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Modification of Starch from Tubers of Caladuim Bicolor with Fatty Acid Derived from Chrysophyllum Albidum Seed Oil: Effect on Physicochemical Parameters

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Abstract:
The interest in starch derived materials is rapidly growing, both in industrial and basic research applications. This could be because of its availability, accessibility and eco-friendliness. This study reports the effect of modification of starch obtained from Caladium bicolor with fatty acids derived from Chrysophyllum albidum oil on the physicochemical properties. The unmodified starch together with modified one was characterized using FTIR and various physicochemical parameters. The results of FTIR analysis reveal vibration frequencies of 3283.62 cm-1, and 1018 cm-1, which affirm the presence of OH, C-O in the modified starch. Whereas the prominent peak at 1647.28 cm-1 assigned to the carbonyl(C=O) which was absent in the unmodified starch showed that modification occurred. The degree of substitution (DS) of modified starch was estimated at 0.79.The results of the physicochemical analysis showed a low amylose content of 16.95% and amylopectin of 83.05% in the unmodified starch. The swelling power, paste clarity, gelatinization temperature, water binding capacity and oil binding capacity of the modified starch were ; 63.5–72.45%, 2.03–3.2A; 76–78oC , 40.5–68.6%, 43.7–53.8% respectively. The result of the paste clarity and water binding capacity suggests that the modified starch could be used in film formation and production of adhesives in industries.

Keywords: Caladium bicolor, Chrysophyllum albidum, gelatinization temperature, Starch, swelling power, paste clarity and water binding capacity.

I. INTRODUCTION

Coronaviruses The industrialization of oil seeds is one of the most important agro-industrial activities in the world today. Oil from plants and animals is employed in the formulation of foods, cosmetics, and drugs in many industrial activities (Nimet et al., 2011). In the absence of carbohydrates, these oils act as insulators to the body's protective layers or internal organs such as the heart and lungs, providing energy to the body. Vegetable oils have received great attention in recent studies as potential alternatives to diesel fuels, health care products, drug delivery processes, food applications, antibacterial activity and alternatives to mineral waxes (Hesterberg et al., 2006). Most of these applications demand some chemical modifications of the vegetable oil structure, aiming to decrease its viscosity or even increase the molecule's reactivity (Ochigbo and Paiko, 2011).

African Star Apple (Chrysophyllum albidum) is one fruit of great economic value in tropical Africa due to its diverse industrial, medicinal and food uses. The tree grows as a wild plant and belongs to the family Sapotaceae, which has up to 800 species and makes up almost half of the order Ebernales (Oboh et al., 2009). The plant has become a crop of commercial value in Nigeria (Ehigiator and Adikwu, 2019). The seeds of this plant have been rarely exploited for the production of oil for commercial purposes, even though they contain about 13 wt % of edible oil. Most often, the seeds are thrown away after the consumption of their juicy pulp (Ochigbo and Paiko, 2011). The fruit pulp is rich in vitamin C and iron (Akubugwo and Ugbogu, 2007) and antinutrient factors (Akaneme, 2008) and shows antioxidant effects via mechanisms including free radical scavenging, decreased lipid peroxidation and increased endogenous blood antioxidant enzyme levels (Adebayo et al., 2011). Eleagnine, tetrahydro-2-methylharman and skatole have been isolated from the seed endosperm of this plant, with eleagnine identified as the main compound responsible for its antimicrobial activity (Aliyu et al., 2007; Idowu et al., 2006). Generally, raw materials of plant origin have been used in industries as modifiers, antibioactics, animal feedstock and adsorption studies (Adebayo et al., 2011; Okocha et al., 2023).

Starch is an attractive raw material due to its abundant supply, low cost, biodegradability, biocompatibility and ease of chemical modification. Indeed, modified starches have been approved for food use, in which they act as thickeners, gelling agents, sizing agents in textiles, and adhesives for paper and paper products (Nsude et al., 2022).The raw form of starch has limited applications; therefore, it does not always have the desired properties for certain types of processing; but when modified, it increases its range of applications. The chemically modified starch has been widely used as an emulsifier, demulsifier, glue and detergent, in plywood, and in the textile industries. Starch modification, which implies the alteration of the physical and chemical characteristics of native starch, is used to improve its functional characteristics and adapt it to specific applications. A common and widely used modification agent is a compound containing a carboxyl group (COO) or a carbonyl group (CO) to form acetates (Singh et al., 2007).

