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Physicochemical properties and storage stability of the raw seed oil of *Huracrepitans*at room temperature

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Abstract
The physicochemical properties and storage stability of *Hura crepitans* raw seed oil are reported. The objective was to study the stability of the oil with respect to time and exposure to light at room temperature. The seeds were collected along Nto Nsek Road, Essien Udim Local Government Area, Akwa Ibom State, Nigeria. The oil was cold-extracted with n-hexane and divided into six portions; three were labeled “light” and kept on the laboratory bench and the other three were labeled “dark” and placed in a dark laboratory locker away from any effects of light. The physicochemical properties were determined using standard methods. It was observed that peroxide value, acid value, free fatty acid, and unsaponifiable matter increased with increase in the number of days of storage. Increase in those values was greater in the oil kept on the laboratory bench than in the oil kept in the dark. Decreases were however observed in the physicochemical properties like iodine value, saponification value, density, vitamin A, absorbance, specific gravity and viscosity. The oil is thus unstable to room temperature storage and should be used as soon as possible after extraction if its wholesome properties are to be maintained. Stray light reaching the oil on the laboratory bench may have aided the observed higher degree of deterioration of the oil under light condition than in the dark condition. Only the fresh oil could be used as industrial oil.

1. Introduction
Hura crepitans, commonly known as *sandbox tree*, is an evergreen tree of the spurge family *Euphorbiaceae* [1, 2]. It is known by its many dark, pointed spines and smooth brown bark. These spines have caused it to be called Monkey no-climb. The tree grows to a height of about 60 meters [3] with large ovate leaves. Besides being a source of seed oil [4], *H. crepitans* has edible uses, industrial and pharmaceutical applications [1, 4, 5-7] but much still need to be done [8]. In particular, the oil has been evaluated for use as a biodiesel feedstock [4, 7-10].
Fishermen use the milky, caustic sap from this tree to poison fish while the Caribs made arrow poison from its sap [11]. The wood is used for furniture under the name "Hura"[12]. Before more modern forms of pens were invented, the trees' unripe seed capsules were sawn in half to make decorative pen sandboxes (also called pounce pots) and hence the name 'sandbox tree' [11]. *H. crepitans* tree is mainly cultivated for shade in private compounds in Nigeria and as a shade plant on highways. Hence its abundance increases daily. Shahidan *et al*.[13] described the possible use of the plant in shade creation and radiation modification to imporove thermal comfort.
Seed oils are vegetable oils that are obtained from the seed endosperm of some plants, rather than the fruit (pericarp). Seed oils serve as important sources of nutritional oils and are of pharmaceutical importance [14]. They also serve as important industrial and domestic materials for various processes particularly as the rise in price of crude oil has put a new shine on the biofuel sector [15]. Vegetable oils play important functional sensory roles in food products, and they act as carriers of fat soluble vitamins A, D, E and K [16]**.** Right from ancient times, the believe has been that oils degrade in physical properties such as color, taste, rancidity, viscosity and lots more,

with time increment, storage conditions as well as storage containers; this deterioration has led to oxidation of the oil thereby producing foul smell and bad taste. Some seed oils such as soybean oil, sunflower oil and date seed oil are known to deteriorate when processed inadequately with the principal decomposition reaction being oxidation [14, 17-19]. Oxidation in seed oil occurs through a free radical mechanism, initially characterized by the emergence of a sweetish and unpleasant odor which progressively worsens until it attains a characteristic smell of rancid fat [20]. Oderinde *et al.* [14] subjected raw *H. crepitans* seed oil to high temperature treatment to study its stability properties and from the results suggested that the seed oil has industrial applications. However, no industrialist or manufacturer ever buys oil and stores it at a high temperature. High temperature treatment of any oil is usually to refine it or as a preliminary step towards conversion of the oil into other products. Despite the reported numerous applications of the seed oil, there is no record of the storage properties of the oil at ambient temperature which should however guide uses and applications.

2. Matherials and Methods

All the reagents used in this work were of analytical reagent grade and were used as obtained without further purification.

2.1 Collection of the seeds and extraction of the seed oil

Mature dry fruits of *H. crepitans* were collected along a village road in Nto Nsek in Essien Udim Local Government Area of Akwa Ibom State, Nigeria. The seeds were carefully removed from the pods; good quality seeds were hand-picked to separate them from the bad ones while the endocarp was gently removed to get the creamy white cotyledons inside. The cotyledons were later oven-dried at a temperature of 105ºC. Finally, the dry cotyledons were ground into powder and used for the extraction of the oil.

