## DETERMINATION OF THE PEROXIDATIVE STATUS OF BRANDED AND UNBRANDED EDIBLE OILS MARKETED IN UMUAHIA, ABIA STATE, NIGERIA

#### UGWU, Paschal, ALAEBO, Prince Ogochukwu, ANUMUDU, Osinachi Fortune, NJOKU, George Chigozie and OKAFOR, Polycarp Nnacheta

Department of Biochemistry, College of Natural Sciences, Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria.

**Correspondence:** Alaebo, P. O. Department of Biochemistry, College of Natural Sciences, Michael Okpara University of Agriculture, Umudike, Nigeria. **Email:** <u>alaebo.prince@mouau.edu.ng</u> **Phone:** +234 8064481954

Received July 22, 2022; Revised August 18, 2022; Accepted August 23, 2022

#### ABSTRACT

Contaminated edible oil cause many disease conditions. The aim of this study was to determine the peroxidative status of frequently consumed edible oils marketed in Umuahia, Abia State, Nigeria. 100 samples of edible oils from six notable markets were bought and analyzed using acceptable physical, chemical and biochemical parameters. The highest and lowest values obtained are – density: unbranded palm oil (0.95  $\pm$  0.05 g/ml) and branded vegetable oil (0.89  $\pm$  0.03 g/ml); iodine value: branded soya oil  $(142.26 \pm 24.69 \text{ g/ml})$  and unbranded vegetable oil  $(57.38 \pm 14.48 \text{ g/ml})$ ; peroxide value: branded vegetable oil (4.43  $\pm$  0.87 meqO<sub>2</sub>/Kg) and unbranded palm oil (3.58  $\pm$ 0.95 meqO<sub>2</sub>/Kg); acid value: unbranded palm oil (40.45  $\pm$  6.62 mgNaOH/g) and branded vegetable oil (0.72 ± 0.22 mgNaOH/g); malondialdehyde value: branded soya oil (0.69 ± 0.58 mg MDA/Kg) and unbranded palm oil (0.36 ± 0.25 mg MDA/Kg); pH: branded soya oil (6.67  $\pm$  0.28) and unbranded palm oil (3.16  $\pm$  2.12); color: unbranded palm oil (0.68  $\pm$  0.04 A) and branded soya oil (0.02  $\pm$  0.01 A). The identified essential fatty acids in branded vegetable oil include eicosatetraenoic acid (1.33 %) and linoleic acid (92.50 %); unbranded vegetable oil include arachidonic acid (85.70 %), while the non-essential fatty acids in branded vegetable oils include oleic acid (73.00 %) and stearic acid (95.80 %); unbranded palm oil include palmitic acid (93.00 %). This study has revealed that unbranded edible oils marketed in Umuahia are highly saturated, adulterated, rancid, not properly refined, and unsafe for consumption.

**Keywords:** Edible oil, Peroxidative status, Physicochemical properties, Biochemical properties, Umuahia, Abia State

#### INTRODUCTION

During the last two decades, food consumption patterns in Umuahia have been changing gradually, and these changes have significantly influenced consumers' choice of edible oils. Forces responsible for shaping the demand for food vary, including economic and demographic factors and lifestyle changes that influence consumers' tastes and preferences (Caswell *et al.*, 2013).

Studies have been done in the general theory of choice-making for products (including food items) with novelty attributes among the consumers (Hu and Chen, 2008; Caswell *et al.*, 2013). The implicit benefit-cost of consumers' choice-making is translated into their utilities, and a choice will be made if the resulting expected utility is greater than the alternative

decision (Hu and Chen, 2008). Because the consumption of edible oils is often associated with particular benefits and costs (Zhang *et al.,* 2012a), which may be either privately or socially relevant, some manufacturers have made an effort to communicate these benefits and costs to influence the consumers' choice of edible oils.

Many unbranded edible oils have been processed in unhygienic conditions and put in plastic containers not properly cleaned. Since consumers want to save costs, they buy them. The question is: how safe is the unbranded edible oil sold in Umuahia?

An investigation has revealed that what the consumers are paying for differs from what is sold. Some sellers add bleached palm oils, shea butter and animal fats to the vegetable oils they sell (Odoh *et al.*, 2017).

The physical and chemical properties of edible oil influence oxidation and hydrolysis reactions, which occur during exposure to light, heat, moisture and air. It is known that the edible oils kept continuously or repeatedly at high temperatures under direct sunlight, in the presence of air and water, are subject to photooxidation, thermal oxidation, polymerization, and hydrolysis, and the resultant decomposition products can adversely affect the quality of the oils, their stability depends on the composition of fatty acids and antioxidants (Crosa *et al.*, 2014).

During the cooking process, different by-products, including alcohols, cyclic compounds, polymers, dimmers, and free fatty acids, are produced as a result of oxidation and hydrolysis reactions, which adversely impact human health (Chen et al., 2013). Also, they play important roles in fried products' flavour, texture and aroma acceptability (Li et al., 2008). Due to the relatively high temperature of frying (150 – 180°C) and repeated heating, various undesired chemical reactions such as fission, hydrolysis, oxidation, polymerization and pyrolysis occur very rapidly in triacylglycerol (Zhang et al., 2012b; Aladedunye, 2015).

Lipids are triacylglycerol formed when three fatty acids are esterified with a molecule of alcohol or glycerol (Ubhayasekera, 2009). Unsaturated fatty acids (UFA) mainly consist of omega-9, omega-6 and omega-3 series and are highly susceptible to oxidation (Johnson and Bradford, 2014; Galano *et al.*, 2015). The oxidation rate depends on the degree of unsaturation and increases with the double bond of fatty acids. When oxygen reacts with unsaturated lipids, a wide variety of oxidation products are produced by lipid peroxidation (Kerrihard *et al.*, 2015).