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Caladium bicolour (family Araceae) is underutilized, inedible; its root tuber is found abundantly in the wild in the south and south-eastern regions of Nigeria. In some areas, C. bicolor is used as an ornamental plant; the leaves and rhizomes are used medicinally as topical applications for boils, wounds, and ulcers. It is used to treat convulsions and as a purgative (Odugbemi, 2008). The potential of its flour for bio-ethanol production using indigenous fungal isolates has been reported (Amadi et al., 2016). Several studies on C. Bicolour show its cellulose has been used in the chemical and pharmaceutical industries.

II. Materials and Methods

Sample Collection and Preparation

Fresh seeds and fruits of Chrysophyllum albidumaying fruits and seeds were bought from Eke Market in Eke town Udi Local Government Area. The seeds were removed from the fruit and dried under ambient conditions for two weeks. The seeds after careful separation from the fleshy mesocarps were first air-dried in the sun at an average temperature of 31°C for 5 days and then the dark brown shell of the separated seeds was cracked mechanically to de-coated the shell and subsequently unveiled the inner cotyledon which were sun-dried for 72 hours. The dried cotyledon was further oven-dried at a temperature of 100°C for 24 hours in a laboratory oven, after which it was ground into fine particle size using an electric blender and stored in air-tight containers until needed for the experiment.

Extraction of Oil from Chrysophyllum Albidium Seeds

The extraction method used for this research was soxhlet extraction and was in line with Betiku et al.,(2016). One hundred grams (100 g) of the powdered Chrysophyllum albidium seeds were used, empty thimble weighed and recorded as W1 and then filled with the milled sample, reweighed and recorded as W2. The round bottom flask was weighed and recorded as W3 and then filled with the solvent (n- hexane) up to two-third of the flask. The reflux condenser was fitted to the top of the extractor and the water flow was turned on. The round bottom flask was placed in the heating mantle and the temperature of the mantle was adjusted to 70oC to bring the solvent to vaporization point. Each extraction took 4 hours for complete extraction. The filtrate was exposed to the atmosphere and the residual solvent was allowed to evaporate. Soxhlet apparatus (1-liter) and n-hexane as solvent were used for the oil extraction. One hundred grams (100 g) of the powdered Chrysophyllum albidium seeds were wrapped with whatmann filter paper and transferred into the thimble of the Soxhlet extractor. The thimble was carefully fixed on a 1- litre capacity round-bottomed flask. About 700 ml of n-hexane was poured to about two third of the volume of the flask and heated at 60°C on a thermostatically controlled heating mantle and allowed to reflux continuously for 4 hrs. Percentage oil yield was determined as expressed and replicate extraction processes were performed.

Extraction of starch

The extraction method used here was reported by Singh et al. (2007). Fresh tubers of Caladium bicolor were washed, peeled and cut into small pieces and blended with distilled water (3:1) for 1 minute using a blender (Sharp SM110, Japan). Then, it was filtered using double-fold cheesecloth. The filtrate was transferred into a beaker and left overnight to allow precipitation of starch on the bottom of the beaker. The supernatant was discarded and the starch precipitate was washed three times with distilled water; then, it was dried in an oven at 45oC until a constant weight was achieved. The dried starch was subsequently pulverized using a grinder and then stored in polyethylene bags until the next step of the experiment. The starch yield was calculated using the equation below.

$$\textbf{Starch\%} = \frac{\boldsymbol{starch\ extracted(g)}}{\boldsymbol{Fresh\ tuber(g)}} \times 100 \qquad (1)$$

Amylose content

The starches were analysed for their amylose content using a colorimetric assay following a modified published protocol (Martinez and Prodolliet, 1996). Five miligram of starch was mixed with 1 mL of 90 % DMSO followed by incubation at 95°C for 1 hour. Afterwards, the sample was diluted with 3 g/L iodine in 90 % DMSO at a ratio of 1:1 and then diluted 10 times with water. Finally, absorbance at 635 nm was measured using a UV-Vis spectrophotometer (Genesys 10S, Thermo Scientific, Loughborough, UK). The Amylose content was reported as a percentage.

