**Enhanced Antioxidation Properties Of Some Local Spices (*afromomum melegueta,* *pipper guineense*, *allium sativum* and *monodora myristica*) On Characteristics Of Palm Oil Consumed In Nigeria.**

Osu Charles I.1\* and E.C. Ogoko2

1Department Of Pure And Industrial Chemistry, University Of Port Harcourt,

PMB 5323, Port Harcourt, Rivers State. Nigeria.

2Department Of Chemistry, National Open University Of Nigeria, 14 – 16 Ahmadu Bello Way. P.M.B. 80067, Victoria Island, Lagos, Nigeria.

\*Corresponding Author: Phone: +2348037783246; E-mail: charsike@yahoo.com; Charles.osu@uniport.edu.ng

**Abstract:** This study revealed the effect antioxidants in the local food additives (*afromomum melegueta,* *pipper guineense*, *allium sativum* and *monodora myristica* ) on the characteristics of palm oil consumed in Nigeria. Also, the effect of contact time of the extracts from the local spices with the palm oil was investigated. The acid value was found to be significantly lower in the four samples treated with the extracts. The acid values ranged from 2.635 to 3.317 mg KOH/g. Free fatty acid (FFA) of oil before and after addition of extracts from the spices used revealed that FFA was found to be significantly higher in oil before addition of the extracts. Sample with *allium sativum* extract had the lowest free fatty acid (1.334 % oleic acid). The values for the effect of contact time ranged from 163.28 to 207.57 mgKOH/g, SV and 13.81 to 14.25 g/100g, IV for sample treated with *afromomum melegueta* extract; 194.83 to 159.09 mgKOH/g, SV and 12.877 to 14.205 g/100g, IV for oil treated with *pipper guineense* extract; 209.68 to 166.38 mgKOH/g, SV and 13.063 to 13.866 g/100g, IV for oil treated with *allium sativum* extract; 192.07 to 160.29 mgKOH/g, SV and 12.88 to 14.386 g/100g g/100g, IV for oil treated *monodora myristica* extract. The values of PV, FFA and AV increase as contact time increases from 0 to 28 days. The values ranged from 4.90 to 9.80 **meg/kg,** PV; 1.556 to 2.88 % oleic acid, FFA and 3.096 to 5.73 mg KOH/g, AV for oil treated with *afromomum melegueta* extract; 4.98 to 9.95 **meg/kg**, PV; 1.417 to 3.54 % oleic acid, FFA and 2.820 to 7.44 mg KOH/g, AV for oil treated with *pipper guineense* extract; 4.95 to 9.90 **meg/kg,** PV; 1.334 to 3.19 % oleic acid, FFA and 2.655 to 6.35 mg KOH/g, AV for oil sample treated with *allium sativum* extract (table 4); 4.90 to 9.82 **meg/kg**, PV; 1.528 to 3.65 % oleic acid, FFA and 3.041 to 7.28 mg KOH/g, AV for oil treated with *momodora myristica* extract. The increase in contact time on addition of the extracts from the different local spices with the palm oil did not retard the development of rancidity.

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**Keywords:** Antioxidation, local spices, palm oil, contact time.

**1. Introduction**

Palm oil (*Eleasis guinneesis*) is an edible vegetable oil obtained from the mesocarp of the oil palm fruits (Oyem, 2011; [Njoku *et al*., 2010](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#676280_ja)). It contains the highest concentration of agriculturally derived carotenoids of the vegetable oils that are widely consumed ([Ahmad *et al*., 2010](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#604526_ja)). Palm oil is a mixture of different [**fatty acid**](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=fatty+acid)**s**\_saturated, unsaturated and polyunsaturated [**fatty acid**](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=fatty+acid)**s**, depending on the presence and number of double bond(s) or indeed the absence of it. However it contains by higher proportion more of the saturated[**fatty acid**](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=fatty+acid)**s** ([Aremu](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10" \l "42360_ja) *[et al](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10" \l "42360_ja)*[., 2006](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10" \l "42360_ja); [Microsoft Student Encarta DVD, 2008](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#59691_b)).