Lipid oxidation products have mutagenic, carcinogenic and cytotoxic properties and are considered risk factors for human health (Keller et al., 2015). These metabolites cause severe health problems, such as the growth of tumour cells through lipid peroxidation as hydroxides of fatty acids are cytotoxic. Oxidation of long-chain fatty acids causes neuromyopathic disease in infants and adults (Olpin, 2005). Oxidation of lipids causes loss of nutritive value and the development of unpleasant flavour (Li et al., 2015). Lipid oxidation reduces the shelf life of many complex food products and the nutritive value of food by limiting the content of essential polyunsaturated fatty acids (PUFA) (Böttcher et al., 2015).

Lipids do not escape damage by reactive intermediates. Lipids are oxidized in several ways, and they may be oxidized enzymatically or via free radical interaction (enzyme independent), or they can also be oxidized in a free radical independent, nonenzymatic manner. Lipoxygenases, cyclooxygenases, and CYPs may catalyze lipid oxidation. Several CYP families have demonstrated the ability to catalyze the formation of hydroxycholesterol and side-chain oxidation products. Free radicalmediated peroxidation of PUFA can occur through distinct mechanisms (Negre-Salvayre et al., 2008). This project aimed at determining the peroxidative status of branded and unbranded edible oils marketed in Umuahia, Abia State, Nigeria, using standard physical, chemical and biochemical parameters as a means to evaluate their quality.

### MATERIALS AND METHODS

**Sample Collection and Storage:** In this study, one hundred (100) samples of edible oils were collected randomly from six notable markets in Umuahia, Abia State, Nigeria

between September and October 2019. These markets include Ishigate, Ndioru, Orie-ugba, Ahiaeke, Ubani and Shoprite. The oils' status, choice of brands or kinds, availability, satisfaction gotten by consumers, and factors that drive purchase were assessed by conducting a market survey in the above-listed markets. The samples labelled "Vegetable oil" were those whose plant sources were not known. The collected samples were transferred into sterilized sample containers wrapped with masking tape (to prevent chemical changes from the environment). Subsequently, the encoded samples were transported to the Animal Nutrition and Biochemistry laboratory, College of Animal Science and Animal Production (CASAP), Michael Okpara University of Agriculture, Umudike, Abia State. Samples were stored in a cool and dry cupboard in the instrumentation room to avoid any form of oxidation. Samples for fatty acid profiling were sent to BGI Laboratories Limited, Port Harcourt, Rivers State, for gas chromatography, mass spectrophotometry tests.

**Physicochemical Properties of the Oils:** The physical components of the oil samples' smoke flash and fire points were estimated according to the method described by Weiss (1963), while the method of Avantina (2010) was used to determine the density, pH, colour and melting point.

The chemical properties of the oils tested were Peroxide Value (PV), Acid Value (AV), Malondialdehyde (MDA) and Value, Iodine Value (IV) to ascertain the level of peroxidation. Fatty acid profile was also done to determine the fatty acid composition of the oil samples. All physicochemical measurements were replicated 2three times. The test methods were based on the standards of the American Oil Chemist's Society (AOCS, 2020), International Union of Pure and Applied Chemistry (Dieffenbacher and Pocklington, 1992), and Food and Agricultural Organization (FAO)/ World Health Organization (WHO) (Codex Alimentarius, 2001). The saponification value was determined using the method described by Lotfy et al. (2015), while the vitamins A and E values were determined by the method described by Codex Alimentarius (1999). Results obtained were compared with the FAO/WHO and NAFDAC standards.

**Statistical Analysis:** The data obtained were subjected to analysis of variance (ANOVA) using Microsoft Office Excel 2007. This was used to obtain the mean values and their standard errors. Inferential statistics were also carried out using the Z-Test in Microsoft Office Excel 2007 to determine the confidence interval and draw logical conclusions from the results.

#### RESULTS

From this survey, both Branded Edible Oils (BEO) and Unbranded Edible Oil (UEO) were patronized by residents of Umuahia. The frequently consumed BEOs are: Branded Soya Oil (BSO) [10 %] and Branded Vegetable Oil (BVO) [15 %], while the most frequently consumed UEOs are: Unbranded Palm Oil (UPO) [15 %] and unbranded vegetable oil (UVO) [60 %].

Peroxidative Status of Frequently Consumed Edible Oils: Peroxide value was significantly higher (p<0.05) in branded vegetable oil (4.43 ± 0.87) than in other edible oils (Table 1). Acid value was significantly higher (p<0.05) in unbranded palm oil (40.45  $\pm$  6.62) than in other edible oils. Iodine value was significantly higher (p<0.05) in branded soya oil  $(142.26 \pm 24.69)$ than in other edible oils. Malondialdehyde value was significantly higher (p<0.05) in branded soya oil  $(0.69 \pm 0.58)$  than in other edible oils. pH was significantly higher (p<0.05) in branded soya oil  $(6.67 \pm 0.28)$  than in other edible oils; Density was significantly higher (p<0.05) in unbranded palm oil  $(0.95 \pm 0.053)$  than in other edible oils, and the colour was significantly higher (p<0.05) in unbranded palm oil (0.68  $\pm$ 0.041) than in other edible oils.