Determination of Acid Value

Into 25cm3 of carbon tetrachloride (CCl4) in 100ml conical flask, 1g of Chrysophyllum albidium oil was added, two drops of phenolpthalin indicator was also added to the mixtures. Titration was done with 0.1M alcoholic potassium hydroxide (KOH) until a colour change was obtained. Blank determination was also carried out (Zhang et al., 2015). This was calculated using the formula;

$$(AV) = \frac{\text{Sample titre value} - \text{blank titre} \times 0.1 \times 56.1}{\text{weight of sample}} \qquad (2)$$

where 0.1= concentration of alcoholic potassium hydroxide (KOH), 56.1= constant.

Determination of Saponification Value (SV) (AOAC methods, 1984)

Oil sample (2g) was measured into 25 ml of 0.5 M ethanolic potash in a conical flask. In another flask, 25 cm^3 of the 0.5 M ethanolic potash were placed without the oil; this was used as a blank. Both flasks were boiled in a water bath for 30 minutes with frequent shaking, and 2 drops of phenolphthalein indicator was added. The titration was done with 0.5 M HCl without delay and with vigorous shaking to get the endpoint and Saponification value (SV) was calculated using the formula:

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$$SV = \frac{\text{Blank titre value} - \text{titre value of sample} \times 28.05}{\text{Weight of sample}} \quad (3)$$

Determination of Iodine Value

The method adopted was specified by ISO 3961 (1989). The sample (0.4g) was placed in a conical flask containing 20 ml of carbon tetrachloride. Thereafter, 25 ml of Dam reagent was added to the flask using a safety pipette influenced chamber. A stopper was then inserted, and the contents of the flask were vigorously swirled. The flask was then placed in the dark for 2 hours and 30 minutes. At the end of this period, 20 mL of 10% aqueous potassium iodide and 125 mL of water were added using a measuring cylinder. The content was titrated with a 0.1 M sodium-thiosulphate solution until the yellow colour almost disappeared. A few drops of 1% starch indicator were added and the titration continued by adding thiosulphate drop-wise until the blue colouration disappeared after vigorous shaking. The same procedure was used for the blank test and other samples.

The iodine value (IV) is given by the expression:

IV = 12.69C (V1-V2) m.

Where: C= concentration of sodium thiosulphate used, V1 = volume of sodium thiosulphate used for the blank, V2 = volume of sodium thiosoulphate used for determination, m = mass of the sample.

Transesterification Reaction of Star Apple Seed Oil and Starch

The method adopted was in line with Issola et al., (2018) and Qiu et al., (2013) and Gaglieri et al., (2021) with slight modification. Starch (12.85 g) and oil(13.35 g) were weighed in a 100-mL round-bottom flask and mixed using a magnetic stirrer. Aluminium chloride (1% of the total mass of starch and oil) was placed in the mixture and heated at temperatures 110°C for 45minutes. The flask was fitted with a condenser and protected from humidity by a calcium chloride trap. At the end of the reactions, mixture was filtered. The starch residue was washed many times with hot ethanol (95%, 50°C) to remove non-reacted oil molecules and the catalyst. Modified starch was dried in an oven at 60°C to constant mass and kept for further characterisation.

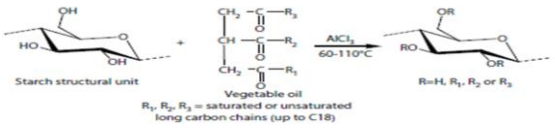

Figure 1: Starch Sstructural Unit.