The oil was extracted using cold extraction method whereby the seed powder was accurately weighed and then soaked in n-hexane for 24 hours. The supernatant was then decanted and allowed to settle. The decant containing the oil extract and the solvent (n-hexane) was put in a rotary evaporator to recover the n-hexane.

2.2 Physiochemical characterization of the seed oil

The various parameters were determined as described by the Association of Official Analytical Chemists, AOAC [21]. All determinations were carried out in triplicates and average results used in plotting the curves.

2.3 Oil stability studies

The extracted oil was then divided into two portions; one portion was kept on the laboratory table where transient light from both electric bulbs and stray sunlight could reach the oil while the other portion was kept in the dark cupboard. All oil samples were kept at those storage conditions throughout the period of analysis; aliquots were only taken out for analysis at the appropriate time interval.

3. Results and Discussion

3.1 Physicochemical properties of the raw seed oil

The physicochemical properties of the raw seed oil are presented in Table1. The oil content of *H. crepitans* seed was found to be 46.02%. The values compare favorably with those obtained by Oyekunle and Omode [22], Okolie *et al*. [4], and Umoren *et al*. [23]. The oil content is also comparable with those of other seed oils like *Cordia sebestena*, 40.3% reported by Agunbiade *et al.*[24] and *Moringa oleifera*, 38.3% reported by Lalas and Tsaknis [25]. Hence, *H. crepitans* seed can be classified as a moderate oil seed. The difference in the oil yield obtained in this study in comparison with literature values could be partly due to differences in location of the plant and time of harvest [1].

3.2 Storage stability

3.2.1 Peroxide value

Peroxide values (PV) are sensitive indicators of the oxidative status of lipids. Pervading off-odors are due to peroxide oxidation products that include aldehydes, ketones and lower molecular weight carboxylic acids [26]. Although the peroxide value is applicable for monitoring peroxide formation in the early stages of oxidation, it is nevertheless highly empirical and its accuracy is questionable [27].

Table 1: Physicochemical parameters of the seed oil of the *H. crepitans* in comparison with literature values

Property/ unit	Values			
Oil content (%)	46.01[a]	47.80[22]	53.61[4]	38.20[23]
Peroxide value (mg/g oil)	6.83	9.10	3.83	2.14
Acid value (mgKOH/g oil)	1.98	4.10	27.09	1.64
Iodine value (mgKOH/g oil)	64.29	149.10	177.66	122.08
Saponification value (mgKOH/g oil)	132.49	202.00	245.98	210.38
Specific gravity	0.92	ND	0.94	ND
Density (g/ml)	0.8634	ND	ND	ND
Free fatty acid (%)	3.33	2.0	14.01	ND
Unsaponifiable matter (%)	4.13	1.20	ND	1.14
Viscosity	19.24	ND	41.50	ND
Vitamin A	2.491	ND	ND	ND
Absorbance (at 233nm)	1.166	ND	ND	ND

a: This work; ND: Not Determined

The effect of period of storage on the formation of primary oxidation products, expressed as peroxide value (PV), versus time of storage is shown in Fig.1. The peroxide value of the fresh oil of *H. crepitans* (6.83mg/g) revealed that the oil was not rancid as rancid oil ranges from 20.00 to 40.00 mg/g [28]. It is seen from Fig.1 that PV increased with increase in the period of storage. From samples exposed to daylight, PV increased sharply to 11.50 mg/g after 7 days, and 14.30 mg/g after 69 days. The PV of the oil stored in darkness (Fig.1) did not reveal such a sharp increase after the first month of storage; PV increased from 6.82 to 10.33 mg/g after 7 days, and in the next 69 days it reached 13.78 mg/g. This indicated a progressive increase in both storage conditions. Deterioration increases with increase in PV values [26].