**Fatty Acid Profile of Unbranded Palm Oil:** This study revealed the presence of 21 chemical substances in palm oil. Their molecular formulas, molar masses, retention time and percentage probability are presented in Table 2. Color (A)

Umuahia, Abia State, Nigeria between September – December 2019						
Oil type / Physicochemical Parameter	Unbranded Palm Oil	Branded Soya Oil	Branded Vegetable Oil	Unbranded Vegetable Oil		
Peroxide value (meqO <sub>2/</sub> kg of oil)	$3.58 \pm 0.95^{a}$	$4.36 \pm 1.11^{b}$	$4.43 \pm 0.87^{b}$	$3.89 \pm 2.08^{ab}$		
Acid value (mgNaOH/g of oil)	$40.45 \pm 6.62^{\circ}$	$0.96 \pm 0.43^{a}$	0.72 ± 0.22 <sup>a</sup>	$5.91 \pm 3.07^{b}$		
Iodine value (mg $I_2/g$ of oil)	$76.19 \pm 25.08^{b}$	$142.26 \pm 24.69^{d}$	$107.83 \pm 15.65^{\circ}$	$57.38 \pm 14.48^{a}$		
Malondialdehyde value (mgMDA/kg of oil)	0.36 ± 0.25 <sup>a</sup>	$0.69 \pm 0.58^{b}$	$0.68 \pm 0.37^{b}$	$0.60 \pm 0.69^{b}$		
рН	$3.16 \pm 2.12^{a}$	$6.67 \pm 0.28^{\circ}$	$6.49 \pm 0.31^{\circ}$	$4.46 \pm 1.68^{b}$		
Density (g/ml)	$0.95 \pm 0.05^{b}$	$0.93 \pm 0.04^{ab}$	$0.89 \pm 0.03^{a}$	$0.90 \pm 0.04^{a}$		

 Table 1: The peroxidative status of frequently consumed edible oils marketed in

 Umuahia, Abia State, Nigeria between September – December 2019

Means on a row with different letter superscript are significantly different (p<0.05)

 $0.68 \pm 0.04^{\circ}$ 

# Table 2: The fatty acid composition of unbranded palm oil marketed in Umuahia, Abia State, Nigeria between September – December 2019

 $0.03 \pm 0.01^{a}$ 

 $0.06 \pm 0.02^{b}$ 

State/ Higena between september				
Compound	Molecular formula	Molar mass (g/mol)	Retention Time (Mins)	% Composition
β-Carotene	C <sub>40</sub> H <sub>56</sub>	536	5.32	96.50
9,12,15-Octadecatrienoic acid, methyl ester	$C_{19}H_{32}O_2$	292	12.63	82.80
Ethyl 9,12,15-Octadecatrienoate	C <sub>20</sub> H <sub>34</sub> O <sub>2</sub>	306	12.63	2.61
Palmitic acid, (2-phenyl-1,3-dioxolan-4- yl)methyl ester	· C <sub>26</sub> H <sub>42</sub> O <sub>4</sub>	418	13.33	93.00
Hexadecanoic acid, (-phenyl-1,3- dioxolan-4-yl)methyl ester, cis-	$C_{26}H_{42}O_4$	418	13.33	6.02
Tripalmitin	$C_{51}H_{98}O_{6}$	806	13.61	98.30
1,2-Dipalmitoylphosphatidylcholine	C <sub>40</sub> H <sub>80</sub> NO <sub>8</sub> P	733	13.61	0.98
Cetyl Stearate	C <sub>34</sub> H <sub>68</sub> O <sub>2</sub>	508	13.77	94.60
Octadecanoic acid, octadecyl ester	C <sub>36</sub> H <sub>72</sub> O <sub>2</sub>	536	13.77	1.66
Ascorbylpalmitate	C <sub>22</sub> H <sub>38</sub> O <sub>7</sub>	414	15.09	96.50
L-(+)-Ascorbic acid 2,6-dihexadecanoat	e C <sub>38</sub> H <sub>68</sub> O <sub>8</sub>	652	15.09	0.96
Palmidrol	C <sub>18</sub> H <sub>37</sub> NO <sub>2</sub>	299	15.60	97.20
Dodecanamide, N-(2-hydroxythyl)-	$C_{14}H_{29}NO_2$	243	15.60	1.94
9,12-octadecadienoic acid	$C_{21}H_{40}O_2Si$	352	16.17	88.20
Linoelaidic acid, trimethylsilyl ester	C <sub>21</sub> H <sub>40</sub> O <sub>2</sub> Si	352	16.17	10.80
Oleic acid, eicosyl ester	C <sub>38</sub> H <sub>74</sub> O <sub>2</sub>	562	17.00	84.00
9-octadecenoic acid(2)-, octadecyl ester	• C <sub>36</sub> H <sub>70</sub> O <sub>2</sub>	534	17.00	6.47
Vitamin E	$C_{29}H_{50}O_2$	430	17.11	71.00
(+)-γ-Tocopherol, 0-methyl	$C_{29}H_{50}O_2$	430	17.11	9.66
Decanoic acid, 1,2,3-propanetriyl ester	C <sub>33</sub> H <sub>62</sub> O <sub>6</sub>	554	17.91	98.30
2-(Octanoyloxy)propane-1,3- diylbis(decanoate)	$C_{31}H_{58}O_6$	526	17.91	0.98

**Fatty Acid Profile of Branded Soya Oil:** This study revealed the presence of 20 chemical substances in soya oil. Their molecular formulas, molar masses, retention time and percentage probability are presented in Table 3.

**Fatty Acid Profile of Branded Vegetable Oil:** This study revealed the presence of 24 chemical substances in branded vegetable oil. Their molecular formulas, molar masses, retention time and percentage probability are presented in Table 4.