Degree of Substitution (DS) of Star Apple Seed Oil Modified Starch

The extent of the esterification reaction was determined by titration (Issola et al., 2018; Jerachaimongkol et al., 2006). Modified starch (0.5 g) was mixed with 10 mL of methanol in a 250-mL flask. Thereafter an aqueous solution of NaOH (10 mL, 1N) was added for the saponification of the ester moieties. The mixture was stirred for 15 minutes. The excess NaOH was determined by titration with an aqueous 1N HCl solution using phenolphthalein as an indicator. A blank test was carried out with unmodified starch. The percentage of substitution was calculated by the following equation:

$$\%\text{Substitution} = \frac{(Vblank - Vsample) \times NHCl \times 0.2115 \times 100}{1000 \times Msample} \quad (4)$$

where V_{blank} and V_{sample} are the volumes in mL of aqueous HCl solution required for the titration of the blank and the sample respectively. N_{HCl} is the normality of the aqueous HCl solution, 211.5 is the mean molecular mass of fatty ester groups and M_{sample} is the dry mass of modified starch used in the experiment. The degree of substitution, defined as the average number of hydroxyl groups per glucose unit that have been substituted, was determined using the percent substitution according to the following equation (Issola *et al*., 2018, and Jiang *et al*., 2012):

$$DS = \frac{162 \times \%substitution}{211.50 \times 100 - [(211.5 - 1) \times \%substitution]} \quad (5)$$

Where 162 is the molecular mass of a glucose unit in starch.

Determination of pH

This was done using a pH meter (model HI 8424 with pH buffer 7). The starch sample (1.5g) was dissolved in a beaker with 10ml of distilled water and stirred properly. The pH meter was inserted into the solution and the reading was taken. The same procedure was repeated in triplicate for both unmodified and modified samples and the average value was recorded.

2.11 Determination of Gelatinization Temperature

Starch sample (1.5g) was dissolved in a beaker with 10ml of distilled water. The mixture was stirred, a thermometer was inserted and the beaker was placed in a water bath. The solution was stirred continuously until its colour became milky and thickened. This is the gel point and the temperature at this point was read off as the gelatinization temperature. The same procedure was repeated in triplicate for unmodified and modified starch samples and the average value was recorded (Martin, 2015).

Determination of Swelling Power and Solubility

The swelling power and solubility were determined following the methods described by Hirsch and Kokini, (2002). The samples were poured into graduated centrifuge tubes appropriately labelled. The solution was stirred and placed in a water bath heated to 95°C while shaking the sample gently to ensure that the starch granules remain in suspension until gelatinization occurs. The gelatinized samples were held at 95°C in the water bath for 1 hour. The samples were cooled to room temperature under running water and centrifuged for 30 minutes at 1000rpm. After centrifuging, the swelling volume was obtained directly by reading the volume of swollen sediment in the tube. The solution was removed from the sediment, placed in a metal dish, weighed, dried at 105°C for 1 hour, weighed and dried again. This technique was repeated three times for both unmodified and modified starch samples

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and the average values were recorded. The starch swelling power and solubility were respectively determined according to equations (5) and (6).

$$\text{Solubility\%} = \frac{Weight\ of\ dry\ supernatant}{Weight\ of\ starch\ sample} \times 100 \quad (6)$$

$$\text{Swelling power} = \frac{Weight\ of\ sediment\ paste}{dry\ mass \times (100 - \%solubility)} \times 100 \quad (7)$$

Water Binding Capacity (WBC)

Water binding capacity was determined using methods by Das *et al.*, (2010) with slight modification. A suspension, 5 g of sample in 75 ml-distilled water was agitated for 1 hour and centrifuged at 3000 rpm for 10 minutes. The free water was removed from the wet starch, which was then drained for 10 minutes. The wet starch was then weighed, the same procedure was repeated in triplicate for the unmodified and modified starch samples and the average value was recorded.

$$\text{WBC \%} = \frac{Wet\ starch(g)}{Dry\ starch(g)} \times 100 \quad (8)$$

Oil-binding Capacity (OBC)

Oil binding capacity of the starches was determined using the methods of Das *et al.* (2010). A suspension, 5 g of starch in 75 ml oil was agitated for 1 hour and centrifuged at 3000 rpm for 10 minutes. The free oil was removed from the wet starch, which was then drained for 10 minutes. The residue was then weighed the same procedure was repeated in triplicate for both unmodified and modified starch samples and the average values was recorded.

$$\text{OBC} = \frac{Weight\ of\ residual\ starch}{weight\ of\ sample} \times 100 \quad (9)$$

Paste Clarity

Paste clarity was measured using the method of Bello-Pérez *et al.*, (1999). Starch (1% w/v) was suspended in water and thereafter heated in a boiling water bath for 30 minutes with shaking. The resulting gel was then analyzed in duplicate for its transmission (%T) at 650 nm using a unicospec UV-2150 spectrophotometer.