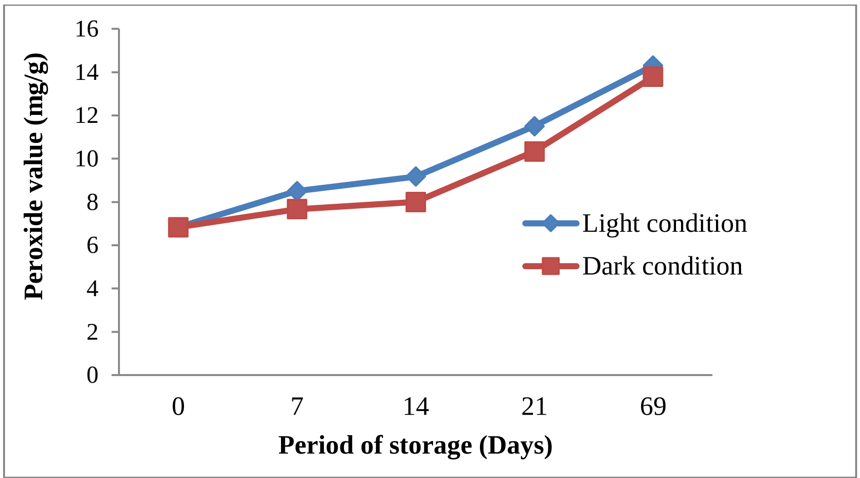

Figure1: Variation of peroxide value against time

3.2.2 Free fatty acid (FFA)

The variation of free fatty acid with period of storage is shown in Fig. 2. Free fatty acid contents increased progressively with increase in the period of storage. The increase was more in the sample stored under light condition. As peroxide value increases, free fatty acid increases [26]. Unsaturated acids have a lower melting point compared to saturated fatty acids of similar chain length [29]. The formation of free fatty acid is generally responsible for the soapy taste in oils [26]. Increase in FFA with storage time implied increase in oxidation and hence instability.

3.2.3 Acid value

The variation of acid value with storage time is shown in Fig. 3. The acid value was quite low at first (1.98 mgKOH/g). For an oil to be applied in cooking, the acid value should fall within the range 0.00 – 3.00mgKOH/g [14]. From Fig. 3, the acid value of the oil increased progressively with period of storage although the increase was higher in the oil kept under light condition. The acid value increased with increase in period of storage. As oil rancidifies, triglycerides are converted into fatty acids and glycerol; causing an increase in acid number. Thus, acid value increased with increase in deterioration.