 $0.06 \pm 0.02^{b}$ 

Compound	Molecular formula	Molar mass (g/mol)	Retention Time (Mins)	% Composition
Cyclopropaneoctanoic acid, 2-octyl-methyl ester	$C_{20}H_{38}O_2$	310	13.56	76.40
10- Nonadecanoicacid, methyl ester	$C_{20}H_{38}O_2$	310	13.56	5.99
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	270	14.34	93.20
Pentadecanoic acid, 14-methyl-,methyl ester	$C_{17}H_{34}O_2$	270	14.34	3.73
Arachidic acid	C <sub>23</sub> H <sub>48</sub> O <sub>2</sub> Si	384	14.82	92.60
Eicosanoic acid	C <sub>23</sub> H <sub>48</sub> O <sub>2</sub> Si	384	14.82	7.01
Docosanoic acid, methyl ester	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	354	15.39	90.90
Methyl 20-methyl-heneicosanoate	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	354	15.39	6.30
9,12-octadecadiiynoic acid, methyl ester	$C_{19}H_{30}O_2$	290	19.18	81.00
Methyl 10,12-octadecadiynoate	$C_{19}H_{30}O_2$	290	19.18	3.24
Vitamin E	$C_{29}H_{50}O_2$	430	19.46	71.00
(+)-γ-Tocophenol,0-methyl	$C_{29}H_{50}O_2$	430	19.46	9.66
γ-sitosterol	$C_{29}H_{50}O$	414	20.62	94.90
β-sitosterol	$C_{29}H_{50}O$	414	20.62	1.93
Methyl 18-methylnonadecanoate	$C_{21}H_{42}O_2$	326	21.59	54.40
Eicosanoic acid, methyl ester	$C_{21}H_{42}O_2$	326	21.59	28.00
Cholesta-3,5-diene	C <sub>27</sub> H <sub>44</sub>	368	21.71	50.50
Cholesterol, chlorodifluoroacetate	$C_{29}H_{45}CIF_2O_2$	498	21.71	5.55
9,12-octadecadienoic acid	$C_{18}H_{32}O_2$	280	52.31	89.50
18-octadec-9-enolide	$C_{18}H_{32}O_2$	280	52.31	5.87

Table 3: The fatty acid composition of branded soya oil marketed in Umuahia, Abia State,Nigeria between September – December 2019

Table 4: The fatty acid composition of branded vegetable oil marketed in Umuahia, AbiaState, Nigeria between September – December 2019

Compound	Molecular formula	Molar mass (g/Mol)	Retention Time (Mins)	% Composition
Octanoic acid	$C_8H_{16}O_2$	144	1.44	96.40
Nonanoic acid	$C_9H_{18}O_2$	158	1.44	0.96
Para-TolylOctanoate	$C_{15}H_{22}O_2$	234	1.98	91.10
Octanoic acid, 3-methylphenyl ester	C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>	234	1.98	5.53
Dodecanoic acid, 3-hydroxypropyl ether	$C_{15}H_{30}O_{3}$	258	3.79	98.00
Dodecanoic acid, 2-hydroxy-1- (hydroxymethyl) ethyl ester	$C_{15}H_{30}O_4$	274	3.79	0.97
3,7-Dimethyloct-6-en-1-yl tetradecanoate	$C_{24}H_{46}O_2$	366	4.65	53.40
3,7-Dimethyloct-6-en-1-yl palmitate	$C_{26}H_{50}O_2$	394	4.65	8.43
Hexadedecanoic acid, 1-methyl-1,3- propanediyl ester	$C_{36}H_{70}O_4$	566	7.88	97.70
Hexadecanoic acid, 1,1-dimethyl-1,2- ethanediyl ester	$C_{36}H_{70}O_4$	566	7.88	1.68
9-hexadecanoic acid, methyl ester	$C_{17}H_{32}O_2$	268	12.42	69.10
Methylhexadec-9-enoate	C <sub>17</sub> H <sub>32</sub> O <sub>2</sub>	268	12.42	20.70
Octadecanoic acid, 2-hydroxy-1- (hydroxymethyl) ethyl ester	$C_{21}H_{42}O_4$	358	20.39	95.80
Octadecanoic acid, 2,3-dihydroxypropyl ester	$C_{21}H_{42}O_4$	358	20.39	2.95
Oleic acid	$C_{18}H_{34}O_2$	282	28.98	73.00
Cis –Vaccenic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282	28.98	5.62
Linoleic acid ethyl ester	C <sub>20</sub> H <sub>36</sub> O <sub>2</sub>	308	30.23	92.50
9,12-octadecanoic acid, ethyl ester	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	308	30.23	2.55
9,12,15-octadecatrienoic acid, phenyl methyl ester	$C_{25}H_{36}O_2$	368	31.39	96.80

5,8.11,14-Eicosatetraenoic acid, phenylmethyl ester	$C_{27}H_{38}O_2$	394	31.39	1.33
Eicosanoic acid, Hexadecyl ester	C <sub>36</sub> H <sub>72</sub> O <sub>2</sub>	536	32.49	98.30
Eicosanoic acid, octadecyl ester	C <sub>38</sub> H <sub>76</sub> O <sub>2</sub>	564	32.49	0.98
Behenic acid, Cyanomethyl ester	C <sub>24</sub> H <sub>45</sub> NO <sub>2</sub>	379	33.53	98.20
Lignoceric acid, Cyanomethyl ester	$C_{26}H_{49}NO_2$	407	33.53	1.34

**Fatty Acid Profile of Unbranded Vegetable Oil:** This study revealed the presence of 28 chemical substances in unbranded vegetable oil. Their molecular formulas, molar masses, retention time and percentage probability are presented in Table 5.

#### DISCUSSION

**Acid Value:** The acid value is defined as the weight in milligram of NaOH required to neutralize 1 g of oil. It is a relative measure of rancidity as free fatty acids are usually formed during the decomposition of glycerides. In normal circumstances, refined oils should be free from any free fatty acids. Oils on hydrolytic and enzymatic decomposition due to chemical or bacterial contamination yield free fatty acids (Keller *et al.*, 2015). Therefore, oils with increased acid value are unsafe for human consumption.