FTIR Analysis

FTIR was carried out to understand the functional group variation before and after modifications of starch of obtained from *C. bicolor*. PerkinElmer 1600 Infrared spectrometer was used for the detection of various functional groups introduced during the modification. The spectra are collected by the spectrometer with 32 running scans at a resolution of 4 cm^{-1} for each sample within the 650–4000 cm^{-1} range. The "find peak tool" functionality of Nicolet software was used to determine the positions of significant transmittance peaks at a particular wave number.

III. Results and Discussion

Physical and Chemical Properties of Chrysophyllum Albidum Seed Oil

The physical and chemical properties of Chrysophyllum albidum Seed Oil are shown in Table 1.

TABLE 1: PHYSICAL AND CHEMICAL ANALYSIS OF CHRYSOPHYLLUM ALBIDUM SEED OIL.

	Parameters	Reported Values
1	Refractive index	1.489at 30 ^{0}C
2	Odour	Agreeable
3	Colour	Brown red
4	Oil content (%)	10.25
5	Specific gravity	0.84
6	Acidic value(mgKOH/g)	4.2
7	Saponification value(mgKOH/g)	205.45
8	Iodine value(mg/g)	40
9	Free fatty acid(mgKOH/g)	2.86

The result shows that Chrysophyllum albidum seed oil has a relatively high refractive index. The refractive index indicates the level of optical clarity of the crude oil sample relative to water. The oil had a refractive index of 1.49, which agreed with Adebayo et al. (2012), who worked on solvent extraction and characterization of oil from African Star Apple Chysophyllum albidum. Chrysophyllum albidum seed oil has a specific gravity of 0.84 at 30^{o}C, which is consistent with Ominyi et al. (2016), who worked on extraction, characterization and fatty acid profile of African star apple seed oil (Chrysophyllum albidum), which has a specific gravity of 0.89 at 25∘C, and 0.83 at 25◦C.

The oil content was in line, with a value of 10.25% as compared to that of 12% recorded by Zahir et al. (2017) and 8.05% and 12.70% by Ominyi et al. (2016). This indicates that the seed may not be a good source of abundant oil. The low oil content could be attributed to variation in genes, climate, plant species, soil condition and improper processing techniques such as prolonged exposure of harvested seeds to sunlight which is capable of impairing the oil yield considerably Akbar et al. (2009).

The saponification value (SV) is related to the average molecular mass of fatty acids in the oil sample. The saponification value obtained was 205.45 mg/KOH/g, which was higher than that of Ominyi et al. (2016), who reported 90.71 mg/KOH/g, but lower than that of Musa et al. (2015), who reported 228.4 mg/KOH/g on Chrysophyllum albidum seed oil research. The high saponification value suggests the oil could be suitable in the production of liquid soap, shampoos and lathering shaving creams (Akbar et al. 2009). The high saponification value can be attributed to process parameters such as extraction time, the temperature of extraction and particle sizes of the milled seeds, as reported by Mahale and Goswami-Giri (2011).

The free fatty acid of Chrysophyllum albidum seed oil was estimated at 2.86 mg/KOH/g, which is greater than 2.25 mg/KOH/g (Adebayor et al., 2012) ,and less than 9.90 mg/KOH/g (Akbar et al., 2009). Low free fatty acid content is indicative of low enzymatic hydrolysis. This could be advantageous because oil containing a high concentration of free fatty acids develops an unfavourable composition during storage (Mahale and Goswami-Giri, 2011).