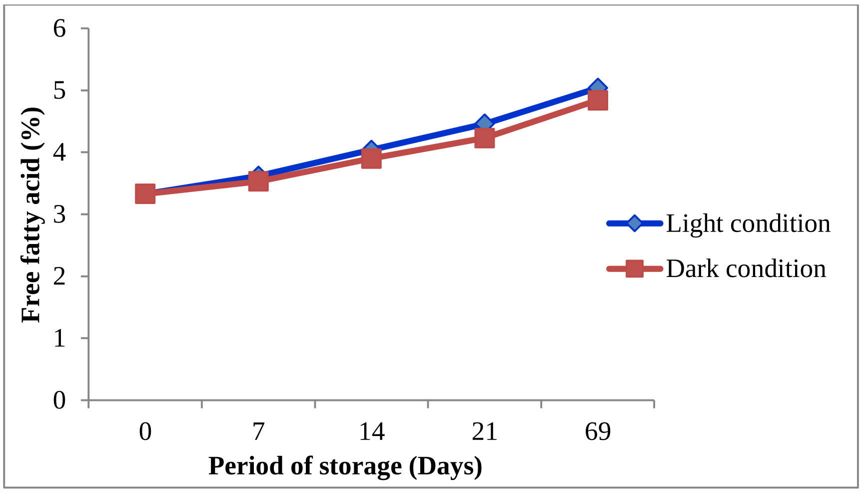

Figure 2: Variation of free fatty acid against time

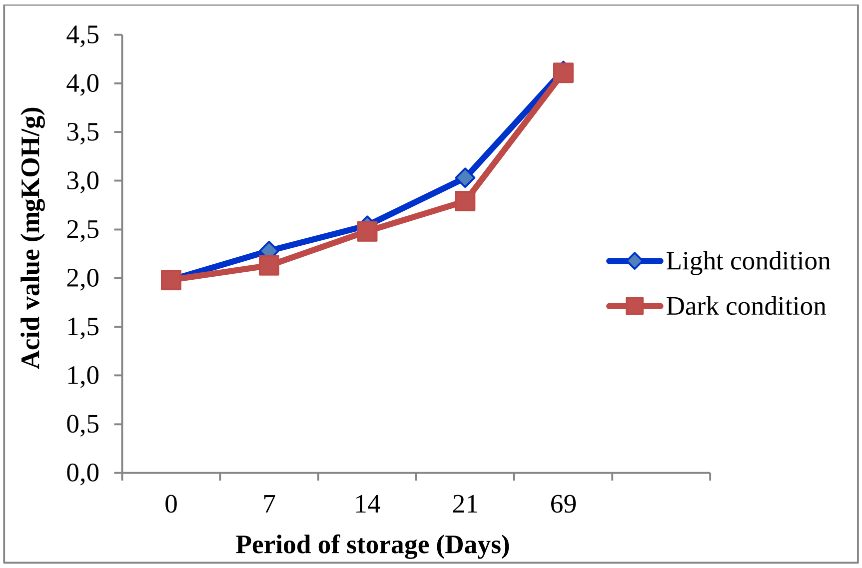

Figure 3: Variation of acid value against time

3.2.4 Iodine value

Iodine value is a measure of the degree of unsaturation in an oil and it is an identity characteristic of native oil [14]. As observed in Fig. 4, iodine value tended to decrease with increase in storage time. The iodine value was low but similar to that of *Moringa oleifera*, 65.58 obtained by Lalas and Tsaknis [25]. This indicated that the oil is unsaturated. The iodine value suggested the presence of unsaturated fatty acids, which are essential in food oils and this places the oil in a semi-drying group [23]. The decrease in iodine value was higher in the oil stored under light conditions. As storage time increased, iodine value decreased progressively indicating reduction in the level of unsaturation of the oil.

3.2.5 Saponification value

Saponification value (SV) is a measure of the average molecular weight of the fat and oil [29]. The higher the SV, the lower the average molecular weight and chain length of the constituent fatty acids making up the triglyceride molecule [26]. The variation of the saponification value with respect to storage time is presented in Fig. 5. Saponification value, however, decreased with increase in storage time; the decrease is greater in the oil stored under the light condition. The high saponification value for *H. crepitans* raw seed oil implies that the oil is richer in short-chain fatty acids, oleic acid and linoleic acid [5]. Short chain fatty acids are of lower melting points and are more soluble in water than the long-chain fatty acids [5]. The high saponification value also implied that the oil could be used for cosmetic purposes [23].

