest (86.3 mg I_2/100 g oil). The best unsaturated traditional oil was melon oil followed by marula traditional oil and ximenia oil. The highest saponification value (lowest molecular mass) was that of the marula traditional oil (317.2 mg KOH/g oil) followed by olive oil (144 mg KOH/g oil), marula cooking oil (134.4 mg KOH/g oil), sunflower oil (126 mg KOH/g oil) and the lowest is the ximenia oil (113.6 mg KOH/g oil). The average molecular weight of the triacylglycerols in marula traditional oil is lowest and ximenia oil is the highest. The acid value must not be too high; because it is a result of the breakdown of triacylglycerols. High acid value causes the oil to turn sour. The highest acid value (and free fatty acids, respectively) is marula traditional oil (9.05 mg KOH/g of lipid), followed by marula cosmetics oil (8.08 mg KOH/g of lipid), marula cooking oil (7.997 mg KOH/g of lipid), sunflower oil (1.941 mg KOH/ g of lipid), olive oil (1.571 mg KOH/g of lipid). The lowest acid values were that of melon oil (1.318 mg KOH/g of lipid). It should be noted that the marula oils were kept in the laboratory for sometime before the analysis, which may have led to increasing the acid value. The highest ester value was marula traditional oil (308.16 mg KOH/ g of lipid), followed by olive oil (142.5 mg KOH/ g of lipid), melon oil (142.4 mg KOH/g of lipid), marula cooking oil (126.44 mg KOH/ g of lipid), sunflower oil (124 mg KOH/ g of lipid) and the lowest was ximenia oil (106.93 mg KOH/ g of lipid). The ester value of ximenia oil is the lowest among traditional oils followed by marula cooking oil and melon oil.

Foods which contain high concentrations of unsaturated lipids are particularly susceptible to lipid oxidation. Lipid oxidation is one of the major forms of spoilage in foods, because it leads to the formation of off-flavours and toxic compounds and is measured by the peroxide value (Analytical methods to measure the constants of fats and oils, 2011). The highest peroxide value was that of olive oil (39.7 mEq peroxide/kg fat), followed by melon oil (19.8 mEq peroxide/kg fat), sunflower oil (14.038 mEq peroxide/kg fat), ximenia oil (4.287 mEq peroxide/kg fat), marula traditional oil (3.8 mEq peroxide/kg fat), marula cooking oil (2.657 mEq peroxide/kg fat) and the lowest was marula cosmetics oil (1.329 mEq peroxide/kg fat). The peroxide value of marula cosmetics oil is the lowest followed by marula cooking oil and then ximenia oil. High levels of cholesterol in blood (more than 200 mg/100 ml serum) can damage arteries and are potentially linked to diseases such as those associated with the cardiovascular system (heart diseases). Highest cholesterol content was in sunflower oil (0.166 mg/ml oil), followed by melon oil (0.141 mg/ml oil), ximenia oil (0.116 mg/ml oil), marula traditional oil (0.057 mg/ml oil), olive oil (0.036 mg/ml oil), marula cooking oil (0.032 mg/ml oil) and lowest was marula cosmetics oil (0.027 mg/ml oil). The cholesterol level of marula cosmetics oil has the lowest cholesterol content followed by marula cooking oil and then marula traditional oil.

Conclusion

When looking at the results of different tests above, it is found that melon oil has the highest iodine value (highest unsaturation value), marula traditional oil has the lowest molar mass of the triacylglycerols, melon oil has the lowest acid value, ximenia oil has the lowest ester value, marula cosmetics has the lowest peroxide value and the lowest cholesterol content. It is very hard to say which is the overall best oil, however, marula (refined) cooking oil has low cholesterol content, relatively low acid value, ester value, peroxide value and reasonable saturation. It is close to olive oil in unsaturation level and better than olive oil in ester value, peroxide value and cholesterol level. The physicochemical data obtained, confirm that the traditional oils (edible and inedible) have characteristics that are comparable to their commercial counterparts. This indicates that these traditional oils can be used for cooking purposes. However, further studies to evaluate their toxicity should be conducted next.

Conflict of interests

The author(s) did not declare any conflict of interest.

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