Compared to FAO/WHO recommended standard, none of the oils' mean values were within the normal range of  $\leq 0.6$  mgNaOH/g of oil (Codex Alimentarius, 2001). However, BVO and BSO had close values to the recommended values. This showed that both BVO and BSO may have been decomposed to an extent. This may be attributed to their exposure to sunlight and heat when marketed. Free fatty acid is a carboxylic acid with a long aliphatic chain that can be saturated or unsaturated, normally released by hydrolysis and the oxidative reaction of oil. The percentage of free fatty acids in most oils is calculated based on oleic acid as for unsaturated oils, while for palm oil (saturated oil), it is calculated in terms of palmitic acid. This may be probably one of the reasons for a higher acid value in palm oil. Also, the high acid values obtained for both UVO and UPO may also be attributed to unhygienic modes of production, exposure to sunlight, and moisture or bacteria in containers used for packaging and storage (Yin et al., 2011).

The high acid value for UPO may also be attributed to the high level of carotene, which accelerates oxidative decomposition. Adulteration of unbranded oils, as detected by the iodine value test, may have also caused the high acid values obtained for the acid test.

**Iodine Value:** Compared to standard, the iodine values of the unbranded palm oils were not within the FAO/WHO recommended values of  $50 - 55 \text{ mgI}_2/\text{g}$  (Codex Alimentarius, 2001), while NAFDAC (2019) recommends 80 - 143  $mqI_2/q$  of oil for refined unsaturated edible oils. Branded soya oil and branded vegetable oil contain more UFA, which include monounsaturated fatty acids (MUFA) (73 % oleic acid) and PUFA (92.5 % linoleic acid). The high level of unsaturation makes these oils have higher iodine values than saturated palm oil and unbranded vegetable oils. However, palm oil has a higher iodine value than normal, indicating adulteration of oils with possibly vegetable oils with higher levels of unsaturation to boost production by producers. This was seen in palm oil's high amount of oleic acid (84 %). In the case of UVO, lipid oxidation reduces the shelf life of many complex food products and the nutritional value of food by limiting the content of essential PUFA (Böttcher et al., 2015); the low iodine value of this oil may be attributed to high rate of oxidation.

**Peroxide Value:** Compared to FAO/WHO standard, the peroxide values for all oils were within the normal range ( $\leq 10 \text{ meqO}_2/\text{Kg}$ ) (Codex Alimentarius, 2001). The structural differences between oil molecules influenced some of the oxidative reactions. UPO is highly saturated, and this limited the number of reactions that took place across the double bonds. With reference to the high iodine value of UVO, it was observed that UVO was adulterated, leading to a higher saturation level than normal.

Abia State, Nigeria between September	- December A	2019		
Compound	Molecular formula	Molar mass (g/Mol)	Retention Time (Mins)	% Composition
β-Sitosterol	$C_{29}H_{50}O$	414	1.34	97.30
γ-Sitosterol	$C_{29}H_{50}O$	414	1.34	1.98
β-Carotene	$C_{40}H_{56}$	536	5.32	96.50
Lycopene	$C_{40}H_{56}$	536	5.32	0.96
9,12-octadecadienoic acid	$C_{18}H_{32}O_2$	280	24.45	89.50
18- Octadec-9-enolide	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	280	24.45	5.87
3,7,11,15-tetramethyl-2-hexadecn-1-ol	C <sub>20</sub> H <sub>40</sub> O	296	24.61	41.20
Phytol, acetate	$C_{22}H_{42}O_2$	338	24.68	10.20
Octanamide, N-N-bis(2-hydroxyethyl)	$C_{12}H_{25}NO_3$	231	24.90	98.60
Dodecanamide, N,N-bis(2- hydroxyethyl)	$C_{16}H_{33}NO_3$	287	24.90	0.98
Decanoic acid, ethyl ester	$C_{12}H_{24}O_2$	200	26.08	94.90
Nonanoic acid, 5-methyl-, ethyl ester	$C_{12}H_{24}O_2$	200	26.08	2.20
Dodecanoic acid	$C_{12}H_{24}O_2$	200	27.34	95.20
Tridecanoic acid	$C_{13}H_{26}O_2$	214	27.34	1.71
Myristic acid, 3-methyl phenyl ester	$C_{21}H_{34}O_2$	318	27.86	92.10
Oxalic acid, 2-methylphenyl octadecyl ester	$C_{27}H_{44}O_4$	432	27.86	1.41
Octadecanoic, 2-hydroxy-1,3-prpanediyl ester	$C_{39}H_{76}O_5$	624	28.01	95.70
Distearin	$C_{39}H_{76}O_5$	624	28.01	3.97
Docosanoic acid, 12,2,3-propanetriyl ester	$C_{69}H_{134}O_6$	1058	32.31	19.80
Dodecanoic acid, 1a,2,5,5a,6,9,10a- octahydro-5a-hydroxy-4- (hydroxymethyl)-1,1,7,9-tetramethyl	$C_{32}H_{48}O_6$	528	32.31	16.00
Oleic acid, 3-(Octadeyloxy)propyl ester	$C_{39}H_{76}O_{3}$	592	33.87	93.90
Oleic acid, eicosyl ester	$C_{38}H_{74}O_2$	562	33.87	0.93
Arachidonic acid	$C_{20}H_{32}O_2$	304	35.76	85.70
5,8,11,14-eicosatetraenoic acid, methyl ester	$C_{21}H_{34}O_2$	318	35.76	2.91
β-Tocopherol, 0-methyl-	$C_{29}H_{50}O_2$	430	36.50	30.10
(+)-γ-Tocopherol, 0-methyl-	$C_{29}H_{50}O_2$	430	36.50	26.60
Methyl glycocholate	$C_{39}H_{69}NO_6Si_3$	695	37.60	91.50
β-D-Glucopyranosiuronic acid, 3-(5- ethyl hexahydro-2,4,6-trioxo-5- pyrimidnyl)-1,1-dimethyl-propyl	$C_{27}H_{52}N_2O_{10}Si_3$	648	37.60	0.91