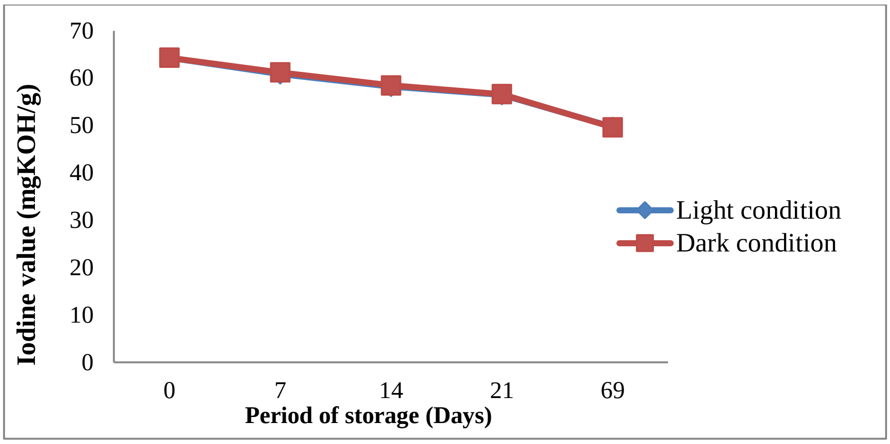

Figure 4: Variation of iodine value against time

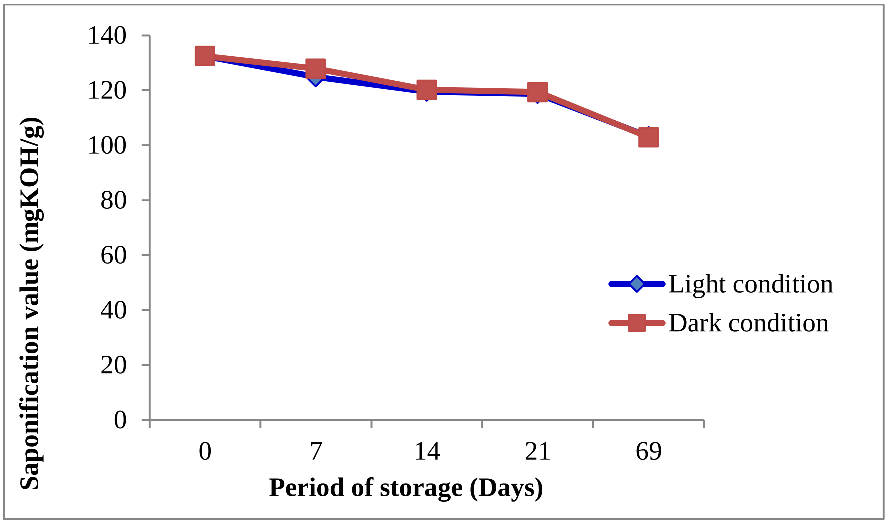

Figure 5: Variation of saponification value against time

3.2.6 Unsaponifiable matter

The variation of unsaponifiable matter with respect to the period of storage is presented in Fig. 6. The unsaponifiable matter increases with increase in storage time.

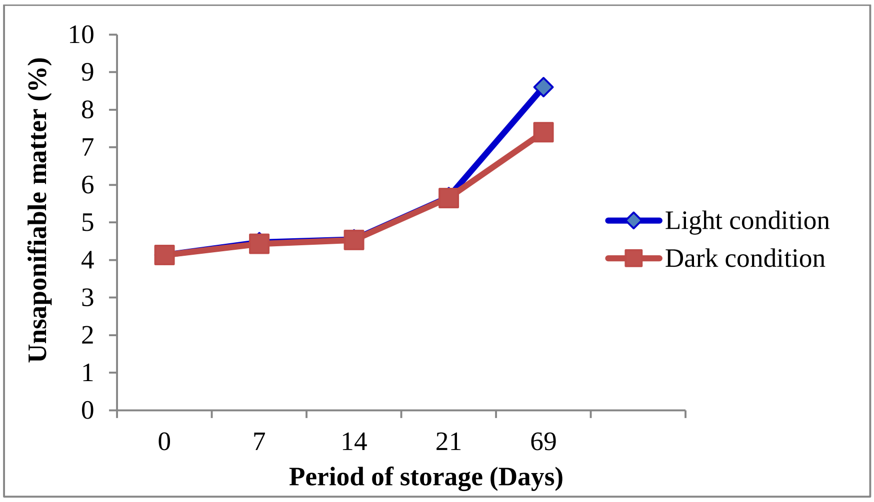

Figure 6: Variation of unsaponifiable matter against time

The initial low unsaponifiable matter content reveals that the oil can be used for cosmetic purposes [23]. Increase in unsaponifiable matter as storage time increased resulted in the deterioration of the oil.

3.2.7 Absorbance

The variation of the absorbance with respect to the period of storage is presented in Fig. 7. There was a marked decrease in the absorbance of the oil, both in the light and dark conditions as the storage time increased. This is because the conjugated diene bond in the oil was broken down as a result of oxidation into ketone and aldehyde groups which led to a decrease in the value of absorbance. The new products formed are more saturated and resulted in the stability of the oil.