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The iodine value is a measure of the degree of unsaturation of vegetable oils, determines the stability to oxidation and allows the overall unsaturation of the fat to be measured quantitatively (Aliyu et al., 2007). The iodine value of the extracted oil was measured and found to be 40 mg/KOH/g. This was higher than that obtained by Musa et al. (2015) but consistent with the value obtained by Aliyu et al. (2007).

The acid value is an important indicator of the oxidation of the oil. It is the weight (mg) of potassium hydroxide required to neutralize the free acid in 1 g of the oil. In good oil, the acid value should be very low (< 0.1) and an increase in acid value is an indicator of oxidation of the oil which may lead to gum and sludge formation besides corrosion (Zahir et al., 2017; Anang et al. 2019). The acid value was also found to be 4.2 mg/KOH/g. This is consistent with 4.50 mg/KOH/g reported by Adebayo et al. (2012), and less than 19.70 mg/KOH/g obtained by Ominyi et al. (2016).

Physical and Chemical Properties of Unmodified Starch of Caladuim Bicolor

The physical and chemical properties of Unmodified Starch of Caladuim bicolor are shown in Table 2.

TABLE 2: PHYSICAL AND CHEMICAL ANALYSIS OF UNMODIFIED STARCH OF CALADUIM BICOLOR

Properties	Reported Values
pH	4.49
Melting point	258
Colour	Pure white
Solubility % at 30 °C	38.50
Gelatinization temp.(°C)	75
Amylose %	16.95
Amylopectin %	83.05
WBC	68.6
OBC (Vegetable oil)%	53.8
OBC (Crude oil)%	42.2
Past clarity	2.013A,0.97%T
Swelling power (%)	72.45

The amylose and amylopectin contents of the unmodified starch are shown in Table 2. Generally, the starch of C. bicolor had a low amylose content of 16.95%, and amylopectin of 83.05%. The amylose content of *C. bicolor* is consistent with Sharlina *et al*., (2017), who worked on *Dioscorea pyrifolia* tubers with starch that contains 44.47 ± 1.86% amylose and Zhang *et al.* (2017), who worked on the physicochemical properties of maca starch, whose apparent and estimated amylose contents ranged from 21.0 to 21.3%. The low amylose content observed in *C. bicolor* starches suggests their use in situations where soft gels/films are needed, such as in the glue, detergent, plywood and textile industries.

Swelling power and water solubility of the unmodified starch are shown in Table 2. The swelling power of starch obtained from unmodified *C. bicolor* was 72.45. Chung *et al*. (2008) found lower values than those presented in the present work. The water solubility analysis in Table 2 shows that at 30 ^{0}C, the unmodified starch of *C. bicolor* has a solubility of 38.5. This is in line with Tang *et al.* (2004) who studied the solubility of barley starches and Sindhu and Khatkar (2016) who worked on the solubility of starch and flour in tartary buckwheat (*F. tataricum*) grains.

According to Sindhu and Khatkar (2016), the swelling power and water solubility index provide evidence of the magnitude of interaction between starch chains in both the amorphous and crystalline domains and provide a measure of starch hydration status. In the same vein, Sharlina *et al.* (2017) opined that the extent of cross-bonding within the granules and the presence of lipids or phosphates affect the swelling and solubility profiles of starches. These suggest that the starch may find application in adhesives, pastes, and glues in the non-food industries (Zhang *et al*. 2017).

The water and oil binding capacity of the starch of *C. bicolor* is shown in Table 2. Water binding capacity was estimated at 68.6, and thus higher than the water binding capacity reported by Nsude *et al.* (2022), who worked on the physicochemical characterization of *Pentaclethra macrophylla benth*. The high water binding capacity of starch is attributed to the extent of hydrogen bonding between water molecules and starch hydroxyl groups as well as the loose association between amylose and amylopectin molecules in starch granules. Jiang *et al.* (2012), who studied the characterizations of starches isolated from five different *Dioscorea L.* species, have resuts in line with the above obtained values. The diversity in staches WBC may be influenced by the dissimilarity in the degree of water-binding area availability inside the granule (El-Halal *et al*., 2015).