 Table 5: The fatty acid composition of unbranded vegetable oil marketed in Umuahia,

 Abia State, Nigeria between September – December 2019

This adulteration caused low peroxide value of UVO. In lipid oxidation, peroxides and hydroperoxides are the predominant reaction products. The reaction products continue to increase until storage conditions change, one or more initiators are depleted, oxygen availability is consumed, or the lipid substrate is exhausted. Since many compounds produced during the termination phase are volatile, their concentration in products may decrease with time (Henry, 2016).

**Density:** With the exception of UPO, all other edible oils had densities within the FAO/WHO

recommended ranges of 0.891 – 0.899 g/ml for refined palm oil, 0.919 – 0.930 g/ml for soya oil (Codex Alimentarius, 2001), and 0.890 – 0.925 g/ml for refined vegetable oil (NAFDAC, 2019). The oils densities decreased with increase in unsaturation and increased with an increase in saturation. The highest density was obtained in UPO due to the presence of high concentration of saturated fatty acid (SFA) in contrast to the lowest density observed for BVO due to the presence of high concentration of MUFA and PUFA. The UPO density was not within the recommended range. This indicated that the UPO sold in Umuahia was adulterated with substances that will help boost profit or were not well refined during production. However, the density ranges of the other three oil types do not mean they are without any adulteration. This is because adulterating these oils with oils of other plant sources will still keep them within the standard range.

**pH:** Acidity is a measure of the extent to which edible oils have been decomposed by the action of light, oxygen, heat, water and (or) other impurities like heavy metal. In general, a pH test is used to detect edible oils' safety. Oils with low pH values are generally rancid and unsafe for consumption. Long-chain fatty acids are degraded during oxidation, and short-chain compounds formed. Highly are acidic compounds are produced, which typically cause low pH and rancid taste (Lee et al., 2004). The low pH detected in UPO and UVO may be attributed to the high level of oil deterioration. This may be probably due to the plastic containers used for storing and packaging of these unbranded edible oils, which have received little or no cleaning, allowing contamination by microbes. These oils were also exposed to light and heat when marketed, leading to oxidation and production of large amounts of acidic compounds as detected in the fatty acid profile. Therefore, unbranded edible oils sold in Umuahia were rancid and unsafe for consumption.

Malondialdehyde Value: The low mean value of MDA obtained for UPO can be attributed to its high content of SFA. BVO and BSO had higher MDA values due to the high contents of UFA. Contrary to this rule, UVO which has been revealed to possess a high saturation level by an iodine test had high level of MDA than expected. This indicated that this oil has undergone a high level of decomposition to give secondary decomposition products. The reason for this may be the high level of arachidonic acid (85.70 %) detected in the fatty acid composition. MDA is an end product generated by decomposing arachidonic acid and larger PUFA (Ayala et al., 2014). If edible oils are chemically more complex and consist of more double bonds with more carboxyl or hydroxyl groups, the chances of becoming rancid are high. The double bonds found in fats and oils play a role in autoxidation. Oils with a high degree of UFA are most susceptible to autoxidation (Sun *et al.*, 2011).

**Colour:** Among the many tests that need to be carried out on edible oils is the colour measurement used to ascertain the quality and determine if the oil has passed through the refining process of bleaching. Crude oils have high pigmentation leading to high colour value, in contrast to edible oils that have passed through the refining process (Choe and Min, 2005).

From the colour of the oils, the soya oil may have received the best treatment with bleaching agents (commonly used are palygorskite and sepiolite) than other oils used in this study during refining. When viewed with the naked eye, it looks almost transparent. UVO though having good colour value appeared very turbid to the eye. This may be attributed to the high amount of beta-sitosterol (97.3 %) and gamma sitosterol (1.98 %) present in these oils. The very rich colour value of palm oil may be attributed to the high content of beta carotenoid (96.5 %), which gives palm oil its dark red colour (Lee, 2003).

Fatty Acid Profile: The presence of eicosatetraenoic acid (an omega-3 fatty acid) in BVO indicated that this oil has the potential to be used as anti-inflammatory, hypocholestrolemic, hypolipidemic, antioxidant and hypotensive agents. This will help reduce oxidative stress, inflammation and platelet aggregation (Rodriguez-Leyva et al., 2010). Linoleic acid and arachidonic acid (omega-6 fatty acids) were detected in BVO and UVO respectively. Linoleic acid is a double UFA occurring widely in plant glycosides. In this particular PUFA, the first double bond is located between the sixth and seventh carbon atoms from the methyl end of the fatty acid (n = 6). Linoleic acid is an essential fatty acid in human nutrition because humans cannot synthesize it (Kaur et al., 2014).