Because of the high cost of animal fats and increased awareness of potential harm from their excessive consumption, the rise of vegetable oils is increasing Arising from the above uses and application of palm oil, it becomes necessary to undertake a study on factors that affects the quality of palm oil. Minor components of vegetable oils include antioxidants, colorants, flavors, and emulsifiers (Onyeka, et al., 2005). Edible oils from plant sources are of interest in various food and application industries.

In terms of oil quality, the free [**fatty acid**](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=fatty+acid) value of oil is an important qualitative parameter. Since fats and oils contain some level of free [**fatty acid**](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=fatty+acid), FFA, there will always be an increase in acidity with time during transport and storage ([Chong, 2000](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#20432_bc); [Syam, *et al*., 2009](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#253509_ja)). This hydrolysis reaction is acid catalyzed and the FFA inherent in palm oil subsequently autocatalyze the hydrolysis reaction ([Chong, 2000](http://scialert.net/fulltext/?doi=ajft.2011.701.704&org=10#20432_bc)).

Since ancient times, spices have been used to improve flavours as well as antioxidant (Adegoke et al. 1999, Rey et al. 2005, Ifesan et al. 2009 a) and antimicrobial properties (Davidson 1997, Ahn et al. 2007, Ifesan et al. 2009 b, Zaborowska et al. 2012) of different types of foods. The tree of *Monodora myristica* (ariwo) is most prevalent in the Southern part of Nigeria and is commonly known as Jamaican or African nutmeg (Ajibola et al., 2013).

Free radicals or oxidative injury now appears the fundamental mechanism underlying a number of human neurologic and other disorders. For instance in diabetes, increased oxidative stress which co-exists with reduction in the antioxidant status has been postulated: Oxygen free-radical can initiate peroxidation of lipids (Atawodi, 2005). Our body is constantly exposed to a variety of oxidizing agents and the body is equally inbuilt with antioxidants to cater for the free radicals generated from the oxidants thus maintaining a balance between the production of free radicals and neutralization by antioxidants. When there is in-balance between formation and neutralization of free radicals by antioxidants, it results to oxidative stress (Azeez et al., 2012; Adom et al., 2003; Liu, 2004; Aruoma 2003).

*Aframomum melegueta* (Roscoe) K. Schum, commonly referred to as Alligator pepper or Grain of paradise belongs to the Zingiberaceae family. It is a spicy edible fruit that is cultivated and occurs throughout the tropics (Owokotomo et al., 2014; Lawal et al., 2007). It is a plant with both medicinal and nutritive value found commonly in the rainforest (Doherty et al., 2010). In Nigeria, the seeds are used in conjunction with other spices in the preparation of local delicacy The chemical composition of seeds of *A. melegueta* has been well studied. A methanolic extract of the seeds was reported to contain gingerdione, paradol, shagaol as the major compounds (Escoubas, et al., 1995). The seeds essential oils have been reported to consist of humulene, β-caryophyllene and their oxides as the major constituents (Ajaiyeoba and Ekundayo, 1999, Meunt et al., 1991). The supercritical CO2 extracted essential oil of *A. melegueta* had been analysed by GC and GC/MS. Forty-three components were detected and identified with the major components asparadol, shogaol, gingerdione, α-humulen, gingerol (Fernandez et al., 2006).

*P.guineense* popularly known as Uziza is an important source of various nutrients and phytochemicals with diverse functions (Elizabeth et al., 2016). Omodamiro and Ekeleme, 2013; Etim et al., 2013 studied the antioxidant activity of *P.guineense.* The result showed that the leaves of this plant exhibited free radical scavenging effects. This could be attributed to the presence of phenolic compounds in the plant which is a major group of compounds that act as primary antioxidants or free radical scavengers. In another study, the seed extracts of *P.guineense* was found to rapidly scavenge nitric oxide in vitro at different intervals (Ngane et al., 2013).