The oil-binding capacity of *C. bicolor* starch is shown in Table 2. The value was estimated at 53.8 for vegetable oil and 42.2 for crude oil. According to the findings, starch has a higher binding capacity for vegetables than crude oil. This corroborates the oil binding capacity due to the structural re-orientation of the starch molecules described by Mbougueng *et al*. (2012). The low water binding capacity of starches could be attributed to the involvement of a larger proportion of the hydroxyl groups in forming hydrogen and covalent bonds between the starch chains than with water (Sharlina *et al*., 2017).

Paste clarity (PC) is an important property that reflects the transparency of a gel. The paste clarity of the unmodified starch was estimated at 0.97%T. The low clarity of cocoyam starch pastes could therefore be due to the presence of amylose molecules with a high susceptibility to retrogradation. This is consistent with Singh *et al*., (2004) research on some properties of corn and potato starches.

The gelatinization temperature of starch, as indicated in Table 2, has a value of 75. This implies that starch contains more amylose, which is strongly bound and requires more energy to dissociate from its inner embedded core than the low amylose starches (Atichokudomchai and Varavinit, 2003). This is in line with the report that starches with high amylose or packed together need a high temperature to fully gelatinize (Mishra and Rai, 2006).

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Physicochemical Properties of Starch of *Caladuim bicolor* Modified with *Chrysophyllum albidum* Seed Oil

The physicochemical properties of *Caladuim bicolor* modified with starch of *Chrysophyllum albidum* seed oil is shown in Table 3.

TABLE 3: PHYSICOCHEMICAL PROPERTIES OF STARCH FROM CALADUIM BICOLOR MODIFIED WITH CHRYSOPHYLLUM ALBIDUM SEED OIL.

Properties	Unmodified Starch	Modified Starch
pH	4.49	6.8
Melting point	258	266
Colour	Pure white	Brown
Solubility%(30°C)	38.50	41.5
Gelatinization temp °C.	75	76
Amylose %	16.95	NA
Amylopectin %	83.05	NA
WBC	68.6	40.5
OBC(Vegetable oil)%	53.8	43.7
OBC(Crude oil)%	42.2	45.2
% Substitution	NA	5.8
DS	NA	0.79
Past clarity	2.013A,0.97%T	3.2A,0.5%T
Swelling power	72.45	63.5

The colour of the starch changed from pure white to brown after several rounds of washings which imply that Caladuim bicolor has adsorption capacity. Chrysophyllum albidum seed oil had no effect on amylose or amylopectin. The water binding and oil binding capacities of Caladuim bicolor starch decrease from unmodified to modify. The WBC decreased from 68.6 for unmodified to 40.5 for modified, when treated with oil, whereas, the OBC decreased from 53.8 for unmodified to 45.2 for modified. It therefore implies that the low WBC is attributed to a low hydrogen bond between the molecule of water and the hydroxyl of the starch. The lower OBC could be associated with crystal structure, crystal size and shape as well as their spatial distribution and order (Marangoni, 2002). The swelling power of the unmodified was higher than the modified. This could be attributed to the degree of substitution and the percentage of fatty acids found in the modified starch.

The degree of substitution of starch is the number of hydroxyl (OH) groups that are changed per D-glucopyranosyl structural unit of the starch polymer. According to Mark and Mehltretter (1972), starch acetates are classified as low DS (0.1), medium DS (0.1-1.0), and high DS (>1.0) acetates based on their DS. The degree of substitution of Caladuim bicolor starch modified with oil of Chrysophyllum albidum seed is medium, as its value (0.79) falls within the range of 0.1–1.0 degree of substitution. This is consistent with Nzikou et al. (2009) finding of low oil content in sesame (Sesamum indicum L.) grown in Congo-Brazzaville.

FTIR Analysis Starch of Caladuim Bicolor Modified with Chrysophyllum Albidum Seed Oil

FT-IR spectroscopy was used to identify the various functional groups present in the oil, starch, and modified starch. The spectral analysis as displayed in Figures 2–3 shows the various peaks of the functional groups present in the starch and modified starch with oil. Frequency vibrations ranging between 3008.01cm−1 and 2853cm−1 showed asymmetric and symmetric stretching of C-H, representing alkane. This is consistent with the findings of Zahir et al. (2017), who investigated the physicochemical properties of corn and mustard oils and discovered 2854.7-2925.8 cm−1 as C-H asymmetric and symmetric stretching vibrations of the aliphatic CH2.

