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Full Length Research Paper

Degradation properties of wild *Adansonia digitata* (Baobab) and *Prosopsis africana* (Lughu) oils on storage

I. I. Nkafamiya, B. A. Aliyu, A. J. Manji, and U.U. Modibbo

Department of Chemistry, Federal University of Technology, Yola Adamawa State, Nigeria.

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The deterioration of *Adansonia digitata* and *Prosopsis africana* oils on storage for 140 days was evaluated using chemical and physical parameters. The chemical parameters evaluated included peroxide value (PV), iodine value (IV), percentage free fatty acids (%FFA), and saponification value (SV). The physical parameters used involved the measurement of infrared (IR) spectroscopy and refractive index (RI). The metallic ions present in the *A. digitata* and *P. africana* oil have been analysed using atomic absorption spectroscopy (AAS). The metallic ions found to be present included calcium (Ca), iron (Fe), zinc (Zn), phosphorus (P), potassium (K) and sodium (Na) with potassium occurred in relatively high amount in *A. digitata oil* (280 ± 1.34 mg/100 g). Systematic variations in these parameters with storage time were observed. These include initial increase followed by decrease in peroxide value, iodine value and increase in free fatty acids, saponification value and refractive index. These changes have been interpreted to be due to some structural changes in the triglyceride leading to the formation of new chemical properties or products over the period of storage. The IR spectra also have given an indication of the rancid state of the oils, due to bands observed at 3470 – 3490, 1745 – 1740, 970 and 870-890 cm^{-1} for hydroperoxides, ester C = O stretching (indicating possible formation/presence of aldehyde, ketones and acids), trans-isomer, peroxides, respectively, which are products of oxidative rancidity.

Key words: Wild plants, *Adansonia digitata, Prosopsis africana,* deterioration, mineral elements, seed, oil.

INTRODUCTION

Adasonia digitata and Prosopsis africana are both wild plants that occur in arid and semi-arid zones of America, Africa and Asia, where 44 species have been reported (Becker et al., 1984). In these regions both plants offer shade and forage for wild life and domestic animals. The indehiscent pods of *P. africana* are palatable to man and animals as well *A. digitata* specie, which can be found growing in Northern Nigeria while *P. africana* specie is found growing in both Northern and Middle-Belt of Nigeria. The seeds of *A. digitata* are used in the preparation of local condiment called “daddawa Higgi” in Michika Local Government Area of Adamawa State, Nigeria (Nkafamiya et al., 2006), while *P. africana* seeds are also used in preparation of local condiment called daddawa Hausawa in most Hausawa States in Nigeria (Barminas et al., 1998). Both condiments are used for flavoring local soups. Apart from flavoring, these products also increase the aesthetic appeal and taste of soups. These seeds offer a convenient and cheap means of providing adequate supplies of minerals, fat, protein, carbohydrate and fiber to the people living with the area (Carlowitze, 1985). Barminas et al. (1998) and Nkafamiya et al. (2006) reported that the seeds from both plants have higher vitamins compared with levels found in cultivated nuts and seeds. In North eastern part of Nigeria where common nuts and seeds like cotton seeds and groundnuts are short in supply, it is possible for seeds from *A. digitata and P. africana* to provide the vitamin and mineral requirements of the local populace.

*Corresponding authors E-mail: iliyankafamiya@yahoo.com.

Fats and oils are the commercially important group of substances classified as lipid (Abraham and Hron, 1992). They are important components in the human diet and more than 90% of the world production is used as food or as ingredient in food production (Elaine, 1990). They serve as rich source of dietary energy. Their fatty acid components are essential nutrients, while their functional and textural characteristics contribute to the flavour and palatability of manufactured and prepared foods (FAO, 1978).

As the oils and fats or their products are used and stored for future use, some changes occur which result in the production of unpleasant tastes and odour. One of the major changes taking place is generally referred to as rancidity (Hill, 1992). The typical sharp unpleasant odour of rancidity is believed to be mainly due to the presence of aldehyde of medium molecular weight and particularly heptylic and nonoic aldehydes. Such compounds may be formed by the oxidation and rapture of fatty acid chain for example, as illustrated in the equation below (Joseph, 1977).