*Monodora myristica* Gaertn. (Annonaceae) is a perennial tree growing in the tropical rainforest from Liberia to Angola. It is a wild plant among the most used as food and drug. In [developing countries](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=developing+countries) several plants give edible products: Fruits, seeds, leaves, flowers, nuts, oils, mushrooms and honey, which take a large place in the local diet and could strongly overcome or ameliorate prevailing food and health problems (Betti and Nzooh, 1998; Okwu, 2001; Tatsadjieu *et al*., 2003; Oboh, 2004; Tchiegang *et al*., 2005). The distinction between food and drug is not always clear. So, the seeds of *Monodora myristica*, in this case, possess these two properties and have carried us to pursue its study.

Earlier studies on *Monodora myristica* have reported the [chemical composition](http://www.scialert.net/asci/result.php?searchin=Keywords&cat=&ascicat=ALL&Submit=Search&keyword=chemical+composition) and the evaluation of antimicrobial activities of essential oils collected in other countries (Cimanga *et al*., 2002; Tatsadjieu *et al*., 2003; Oussou *et al*., 2004; Nguefack *et al*., 2004; Odoh, 2004; Agnaniet *et al*., 2004).

The flavonoids of *M. myristica* was able to scavenge hydroxyl radicals generated by Fenton reaction in a concentration dependent manner (Akinwunmi and Oyedapo, 2013). The results of this study are in agreement with earlier reports of Abdou et al. *(*2010), that extracts of *M. myristica* inhibited the decomposition of deoxyribose.

Flavonoid of *M. myristica* was able to inhibit the action of free radical generated as a result of the reaction of CuSO4 with H2O2 by causing a decrease in the amount of haemoglobin released (Akinwunmi and Oyedapo, 2013).

Addition of natural antioxidants and precursors of plant origin into the frying oils is the best way of enhancing oxidative and flavor stability (Kaleem et al.,2015) Therefore, this study investigate the effect of antioxidant in extracts of selected spices on the characteristics of palm oil consumed in Nigeria. And the effect of contact time of the extracts from the local spices with the palm oil was also investigated.

**2. Material and Methods**

Sample Collection and Preparation.

Pure sample of palm oil and the local spices were obtained from Obior town, Aniocha North, Delta State, Nigeria. There was no need for further purification of the oil since they were already extracted and decanted in a bottle. 10 Ml of the oil were added into five conical flasks each. 10 ml of each of the extract of the local spices were also added to each of the flask and were labeled A, B, C, D and E. Where A, B, C, D and E represents Control, *afromomum melegueta* treated oil, *Pipper Guineense* treated oil, *Allium sativum* treated oil and *monodora myristica* treated oil respectively. The samples were heated for 20 minutes in a water bath maintained at 60 oC and were filtered. The experiment was repeated after 7 days, 14 days, 28 days respectively. The filtrate was used for determination of the effect of the antioxidants on the characteristics of the oil.

**Sample analysis**.

**Determination of Peroxide and Acid Values**

Peroxide value and acid value were determined according to Official American Oil Chemist’s Society (AOCS) methods (AOCS, 1985). The values were expressed as meq of peroxide O2 / kg oil and mg KOH / g oil, respectively.

**Iodine value analyses**

The iodine value (IV), the number of grams of iodine absorbed by 100 parts by weight of the oil or fat, were determined following the method of the AOAC as described by Horwitz (2002); Othman and Ngassapa, (2010).

**Determination of Free fatty acid and Saponification value**

Free fatty acid was determined, as percent by mass oleic, palmitic or lauric acid, and saponification value, as the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from complete hydrolysis of one gram of oil or fat, was determined using the procedures adopted by Jayaraman (1985).

**3. Results**

The physiochemical parameters of the samples studied where presented in table 1 - 5.

