

Effect of Acetic Acid and Alpha-Amylase Modifications on Some Physicochemical Properties of *Xanthosoma sagittifolium* (Cocoyam) Starch

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Abstract

This study was aimed at evaluating the effect of acetic acid and alpha-amylase modifications on the physicochemical properties of *Xanthosoma sagittifolium* (cocoyam) starch. Standard procedures were employed in determining the physicochemical features of the starch. The yield of starch from cocoyam root was 22.30 %. The result showed that of the native and modified starches did not show significant difference in the moisture content, and the swelling capacity of the native and modified starches. The amylose content showed that acetic acid modified starch had significantly ($p < 0.05$) higher amylose content (10.07 ± 0.20 %) than the native and enzyme modified starches. The solubility of the starch was shown to be significantly ($p < 0.05$) higher in the native cocoyam starch (3.75 g/g) than in either acetic acid or enzyme modified starch (3.30 ± 0.02 and 3.04 ± 0.01 g/g) respectively. The gelatinization temperature of the starches was found to be significantly ($p < 0.05$) higher in the modified starch (82.51 ± 0.08 and $81.15 \pm 0.05^\circ\text{C}$) than native starch. The water absorption capacity was significantly higher in native starch (6.65 ± 0.12) than in the modified starches (2.14 ± 0.07 and 2.03 ± 0.04 for acetic acid and enzyme modified starches respectively). It is therefore noteworthy that modification of cocoyam starch may present it a worthy resource material for industrial application as such popularising its utility.

Keywords: Cocoyam starch; Acetic acid modification; Enzyme modification; Solubility; Gelatinization.

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1. INTRODUCTION

Cocoyam (*Xanthosoma sagittifolium*) belongs to the family Aracea and it is the sixth most important root and tuber crops world-wide (Ashogbon, 2017). Cocoyam is consumed in several developing countries of the world. Nevertheless, this food crop is less popular compared to some other tropical root crops like cassava, yam as well as sweet potato (Ashogbon, 2017). Although, in some regions of the world, especially the tropics and sub-tropics, they still serve as staple food for the populace (Adeosun *et al.*, 2017; Coker and Aiyeye, 2019). Cocoyam has several nutritional benefits than most root and tuber crops as its protein content is higher (Boakye *et al.*, 2018) as well as considerable amount of calcium, phosphorus, vitamins A and B vitamins. The high content of carbohydrate present in the crop makes it a good source of starch which may be utilized in both domestic and industrial applications. In certain underdeveloped nations, infants are historically weaned primarily on precooked, wet-milled, and wet-sieved corn starch (Akobundu and

Hoskins, 1987). Recent research have also shown that cocoyam starch may be used to make readily digested and affordable weaning meal for low-income earners in underdeveloped nations (Oti and Akobundu, 2008). Despite the economic importance of cocoyam as a food source in some regions of the tropics and subtropics, little is known about its post-harvest features, which may contribute to the limited use of enhanced post-harvest technologies to retain quality and boost marketing potential. Maize, millet, sorghum, cassava, potatoes, and rice flours were mixed in with wheat flour to increase the usage of local products while lowering the expense of wheat imports. The chemical and (or) physical qualities of native starch limit its usage in many commercial applications, therefore a modified starch is described as a product in which the chemical and (or) physical properties of native starch have been changed.

Starch is a biodegradable substance that is found in abundance in nature (Ashogbon and Akintayo,

2014). Some of natural starch's qualities, such as water insolubility, inclination to retrograde, and instability under various processing conditions of temperature, pH, and shear pressures, limit its use in culinary and medicinal applications (Alcazar-Alay and Meireles, 2015). Modification of starch alleviates these constraints by changing the structural features of starch granules and the physicochemical qualities of starch, as well as increasing its value in the food and nonfood industries (Lopez *et al.*, 2010). Chemical, physical, and enzymatic methods, as well as their mixtures, can all be used to modify starch. Apart from cocoyam flour, cocoyam starch is a shelf-stable intermediate product that can help reduce post-harvest losses in cocoyam corms, which are very perishable and subject to significant post-harvest losses. Unlike cassava and corn starches, cocoyam starch has not found widespread use in the food and non-food industries. Cocoyam starch has been studied for its properties (Aprianita *et al.*, 2014; Gbadamosi and Oladeji, 2013; Awokoya *et al.*, 2012). However, data on the properties of modified cocoyam starch is limited. Starch from cocoyam were chemically and enzymatically altered, and the effects of different degrees of modification on the physicochemical characteristics of modified and native cocoyam starches were investigated.