**Conclusion:** In this study, various physicochemical parameters have been examined for collected

edible oil samples. Acid value test has revealed that unbranded edible oils (unbranded palm oil and unbranded vegetable oil) were highly rancid. It has also revealed that exposure of branded edible oils to heat and sunlight in the markets lead to decomposition. Iodine number test has shown that branded edible oils were highly unsaturated and safe for consumption, unlike the unbranded palm oil with a higher than normal level of unsaturation, indicating adulteration. Unbranded vegetable oil with a lower than normal saturation level also indicated a high oxidation level, and (or) adulteration with animal fats or bleached palm oil has also occurred. Peroxide values were within the standard range; however, this does not mean that the oil was safe for consumption since manv compounds produced durina the termination phase of autoxidation are volatile, and their concentration in products begins to decrease with time. The colours for all oil samples were good. Higher than standard value for unbranded palm oil density has revealed that this oil was not well refined before being sent to the markets and (or) was adulterated. pH is low for unbranded vegetable oil and unbranded palm oil, indicating that these oils are rancid. Higher than expected MDA value in unbranded vegetable oil indicate that these oils have undergone a high level of decomposition to give secondary decomposition products. This study has revealed that even though the edible oils studied have nutritive values (as detected by fatty acid profile), unbranded edible oils sold in Umuahia do not conform to NAFDAC and FAO/WHO standard values for almost all parameters measured. Therefore, it can be concluded that the unbranded edible oils sold in Umuahia are highly saturated, adulterated, rancid, and not well refined. These oils were unsafe for consumption.

#### ACKNOWLEDGEMENTS

In a special way, we wish to thank Mr. Christian Nwachukwu, the Chief Technologist of Animal Nutrition and Biochemistry Laboratory, College of Animal Science and Animal Production (CASAP), Michael Okpara University of Agriculture, Umudike, Abia State, for providing us with all the assistance we needed in the laboratory.

#### REFERENCES

- ALADEDUNYE, F. A. (2015). Curbing thermooxidative degradation of frying oils: current knowledge and challenges. *European Journal of Lipid Science and Technology*, 117(11): 1867 – 1881.
- AOCS (2020). *Official Methods and Recommended Practices of the AOCS.* 7<sup>th</sup> Edition, American Oil Chemists' Society, Champaign, Illinois, United States.
- AVANTINA, S. (2010). *Textbook of Food Science and Technology.* 2<sup>nd</sup> Revised and Enlarged Edition, IBDC Publishers, Lucknow, Uttar Pradesh 226001, India.
- AYALA, A., MUÑOZ, M. F. and ARGÜELLES, S. (2014). Lipid peroxidation: production, metabolism, and signaling mechanisms of malondialdehyde and 4-hydroxy-2nonenal. *Oxidative Medicine and Cellular Longevity*, 2014: 360438. <u>https://doi.or</u> g/10.1155/2014/360438
- BÖTTCHER, S., STEINHÄUSER, U. and DRUSCH, S. (2015). Off-flavour masking of secondary lipid oxidation products by pea dextrin. *Food Chemistry*, 169: 492 – 498.
- CASWELL, J. A., YAKTINE, A. L. and NATIONAL RESEARCH COUNCIL (2013). Individual, household, and environmental factors affecting food choices and access. In *Supplemental Nutrition Assistance Program: Examining the Evidence to Define Benefit Adequacy.* National Academies Press, Washington, DC, USA.
- CHEN, W. A., CHIU, C. P., CHENG, W. C., HSU, C. K. and KUO, M. I. (2013). Total polar compounds and acid values of repeatedly used frying oils measured by standard and rapid methods. *Journal of Food and Drug Analysis*, 21(1): 58 – 65.
- CHOE, E. and MIN, D. B. (2005). Chemistry and reactions of reactive oxygen species in foods. *Journal of Food Science*, 70(9): R142 R159.

- CODEX ALIMENTARIUS (1999). Recommended Methods of Analysis and Sampling CXS 234-1999. Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission. https://www.fao.org/fao-who-codexalim entarius/sh-proxy/en/?lnk=1&url=https% 253A%252F%252Fworkspace.fao.org% b252Fsites%252Fcodex%252FStandard s%252FCXS%2B234-1999%252FCXS\_2 34e.pdf
- CODEX ALIMENTARIUS (2001). *Codex Standard for Named Vegetable Oils (CODEX-STAN 210 - 1999).* Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission. <u>https://www.fao.org/3/y2774e/y2774e0</u> <u>4.htm</u>
- CROSA, M. J., SKERL, V., CADENAZZI, M., OLAZÁBAL, L., SILVA, R., SUBURÚ, G. and TORRES, M. (2014). Changes produced in oils during vacuum and traditional frying of potato chips. *Food Chemistry*, 146: 603 – 607.
- DIEFFENBACHER, A. and POCKLINGTON, W. D. (1992). *Standard Methods for the Analysis of Oils, Fats and Derivatives.* 1<sup>St</sup> Supplement to the 7<sup>th</sup> Revised and Enlarged Edition, Commission on Oils, Fats and Derivatives, Applied Chemistry Division, International Union of Pure and Applied Chemistry (IUPAC), Blackwell Scientific Publications, Oxford.
- GALANO, J. M., LEE, Y. Y., DURAND, T. and LEE, J. Y. (2015). Special Issue on "Analytical Methods for Oxidized Biomolecules and Antioxidants" The use of isoprostanoids as biomarkers of oxidative damage, and their role in human dietary intervention studies. *Free Radical Research*, 49(5): 583 – 598.
- HENRY, L. N. (2016). Effect of light and air on the quality and stability of selected vegetable oils. *International Journal of Innovative Research in Science, Engineering and Technology*, 5(5): 6609 – 6616.
- HU, W. and CHEN, K. Z. (2008). Consumers' purchasing intentions for vegetable oil in the presence of generic or specific information on genetic modification.

*Journal of Agribusiness*, 26(2): 135 – 155.