**Table 1.** **Characteristics of Palm Oil before and after treatment with different extracts from local spices**.

|  |  |  |
| --- | --- | --- |
| **Parameters** | **TREATMENT** |  |
| **A** | **B** | **C** | **D** | **E** |
| **SV (mg/gKOH)** | **176.00** | **207.57** | **194.68** | **209.68** | **192.07** |
| **PV(meg/kg)** | **4.90** | **4.90** | **4.98** | **4.95** | **4.90** |
| **IV (** g/100g**)** | **14.183** | **14.253** | **12.877** | **13.063** | **14.386** |
| **FFA(**% oleic acid**)** | **1.667** | **1.556** | **1.417** | **1.334** | **1.528** |
| **AV (mg/g oil)** | **3.317** | **3.096** | **2.820** | **2.655** | **3.041** |

SV = saponification, AV=Acid Value, IV =Iodine Value, FFA= Free Fatty Acid, PV = Peroxide Value

**Table 2 Table 2. Effect of Time on the Characteristics of Palm Oil after treatment with *Afromomum Melegueta***

|  |  |
| --- | --- |
| **Parameters** | **TIME (DAYS)** |
| **0 DAY** | **7 DAYS** | **14 DAYS** | **28 DAYS** |
| **SV (mg/gKOH)** | **207.57** | **204.50** | **184.76** | **163.28** |
| **PV(meg/kg)** | **4.90** | **9.80** | **4.97** | **9.80** |
| **IV (** g/100g**)** | **14.253** | **14.13** | **14.21** | **13.81** |
| **FFA(**% oleic acid**)** | **1.556** | **1.71** | **2.22** | **2.88** |
| **AV (mg/g oil)** | **3.096** | **3.407** | **4.42** | **5.73** |

**Table 3. Effect of Time on the Characteristics of Palm Oil after treatment with *PIPPIER GUINEENSE***

|  |  |
| --- | --- |
| **Parameters** | **TIME (DAYS)** |
| **0 DAY** | **7 DAYS** | **14 DAYS** | **28 DAYS** |
| **SV (mg/gKOH)** | **194.83** | **188.40** | **180.87** | **159.09** |
| **PV(meg/kg)** | **4.98** | **9.95** | **4.99** | **9.80** |
| **IV (** g/100g**)** | **12.877** | **14.205** | **13.92** | **13.56** |
| **FFA(**% oleic acid**)** | **1.417** | **2.147** | **3.74** | **3.54** |
| **AV (mg/g oil)** | **2.820** | **4.274** | **7.44** | **7.05** |

**Table 4. Effect of Time on the Characteristics of Palm Oil after treatment with *ALLIUM SATIVUM***

|  |  |
| --- | --- |
| **Parameters** | **TIME (DAYS)** |
| **0 DAY** | **7 DAYS** | **14 DAYS** | **28 DAYS** |
| **SV (mg/gKOH)** | **209.68** | **191.19** | **188.87** | **166.38** |
| **PV(meg/kg)** | **4.95** | **9.90** | **5.00** | **9.85** |
| **IV (** g/100g**)** | **13.063** | **13.866** | **13.67** | **13.51** |
| **FFA(**% oleic acid**)** | **1.334** | **1.585** | **2.28** | **3.19** |
| **AV (mg/g oil)** | **2.655** | **3.154** | **4.54** | **6.35** |

**Table 5. Effect of Time on the Characteristics of Palm Oil after treatment with *MONODORA MYRISTICA***

|  |  |
| --- | --- |
| **Parameters** | **TIME (DAYS)** |
| **0 DAY** | **7 DAYS** | **14 DAYS** | **28 DAYS** |
| **SV (mg/gKOH)** | **192.07** | **182.88** | **179.43** | **160.29** |
| **PV(meg/kg)** | **4.90** | **9.82** | **4.90** | **9.80** |
| **IV (** g/100g**)** | **14.386** | **14.142** | **13.31** | **12.88** |
| **FFA(**% oleic acid**)** | **1.528** | **2.525** | **3.65** | **3.56** |
| **AV (mg/g oil)** | **3.041** | **5.025** | **7.26** | **7.08** |