$CH_2\ (CH_2)_7CH{=}CH\ (CH_2)_7CO_2R \longrightarrow +O_2CH_2\ (CH)_7CHO$ + other oxidation products (Oleic acid glyceride) (Oxygen) Nonoic aldehyde (ketones, alcohols, acids etc)

During the period of storage and usage in the process of food preparation, fats and oils or their products are at the same time exposed to air which results in a complex series of reactions that generating a wide spectrum of new components, both volatile and non-volatile, that may have important physiological effects. From the nutritional viewpoint, the non-volatile products of degradation are more important, because they remain in the oil, and absorbed by the food items processed and are later consumed (Soriguer et al., 2003). The functional sensory and nutritional qualities of stored fats and oils or their products are also changed during storage and a point may be reached where high quality foods can no longer be prepared in them (Fritsch, 1981).

Studies have also revealed that the higher the degree of unsaturation (high iodine value), the greater the tendency of the fat to oxidative rancidity (Joseph, 1977). As the concentration of peroxides increases, complex chemical changes occur leading to further oxidation forming diperoxides and ultimately to polymer formation. Fission reactions are likely forming aldehydes, semi-aldehydes, aldehydro-glycerides, hydroxy-compounds and subsequently organic acids. Dehydration leads to formation of keto-glycerides and dihydroxy-glycerides. The resulting compounds produce rancidity or off-flavour (Evans et al., 1974 and Egan et al., 1990).

With time, the oils and fats from both *A. digitata* and *P. africana* have a tendency to go bad during storage. It was therefore the objective of this research work to determine the onset of deterioration of *A. digitata* and *P. africana* oils. The result of this research will assist the users of these oils to know the storage period and aware of the rejection point (when the stored oils are no longer good for food preparation) so as to safeguard them from using oils that have gone bad.

MATERIALS AND METHODS

Samples used and chemical analysis

Plant samples were collected from Nkafamiya, Michika Local Government Area of Adamawa State of Nigeria. Samples were dried under room temperature and made into powder for subsequent analysis. The oils from the seeds were soxhlet extracted with petroleum ethers (40 - 60°C). All the reagents used were of analytical grades. The oil was stored for 140 days at room temperature (30 ± 2°C) under vacuum and chemical parameters were tested at two weeks intervals over the said period. The chemical parameters (peroxide value, iodine value, percentage free fatty acidss and saponification value) were tested based on America Oil Chemist Society (AOAC, 1980)

Atomic absorption spectroscopy (AAS) analysis

Sample for AAS study were prepared by dry ashing and 150 g of sample were charred at high temperature (600°C) for two days followed by heating in muffle furnace at 400°C for 2 h. This was followed by addition of distilled water and acid solution to a set volume (50 cm^3). Aqueous solution was transferred to propylene bottle for subsequent AAS analysis (AOAC, 1980; Eromosele and Eromosele, 1992)

Determination of peroxide value (PV)

Five grams of the oil was dissolved in 30 ml of glacial acetic acid: chloroform (3:2, v/v). 0.5 ml of saturated KI was added and I_2 was liberated by the reaction with the peroxide. The solution was then titrated with standardized sodium thiosulphate using starch indicator. The peroxide value (PV) was determined from the following equation:

PV (mEq/Kg) = [(S-B) x M x 1000] / Sample weight (g)

Where S = sample titre value, B = blank titre value and M = molarity of $Na_2S_2O_3$.

Determination of iodine value (IV)

0.1 M iodine monochloride in acetic acid was added to 0.2 g of the oil dissolved in cyclohexane. The mixture was allowed to stand for 10 min, to allow for halogenation. 0.1 M of KI solution was added to reduce excess iodine monochloride to free iodine. The liberated iodine was titrated with a standardized solution of 0.1M sodium thiosulphate using starch indicator. The iodine value was calculated from the following equation:

IV = [(B-S) x M x 12.69] / Sample weight (g)

Where B = blank titre value, S = sample titre value, M = molarity of $Na_2S_2O_3$ and 12.69 = conversion factor from Meq. $Na_2S_2O_3$ to gram iodine (molecular weight of iodine is 126.9 g).

Determination of percentage free fatty acidss (%FFA)

Two grams of well-mixed sample was accurately weighed into a

Table 1. Mineral composition (mg/100g) of *Adasonia* digitata and *Prosopsis africana* before storage.