The peaks at 1018cm-1, 1022.31cm-1 and 1153.74 cm-1, in Figure 2 were attributed to the C–O bond stretching. Other characteristic absorption bonds were observed at around 1639.55 cm-1, corresponding to the tightly bound water (H2O) in the starch, an extremely broad band at around 3367.11 cm-1, resulting from the vibration of the hydroxyl group (O–H); and at around 2930.90 cm-1, attributed to the C–H vibration stretch (Nzikou et al., 2009; El-Badry and Ali, 2015; Zahir et al. 2017).

The modification of Caladuim bicolor starch with Chrysophyllum albidum oil is represented with an FTIR as shown in Figure 3. The peak at 1647.28 cm−1 became more prominent, while the intensity of the peak at 3367.11 cm1 decreased. This could affirm that there was modification with a high degree of substitution of the starch using Chrysophyllum albidum oil. The fatty acid of the oil most possibly reacts with the hydroxyl of the starch, thus increasing the size of the peak at 1647.28 cm1 and reducing the peak at 3367.11 cm-1. This is in line with Eze (2012), who worked on the physico-chemical properties of oil from some selected underutilized oil seeds and starch.

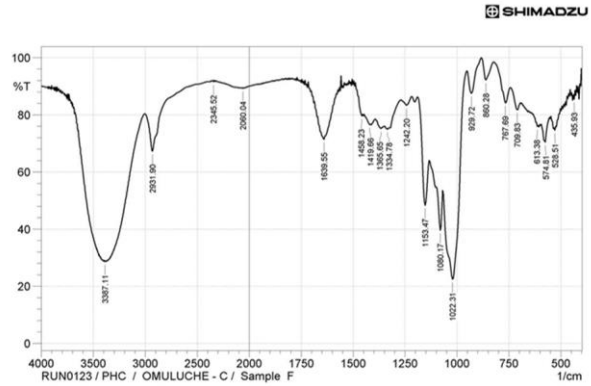

Figure 2: Ftir Of Unmodified Starch Of Caladuim Bicolor.

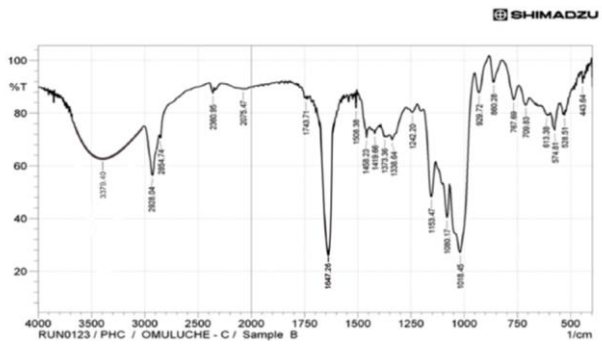

Figure 3: Ftir Of Caladuim Bicolor Starch Modified With Chrysophyllum Albidum Seed Oil.

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IV. Conclusion

The study showed that Caladuim bicolor contained starch and Chrysophyllum albidum has low oil content. Based on the physicochemical analysis, the isolated starch of C. bicolor can be modified with fatty acids of Chrysophyllum albidum oil. The findings showed that modified starch has a lower water and oil binding capacity and swelling power than native starch and greater paste clarity, gelatinization temperature, and solubility than unmodified starch. This change in physicochemical properties from unmodified to modified starch could be associated with the reaction of fatty acids and the hydroxyl group (OH) of starch. The FTIR results reveal some functional groups attributed to starch, and also confirm an increase in the intensity of the peak attributed to the carbonyl functional group. The findings also estimated a degree of substitution that is within a commercially acceptable starch range of 0.01–0.20 DS and has been used for film formation, adhesion, thickening, stabilising, and texturizing (Ma'arif and Aditama, 2019).In line with the findings of this study, C. bicolor starch modified with fatty acids from Chrysophyllum albidum oil could be a viable source of adhesives, detergents, plywood, pastes, and glues in the non-food and textile industries.

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