**4. Discussions**

Characteristics of palm oil before and after treatment with extract from different local spices were shown in table 1. The saponification value of the untreated oil was lower than that of treated oil. The results ranged from 176.00 to 209.68 mgKOH/g. The saponification values increase as the extracts were added. The peroxide value presented in table 1 above ranged from 4.90 to 4.98 meg /kg, there is no significant difference between the untreated and treated sample. There is no increase in the peroxide values when the extracts were added. The treated oils will not be susceptible to autoxidation. This is attributed to the antioxidant present in the extracts. Detection of [peroxide](https://en.wikipedia.org/wiki/Peroxide) gives the initial evidence of rancidity in unsaturated fats and oils (Grossi et al., 2015). Other methods are available, but peroxide value is the most widely used. It gives a measure of the extent to which an oil sample has undergone primary oxidation. The peroxide concentration, usually expressed as peroxide value, is measured by oxidation or rancidity in its early stages and should be not more than 10 (milliequivalents peroxide/1000g sample) in cooking oil (O’Brien, 2009). The [double bonds](https://en.wikipedia.org/wiki/Double_bond) found in fats and oils play a role in [autoxidation](https://en.wikipedia.org/wiki/Autoxidation). Oils with a high degree of [unsaturation](https://en.wikipedia.org/wiki/Unsaturated_fat) are most susceptible to autoxidation. [Peroxides](https://en.wikipedia.org/wiki/Peroxide) are intermediates in the autoxidation reaction. Autoxidation is a [free radical reaction](https://en.wikipedia.org/wiki/Free_radical_addition) involving [oxygen](https://en.wikipedia.org/wiki/Oxygen) that leads to deterioration of fats and oils which form off-flavours and off-odours. Peroxide value, concentration of peroxide in an oil or fat, is useful for assessing the extent to which spoilage has advanced.

The peroxide value is determined by measuring the amount of iodine which is formed by the reaction of peroxides (formed in fat or oil) with iodide ion.

2 I- + H2O + ROOH → ROH + 20H- + I2

The base produced in this reaction is taken up by the excess of acetic acid present. The iodine liberated is titrated with sodium thiosulphate.

2S2O32- + I2 → S4O62- + 2 I-

Iodine numbers are often used to determine the amount of unsaturation in [fatty acids](https://en.wikipedia.org/wiki/Fatty_acid). This unsaturation is in the form of double bonds, which react with iodine compounds. The higher the iodine number, the more C = C bonds are present in the fat (Thomas, 2002). The iodine value presented in table 1 above ranged from 12.817 to 14.386 meg / kg. There is no significant different in the values obtained.

The acid values were presented in table 1 above. The acid value was found to be significantly lower in the four samples treated with the extracts. The acid values ranged from 2.635 to 3.317 mg KOH/g. Free fatty acid (FFA) of oil before and after addition of extracts from the spices used revealed that FFA was found to be significantly higher in oil before addition of the extracts. Sample with *allium sativum* extract had the lowest free fatty acid (1.334 % oleic acid) (table 1.) The decrease in free fatty acids could be attributed to antioxidation of fats by the extracts. Antioxidants act as a defense mechanism that protect against deleterious effects of oxidative reactors produced by reactive oxygen species (ROS) in a biological system (Oladoye et al., 2014; Jayachitra and Krilhiga, 2010), Antioxidants have been reported to prevent oxidative damage caused by ROS by reacting with free radicals, chelating, and catalytic metals and also by acting as oxygen scavengers (Tanizawa et al., 1992), (Maggio et al., 2002). The antioxidants in biological system can be either enzymatic or nonenzymatic. The enzymatic antioxidants include catalase, superoxide dismutase and glutathione which catalyze neutralization of many types of free radicals (Jacob, 1995; Fasoyiro et al., 2006), while the nonenzymatic antioxidants include vitamin C, Selenium, vitamins E, Carotenoids, and Polyphenols.