Seed	P	Ca	K	Na	Zn	Fe
Adasonia digitata	6.00±0.02	58.90±2.34	280.00±1.34	6.07±0.04	3.60±0.04	6.36±0.42
Prosopsis africana	275.13±1.83	118.73±2.43	278.12±1.43	5.06±0.03	3.46±1.04	5.63±0.24

Values are means ± SD for 3 determinations

conical flask into which 10 ml of neutralized 95% ethanol and phenolphthalein were added. This was then titrated with 0.1 M NaOH, shaking constantly until a pink colour persisted for 30 s. The free fatty acid was calculated as follows:

%FFA = (V× M × 2.82 mg) / Sample weight (g)

Where V = Volume of NaOH, M = molarity of NaOH and 2.82 = conversion factor for oleic acid.

Determination of saponification value (SV)

Two grams of the oil sample was added to excess alcoholic KOH. The solution was heated for two minutes to saponify the oil. The unreacted KOH was back-titrated with standardized 0.1 M HCl using phenolphthalein indicator. The saponification value was calculated from the following equation:

SV = [(S-B) x M x 56.1] / Sample weight (g)

Where S = Sample titre value, B = blank titre value, M = molarity of the HCl and 56.1 = the molecular weight of KOH.

Physical parameters

The refractive index (RI) and infrared (IR) spectrum were also determined using the method described by AOAC (1980).

Test for the presence of aldehyde in the oil

The presence of aldehyde in the oils was carried out by the method described by Cocks and Van (1997).

RESULTS AND DISCUSSIONS

The mineral composition of the oil is presented in Table 1. The oil contains calcium (Ca), iron (Fe), zinc (Zn) phosphorus (P), potassium (K) and sodium. Of these potassium occurs in relatively higher amount (280 ± 34 mg/100 g and 278.12 ± 1.43 mg/100 g) for *A. digitata* and *P. Africana*, respectively. Higher values of P and Ca were determined in *P. africana* oils compared to *A. digitata.* However, Na, Zn and Fe values were not very much different with relatively lower values of *P. africana.*

The variation of peroxide value with storage time in days is presented in Figure 1. It was observed that the peroxide value for the oils increased with time of storage and passed through a maximum. The initial increase in peroxide value values up to a maximum may be due to the fact that the rate of production of peroxide out weighs

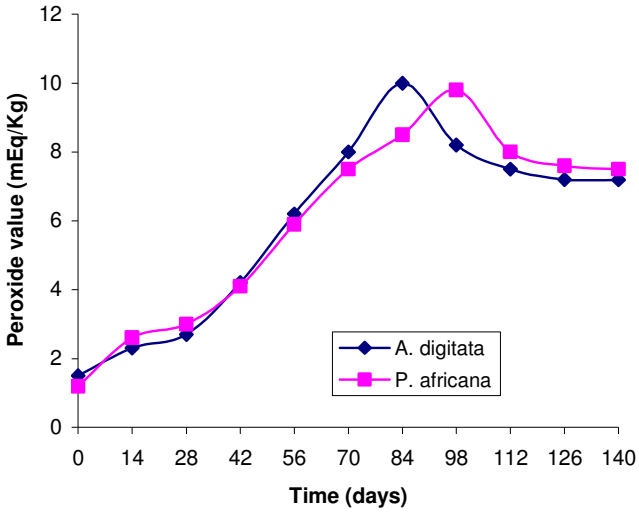

Figure 1. Variation of peroxide value of *Adansonia digitata* and *Prosopsis africana* oils during storage.

the rate of decomposition of the peroxide. The decrease in peroxide value values may also suggest that the rate of consumption of the peroxide out weighs the rate of production. The maximum peroxide value value for *A. digitata* was attained after 84 days, and the change in peroxide value values appears to be more rapid throughout the period of study than that of *P. africana* in which the maximum peroxide value was obtained after 98 days. Since the change is more rapid in the peroxide value of *A. digitata*, it might be possible that the oil or the products prepared using the seeds deteriorate fast. This may be due to many factors, which include the initial amount of fatty acids present and the presence of metallic ions, which is one of the factors that promote or enhances oxidation after the formation of hydro peroxide (Rossell, 1984).