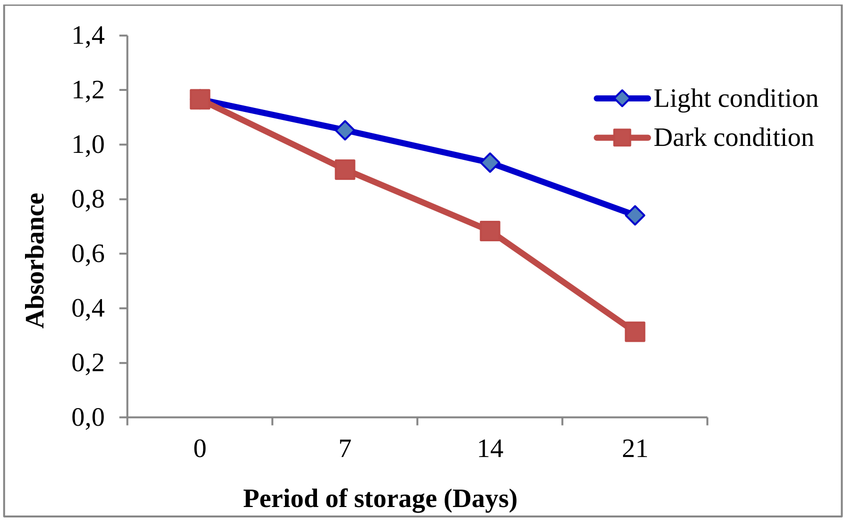

Figure 7: Variation of absorbance against time

3.2.8 Density

The decrease in weight may be attributed to partial evaporation of other volatile compounds. As oxidation proceeded, oxygen was incorporated into unsaturated fatty acids and more hydroperoxides were formed. The hydroperoxides formed are less dense than the initial oil components [18], thus, the density of the oil decreased with increase in storage time (Fig. 8).

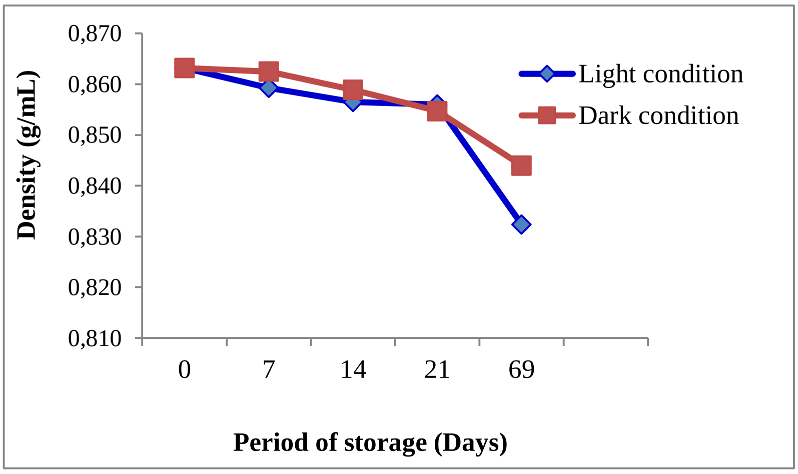

Figure 8: Variation of density against time

3.2.9 Specific gravity

The specific gravity of the oil fitted into the range of values of specific gravities for industrially established vegetable oils [30]. However, as the oil deteriorated with storage, specific gravity decreased progressively. The oil stored in the light condition deteriorated faster than the oil stored in the dark condition (Fig. 9). Decrease in specific gravity implied increase in deterioration with storage.

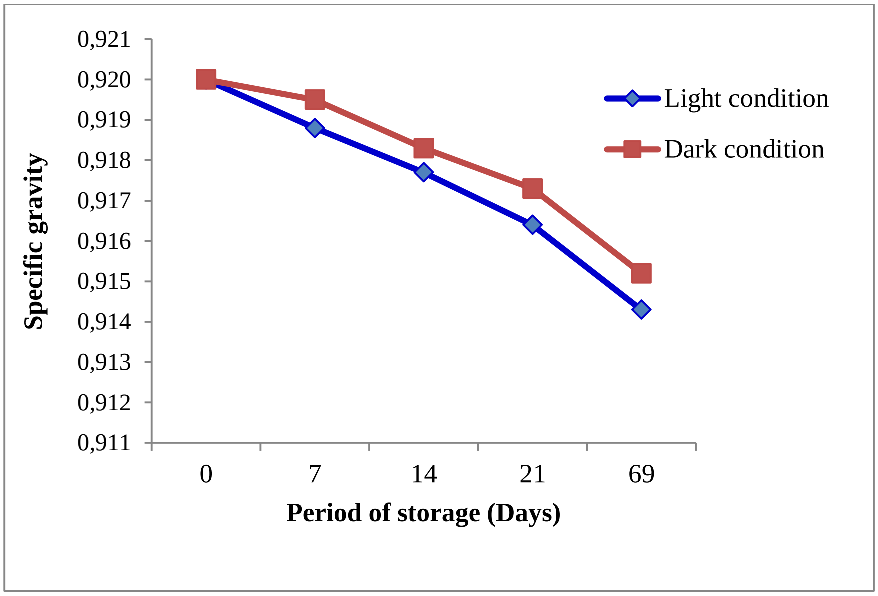

Figure 9: Variation of specific gravity against time

3.2.10 Viscosity

The viscosity of a liquid is required for the design of heat transfer equipment, process piping design and pressure drop determination [31]. The variation of viscosity with storage time is presented in Fig.10. The viscosity of the oil decreased with increase in storage time for both samples. As storage time increased, the viscosity of the oil reduced due to deterioration of the oil. The viscosity value of the fresh oil implied that the oil might be utilized as a lubricating oil base stock and this has been reported by others [4, 7-10].