- JOHNSON, M. A. C. B. and BRADFORD, C. (2014). Omega-3, omega-6 and omega-9 fatty acids: implications for cardiovascular and other diseases. *Journal of Glycomics and Lipidomics*, 4(4): 123. <u>https://doi. org/10.4172/2153-0637.1000123</u>
- KAUR, N., CHUGH, V. and GUPTA, A. K. (2014). Essential fatty acids as functional components of foods-a review. *Journal* of Food Science and Technology, 51(10): 2289 – 2303.
- KELLER, J., CAMARÉ, C., BERNIS, C., ASTELLO-GARCÍA, M., DE LA ROSA, A.P.B., ROSSIGNOL, М., DEL SOCORRO SANTOS DÍAZ, M., SALVAYRE, R., NEGRE-SALVAYRE, A. and GUÉRAUD, F. (2015). Antiatherogenic and antitumoral properties of Opuntia cladodes: inhibition of low density lipoprotein oxidation by vascular cells, and protection against the cytotoxicity of lipid oxidation product 4-hydroxynonenal in a colorectal cancer cellular model. Journal of Physiology and Biochemistry, 71(3): 577 - 587.
- KERRIHARD, A. L., PEGG, R. B., SARKAR, A. and CRAFT, B. D. (2015). Update on the methods for monitoring UFA oxidation in food products. *European Journal of Lipid Science and Technology*, 117(1): 1 – 14.
- LEE, J., KOO, N. and MIN, D. B. (2004). Reactive oxygen species, aging, and antioxidative nutraceuticals. *Comprehensive Reviews in Food Science and Food Safety*, 3(1): 21 – 33.
- LEE, R. F. (2003). Photo-oxidation and phototoxicity of crude and refined oils. *Spill Science and Technology Bulletin*, 8(2): 157 – 162.
- LI, J., SOLVAL, K. M., ALFARO, L., ZHANG, J., CHOTIKO, A., DELGADO, J. L. B., CHOULJENKO, A., BANKSTON, D., BECHTEL, P. J. and SATHIVEL, S. (2015). Effect of blueberry extract from blueberry pomace on the microencapsulated fish oil. *Journal of Food Processing and Preservation*, 39(2): 199 – 206.

- LI, Y., NGADI, M. and OLUKA, S. (2008). Quality changes in mixtures of hydrogenated and non-hydrogenated oils during frying. *Journal of the Science of Food and Agriculture*, 88(9): 1518 – 1523.
- LOTFY, H. R., MUKAKALISA, C. and RAIDRON, C. (2015). Analysis of different Namibian traditional oils against commercial sunflower and olive oils. *African Journal of Food Science*, 9(6): 372 – 379.
- NAFDAC (2019). *Fats and Oils Regulations 2019.* National Agency for Food and Drug Administration and Control (NAFDAC), Abuja, Nigeria. <u>https://www.nafdac.gov.</u> ng/wp-content/uploads/Files/Resources /Regulations/Food Regulations/Fats-an <u>d-Oils-Regulations-2019.pdf</u>
- NEGRE-SALVAYRE, A., COATRIEUX, C., INGUENEAU, C. and SALVAYRE, R. (2008). Advanced lipid peroxidation end products in oxidative damage to proteins. Potential role in diseases and therapeutic prospects for the inhibitors. *British Journal of Pharmacology*, 153(1): 6 – 20.
- ODOH, C. K., AMAPU, T. Y., ORJIAKOR, I. P., MARTINS, P. E., SEIBAI, B. T., AKPI, U. K., UGWU, C. S., LERUM, N. I. and NWANKWEGU, A. S. (2017). Assessment of mold contamination and physicochemical properties of crude palm oil sold in Jos, Nigeria. *Food Science and Nutrition*, 5(2): 310 – 316.
- OLPIN, S. E. (2005). Fatty acid oxidation defects as a cause of neuromyopathic disease in infants and adults. *Clinical Laboratory*, 51(5-6): 289 – 306.
- RODRIGUEZ-LEYVA, D., BASSETT, C. M., MCCULLOUGH, R. and PIERCE, G. N.



(2010). The cardiovascular effects of flaxseed and its omega-3 fatty acid, alpha-linolenic acid. *Canadian Journal of Cardiology*, 26(9): 489 – 496.

- SUN, Y. E., WANG, W. D., CHEN, H. W. and LI, C. (2011). Autoxidation of unsaturated lipids in food emulsion. *Critical Reviews in Food Science and Nutrition*, 51(5): 453 – 466.
- UBHAYASEKERA, S. K. A. (2009). *Sterols and Oxysterols: Occurrence and Analysis in By-Products Feed Fats and Animal Tissues.* Doctoral Thesis, Department of Food Science, Faculty of Natural Resources and Agricultural Sciences, Swedish University of Agricultural Sciences, Uppsala.
- WEISS, T. J. (1963). Fats and oils. *In:* HEID, J. L. and JOSLYN, M. A. (Eds.). *Food Processing Operations, Volume 2, Their Management, Machines, Materials, and Methods.* AVI Publishing Company, Westport, Connecticut, USA.
- YIN, H., XU, L. and PORTER, N. A. (2011). Free radical lipid peroxidation: mechanisms and analysis. *Chemical Reviews*, 111(10): 5944 – 5972.
- ZHANG, C., BAI, J. and WAHL, T. I. (2012a). Consumers' willingness to pay for traceable pork, milk, and cooking oil in Nanjing, China. *Food Control*, 27(1): 21 – 28.
- ZHANG, Q., SALEH, A. S., CHEN, J. and SHEN, Q. (2012b). Chemical alterations taken place during deep-fat frying based on certain reaction products: a review. *Chemistry and Physics of Lipids*, 165(6): 662 – 681.

This article and articles in Animal Research International are Freely Distributed Online and Licensed under a Creative Commons Attribution 4.0 International License (CC-BY 4.0) https://creativecommons.org/licenses/by/4.0/