The iodine value for the oil shows non-uniform increase followed by a constant decrease. The fluctuating values may be due to dehydrogenation and saturation. The decrease in iodine value values is an indication of lipid oxidation, since there is a decline in unsaturation during oxidation (Figure 2). Holiday and Pearson (1974) have also reported similar observation for the oil from soya bean. As in the case of peroxide value, the iodine value of *A. digitata* also decreases faster than that of *P. africana.* Since decrease in iodine value indicate lipid oxidation, the *A. digitata* oil or products prepared using the seed will deteriorate fast.

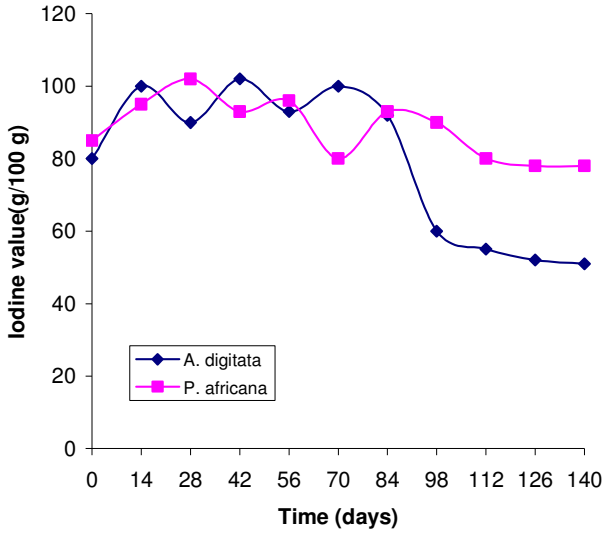

Figure 2. Variation of iodine value of *Adansonia digitata* and *Prosopsis africana* oils during storage.

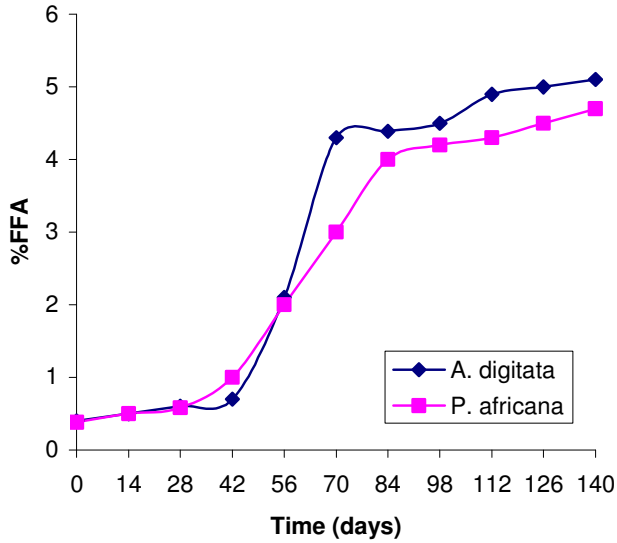

Figure 3. Variation of free fatty acids of *Adansonia digitata* and *Prosopsis africana* oils during storage.

The values for free fatty acids over the period study showed an initial increase with storage time. The increase in free fatty acids suggests those reactions which led to the formation of free fatty acidss, occurred during storage process (Figure 3). Joseph (1979) and Magnus (1992) have reported similar observation for the oils from damaged soya bean and cotton seeds.

The pattern of change in saponification value (SV) showed little increase over the period of study, with storage time. This behaviour is parallel to other trends observed in the variation of other parameters for the oils. The increase in saponification value may indicate oxidation and the decrease suggest the unset of oxidation (Figure 4). From the Figure 4, we can see that there are three transitions. The first transition suggest the formation of lower molecular weight oxidation products, that is peroxide and hydro peroxide which decomposed to give higher molecular weight oxidation products like aldehydes and ketones in the second transition. The third transition also suggests the on set of oxidation (Rossell, 1984).

The refractive index value of the oils increased with storage time (Figure 5). This may be due to production of oxidation products. Studies have shown that refractive index increases by value of 0.001 as rancid odour is noticeable (Rossell, 1984). This also confirmed the result obtained from the saponification value.

To confirm the oxidation of the oil, a chemical test was carried out to test for the presence of aldehyde, which is responsible for unpleasant odours in oils. The test shows that at the beginning of the study, aldehyde was absent and present at the end of the study.