2. MATERIALS AND METHODS

2.1 Collection of Plant Sample

Fresh roots of cocoyam (*Xanthosoma* sp) were obtained from the Ultra-Modern Market, Minna, Niger State, Nigeria.

2.2 Extraction of Cocoyam Starch

Cocoyam starch was extracted using the method described by Mweta (2009). The fresh cocoyam roots were peeled and cut into small pieces and ground into slurry. The slurry was screened through a muslin cloth and washed thoroughly with portable water. The

slurry was allowed to settle properly, thereafter, the supernatant was decanted and the residual wet cakes of the starch were dried at ambient temperature, ground into powder, packaged into polyethylene bag and stored prior to analysis (Figure 1). The percentage yield was calculated from the initial and final weights obtained:

$$\% \text{ Starch yield from fresh roots} = \frac{\text{weight of cocoyam flour}}{\text{weight of unpeeled roots}} \times 100$$

2.3 Preparation of enzyme-hydrolyzed starch

The production of Enzyme-hydrolyzed starch was carried out by the method described by the World Intellectual Property Organization (WIPO, 1997). To an aqueous suspension of cocoyam starch (30 % w/v) was added 15 mL of enzyme (α -amylase extracted from maize) at pH 6.0 and temperature of 37 °C with constant stirring for the 20 min. Afterwards, the action of the enzyme was terminated by lowering the pH to 2.5 with 0.1 M HCl. The reaction medium was subsequently neutralized by raising the pH to 7 using 0.1 M NaOH. The resulting product was separated from the reaction medium after settling down. The product was washed several times with distilled water and then dehydrated with 100 mL of ethanol (95 % v/v). The dehydrated product was air-dried and powdered after decanting the ethanol.

2.4 Preparation of Acetylated Starch

The method of Sathe and Salunkhe (1981) was adopted. Native cocoyam starch (35 g) was dispersed in distilled water and stirred for 20 minutes. The pH of the slurry obtained was adjusted to 8.0 using 1.0 M NaOH. Acetic anhydride (5 mL) would be added slowly to the mixture while maintaining a pH range of 8.0. The reaction will proceed for 5 minutes after the addition of concentrated acetic anhydride. The pH 8.0 of the slurry will be adjusted to 4.5 using 0.5 M HCl, then filtered, washed four times with distilled water and air dried at 30+2 °C for 48 hrs.

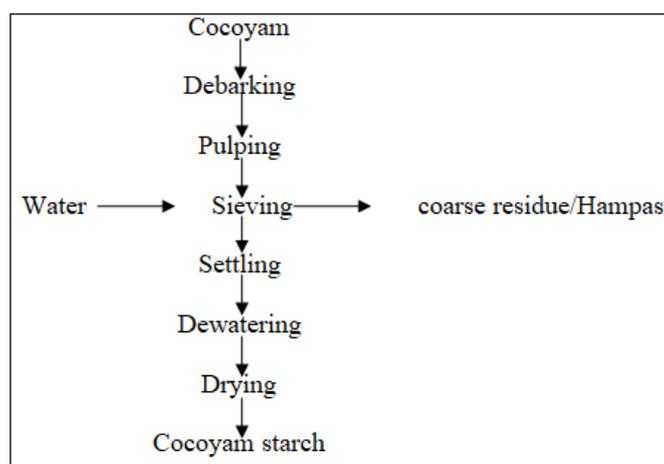


Figure 1: Schematic Flow Chart for Cocoyam Processing

2.5 Physicochemical Tests on Modified Starches

2.5.1 Determination of Moisture Content

The moisture content of cocoyam flour was determined using a method described by ASAE (2003). Five grams of the starch was weighed and dried to constant weight at a temperature of 100°C. The loss in weight was determined and expressed as percentage moisture content:

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100$$

Where W_1 = initial weight, W_2 = final weight

2.5.2 Determination of Starch Swelling Capacity and Solubility

Swelling capacity was determined according to the method described by Adeleke and Odedeji (2010) with modification. One (1.0) gram of starch sample was weighed into a test tube into which 15 mL of distilled water was added. The mixture was heated in a water bath at a temperature of 60 °C for 30 minutes with continuous stirring. In the end, the test tube was centrifuged at 2000 rpm for 10 min. The supernatant was carefully decanted and weight of the starch paste taken. Five mL of the clear supernatant solution was heated to dryness and the weight of the dried residue with reference to the volume of the solution was determined accordingly as the percentage solubility of the starch in the solvent and the swelling capacity was calculated as follows:

$$\text{Swelling capacity (g/g)} = \frac{\text{Weight of starch paste}}{\text{Weight of dry starch}}$$

$$\text{Solubility (\%)} = \frac{\text{Dry supernatant weight}}{\text{Initial sample weight}} \times 100$$

2.5.3 Determination of Amylose Content

A simplified colorimetric method described by Sowbhagya and Bhattacharya (1971) was adopted with modification. Exactly 0.1 g of the starch was weighed into 100 mL volumetric flask and 1 mL of 95 % (v/v) ethanol was added to wet the sample. Then, 10 mL of 0.5 M KOH was added and the mixture was slightly heated and held overnight at ambient temperature. The mixture was diluted to the mark with distilled water. Five (5.0) mL aliquot of the diluted solution was pipetted into another 50 mL volumetric flasks and three (3.0) drops of 0.1 % phenolphthalein solution was added. The resulting solution was neutralized by adding in drop-wise 1 M HCl until neutral pH was achieved. Three (3.0) drops of 0.2 % of iodine solution was added and made to mark with distilled water. The absorbance of sample was measured at 630 nm. The measurement of the amylose was determined from a standard curve developed using amylose and amylopectin blends. The percentage amylose was calculated using the formula below:

$$\text{Absorbance of sample} \times \text{gradient factor} \times \text{dilution factor}$$

2.5.4 Determination of Gelatinization Temperature of Starch

This was evaluated using the method as described by Adewumi *et al.*, (2020). One (1.0) gram of the starch sample was hydrated in 10 mL distilled water and heated to form gel. The gelatinization temperature was read with a thermometer suspended in the starch slurry.

2.5.5 Determination of Water Absorption Capacity (WAC) of Starch

One (1.0) g of the starch sample was suspended in fifteen (15.0) mL of distilled water and agitated at intervals for 2 hr and centrifuged at 4000 rpm for 10 min. The supernatant was measured and the weight of the supernatant was taken (Köhn *et al.*, 2015). WAC was calculated thus:

WAC = amount of water added – amount of water decanted after centrifugation

3. RESULTS AND DISCUSSION

The result of the present study showed a yield of (22.30 %) of starch from cocoyam (Table 1). Aprianita *et al.*, (2014) reported a similar yield of 21.1 % cocoyam starch. However, the high yield is not in agreement with the 11.47 % of cocoyam starch yield report by Arawande and Ashogbon (2019). Okunade and Arinola (2021) also reported a low starch yield of 11.28% for red cocoyam and 9.02% for white cocoyam. Arinola (2019) reported 11.00 % and 10.20 % for red and white cocoyam starches respectively. Lawal (2004) declared starch yield of 30 to 62 % for new cocoyam starch which is higher than reported in the present study. The variation of starch yield may be attributed to the origin and genetic differences of carbohydrate source, maturity stage of crop, and extraction method employed in isolating the starches (Awolu *et al.*, 2020). The appreciable accumulation of starch in the fresh roots as shown in this study would be of significant importance in domestic and industrial starch utilization (Arawande and Ashogbon, 2019).

Figure 2 showed that there was no significant ($p < 0.05$) difference in the moisture content. However, it ranged from 10.74 ± 1.04 % in acetic acid modified starch to 11.31 ± 0.72 % in enzyme modified starch. This is lower than 15.05 % reported by Arawande and Ashogbon (2019) but relatively similar to 9.36 % reported by Oladebeye *et al.*, (2010). The result of moisture content obtained in the present study is within the 10 % stipulated standard of the revised regulation of the Standards Organisation of Nigeria (1988) so as to prolong its shelf life over a long storage period. Akubo (1997) reported that the lower the initial moisture content of a product to be stored, the better the storage stability of the product. Therefore, the moderate moisture content of the starch suggests its stability against microbial activity (Arawande and Ashogbon, 2019).