Specific type of rancidity involving oxygen damage to foods, and this type of rancidity is called "oxidative rancidity." During the process of oxidative rancidity, oxygen molecules interact with the structure of the oil and damage its natural structure in a way that can change its odour, its taste, and its safety for consumption. Oxidation of fats, generally known as rancidity, is caused by a biochemical reaction between fats and oxygen. In this process the long-chain fatty acids are degraded and short-chain compounds are formed. One of the reaction products is butyric acid, which causes the typical rancid taste.

Rancidification is the decomposition of fats, oils and other lipids by hydrolysis or oxidation, or both. Hydrolysis will split fatty acid chains away from the glycerol backbone in glycerides. These free fatty acids can then undergo further auto-oxidation. Oxidation primarily occurs with unsaturated fats by a free radical-mediated process. These chemical processes can generate highly reactive molecules in rancid foods and oils, which are responsible for producing unpleasant and noxious odours and flavours. These chemical processes may also destroy nutrients in food. Under some conditions, rancidity, and the destruction of vitamins, occurs very quickly.

Natural anti-oxidants include flavonoids, polyphenols, ascorbic acid (vitamin C) and tocopherols (vitamin E). Synthetic antioxidants include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl 3,4,5-trihydroxybenzoate also known as propyl gallate and ethoxyquin.

The natural antioxidants tend to be short-lived, so synthetic antioxidants are used when a longer shelf life is preferred. The effectiveness of water-soluble antioxidants is limited in preventing direct oxidation within fats, but is valuable in intercepting free radicals that travel through the watery parts of foods.

The effect of time on the characteristics of palm oil after treatment with the extracts from the different local spices used were presented in table 2 to 5. Saponification values and iodine values decreases as contact time increases from 0 to 28 days. The values ranged from 163.28 to 207.57 mgKOH/g, SV and 13.81 to 14.25 g/100g, IV for sample treated with *afromomum melegueta* extract; 194.83 to 159.09 mgKOH/g, SV and 12.877 to 14.205 g/100g, IV for oil treated with *pipper guineense* extract; 209.68 to 166.38 mgKOH/g, SV and 13.063 to 13.866 g/100g, IV for oil treated with *allium sativum* extract (table 4); 192.07 to 160.29 mgKOH/g, SV and 12.88 to 14.386 g/100g g/100g, IV for oil treated *monodora myristica* extract (table 5).

The values of PV, FFA and AV increase as contact time increases from 0 to 28 days. The values ranged from 4.90 to 9.80 **meg/kg**, PV; 1.556 to 2.88 % oleic acid, FFA and 3.096 to 5.73 mg KOH/g, AV for oil treated with *afromomum melegueta* extract (table 2); 4.98 to 9.95 **meg/kg**, PV; 1.417 to 3.54 % oleic acid, FFA and 2.820 to 7.44 mg KOH/g, AV for oil treated with *pipper guineense* extract (table 3); 4.95 to 9.90 **meg/kg**, PV; 1.334 to 3.19 % oleic acid, FFA and 2.655 to 6.35 mg KOH/g, AV for oil sample treated with *allium sativum* extract (table 4); 4.90 to 9.82 **meg/kg**, PV; 1.528 to 3.65 % oleic acid, FFA and 3.041 to 7.28 mg KOH/g, AV for oil treated with *momodora myristica* extract (table 5). The values of FFA and AV obtained were higher than the specification recommended by FAO/WHO (1.376 and ≤ 0.6 respectively). The increase in contact time on addition of the extracts from the different local spices did not retard the development of rancidity.

**Conclusion**

The decrease in free fatty acids could be attributed to antioxidation of fats by the extracts. Antioxidants in the spices are often added to oil in order to retard the development of rancidity due to oxidation.  In addition, rancidification can be decreased, but not completely eliminated, by addition of food additives (spices), storing fats and oils in a cool dark place with little exposure to oxygen or free radicals.

**Corresponding Author:**

Dr.Osu, Charles Ikenna.

Department of Department Of Pure And Industrial Chemistry, University Of Port Harcourt, PMB 5323, Port Harcourt, Rivers State. Nigeria. Phone: +2348037783246;

E-mail: charsike@yahoo.

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