The IR spectroscopy of both oils showed bands at 3470 – 3494 cm^{-1} which strongly suggest the presence of hydroperoxide, 1745 – 1740 cm^{-1} suggest ester C = O stretching which indicates possible formation/presence of

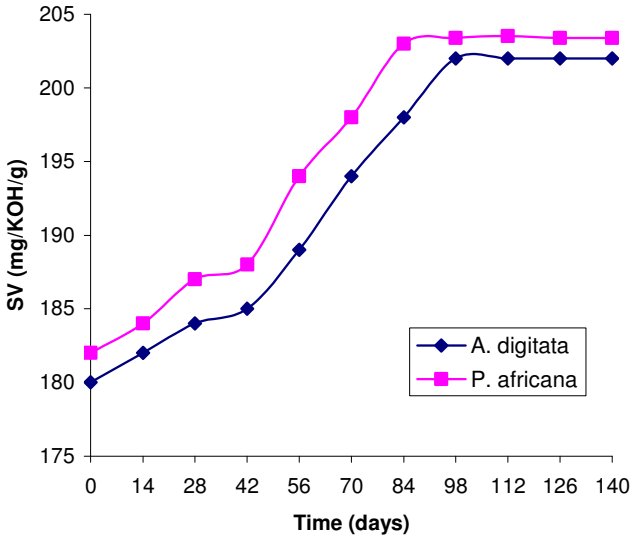

Figure 4. Variation of saponification value of *Adansonia digitata* and *Prosopsis africana* oils during storage.

aldehyde, ketones and acids, 1650 – 1654 cm^{-1} suggests conjugation of double bond and bands at 159 - 1164 and 1100 cm^{-1} also suggests presence of methyl ester and secondary alcohol. Others at 970, 853 - 890 and 797 - 799 cm^{-1} suggests the presence of trans-isomer, peroxides and epoxy (Coates, 2004). These bands are tentatively indicating the formation of new compounds (due to decomposition of hydroperoxide), which were not present at the beginning of the study but were detected at the end of the study. These compounds are assumed to be products of degradation, which are responsible for the deterioration of the oil.

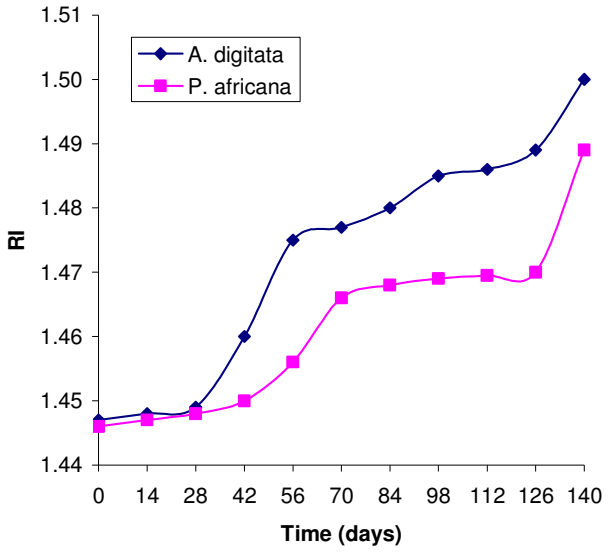

Figure 5. Variation of refractive index of *Adansonia digitata* and *Prosopsis africana* oils during storage.

In conclusion, from the changes of the chemical and physical parameters, it can be concluded that the rejection point of the oil can be assigned tentatively to be 84 days for *A. digitata* and 98 days for *P. africana* after extraction. At this point all the parameters used for monitoring the deterioration showed clear and sharp variations which suggests that the oil had gone bad such that it may not be advisable to keep on using the oil in food preparation. However, such oils can put into other uses like soap making. The shelf life of the oils can be prolonged by storing the oils at relatively low temperatures (below 30°C). Exposing the oils to air or radiation may result into complex series of reaction generating wide spectrum of new components. In addition the moisture content should be reduced coupled with the addition of antioxidants like butylated hydroxyanisole (BHA), which break the oxidation chain by containing the free radicals or acting as hydrogen donors. The antioxidants also direct the breaking down of peroxide into stable substances that do not promote further oxidation.

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