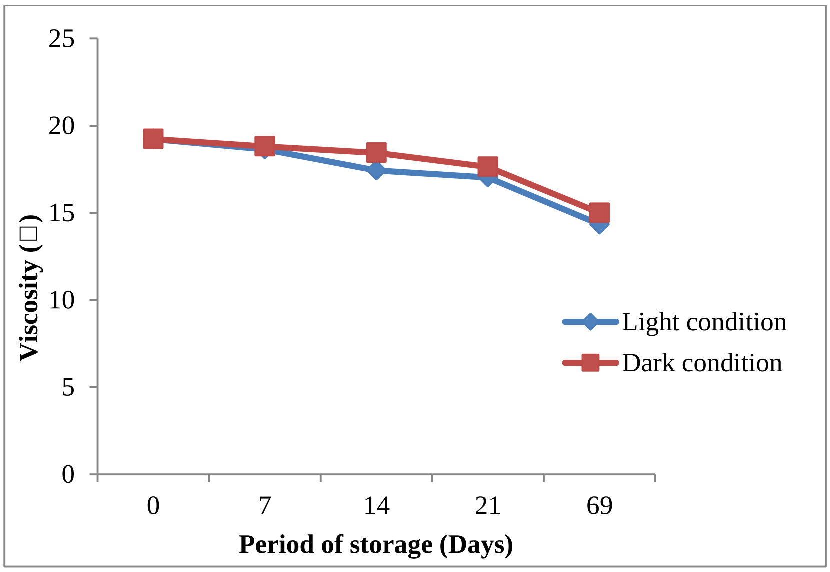

Figure 10: Variation of viscosity against time

3.2.11 Vitamin A

Vitamin A is a fat-soluble vitamin, which is essential for normal vision, bone growth and health of the immune system [32]. The variation of vitamin A with time of storage is presented in Fig. 11. The vitamin A content of the oil decreased with increasing storage time; the decrease was greater in the oil stored under light condition. As storage time increased, the vitamin A was broken down by oxidation into carboxylate groups. Thus, vitamin A content decreased with increase in deterioration of the oil.

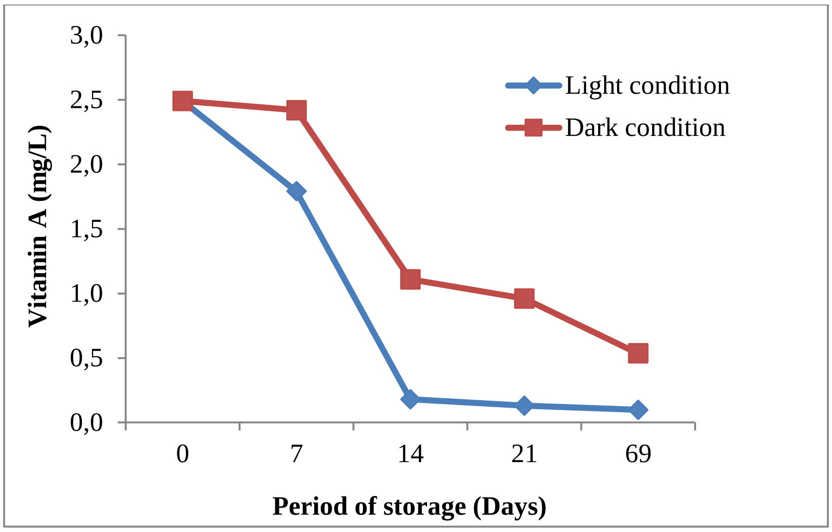

Figure 11: Variation of vitamin A content against time

Conclusions

Findings from this study reveal that the raw seed oil of *H. crepitans* is unstable to storage at room temperature. This instability is higher in the presence of light. Since the raw oil is reported to have good industrial potentials, it should be used immediately after extraction if its wholesome properties are to be preserved.

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