The solubility of the starch was shown to be significantly ($p < 0.05$) higher in the native cocoyam starch (3.75 ± 0.05 %) than in either acetic acid or enzyme modified starch (3.30 ± 0.02 and 3.04 ± 0.01 %) respectively (Figure 1). Solubility and water absorption capacity are significantly higher with lower gelatinization temperature in native starch. There was no significant difference in the swelling capacity between the native and modified starches. These phenomena did not agree with myriad reported findings for modified starches. This could be attributed to low (≤ 5.0 min) reaction time, concentration of reactant for better modification. The solubility of native cocoyam starch was significantly higher than that obtained for modified starches. No significant difference was observed in solubility between the starch-acetate and enzyme-hydrolyzed-starch. The elevated solubility of the native starch is attributed to the significant presence of hydrophilic substituting groups which allows water retention due to their hydrogen bonds forming capacity and this singular factor ensures high retention of water that goes into the granules (Awolu *et al.*, 2020). Hence, low solubility can be a valuable asset in the manufacture of some starch base products such as films.

The amylose content of the starches is presented in Figure 2. The result showed that acetic acid modified starch had significantly ($p < 0.05$) higher amylose content (10.07 ± 0.20 %) than the native (9.57 ± 0.05 %) and enzyme modified (9.64 ± 0.14 %) starches. There was no significant difference in the amylose content between the native and the modified starches. Starch consists of two types of molecules; amylose and amylopectin. Normal starches contain 20-30 % amylose; the difference being made up by amylopectin. Waxy and high amylose starches contain less than 15% and greater than 40% amylose, respectively (Nalin *et al.*, 2015). However, the relative proportion of amylose to amylopectin may vary from crop to crop and with variety. The amylose content value for cocoyam starches ranges from 3 – 43 % depending on variety as reported by Moorthy, (2002) and Tian *et al.*, (1991). The results of the amylose of the cocoyam starch produced in this study was in consonance with the range in the literature (3 - 43%) as stated above. The amylose content of cocoyam starch was lower than the 23.05 ± 0.02 % reported by Arawande and Ashogbon, (2019). The result of this study also varies from 16 - 30% reported by Aboubukar *et al.*, (2008). The difference in value might be as a result of difference in species and agricultural environment where the plants were cultivated (Jacob and Adeleke, 2019). The amylose and amylopectin contents of starches are important as they affect pasting, gelatinization, retrogradation, swelling power and enzymatic vulnerability of starches (Capule and Trinidad, 2016).

The gelatinization temperature of the starches was found to be significantly ($p < 0.05$) higher in the modified starch (82.51 ± 0.08 and 81.15 ± 0.05 °C for acetic and enzyme modified starch respectively) than native starch (80.41 ± 0.03 °C) (Figure 3). Gelatinization is the process whereby starches undergo an irreversible change under heat and absorb water with swelling thereby making the granules swell more and become a paste rather than a dispersion which it forms in cold water (Kolawole *et al.*, 2013). The gelatinization temperature provides an indication of the minimum temperature required to cook a given sample and it has implications on the stability of other components in a formula and also indicates energy cost (Kolawole *et al.*, 2013). The gelatinization temperature of the modified starches were found to be significantly higher than that observed in the native starch, thus confirming the hypothesis that given the elevated content of high molecular weight amylopectin, more energy will be required to dissociate the chains (Coronell-Tovar *et al.*, 2019). In this findings, all the starch types have gelatinization temperature similar to that reported for *C. esculenta* (82.5 °C) but higher than the value found for *Xanthosoma* sp. (78 °C). Since cocoyam flour possesses a high gelatinization temperature, its use can be recommended for products that require high processing temperatures, such as canned foods (Hernández-Medina *et al.*, 2008).

The water absorption capacity was significantly higher in native starch (6.65 ± 0.12) than in the modified starches (2.14 ± 0.07 and 2.03 ± 0.04 for acetic acid and enzyme modified starches respectively). The variations in water binding capacity values indicated differences in the degree of engagement to form hydrogen and covalent bonds between starch chains and the degree of availability of water binding sites (Hoover and Sosulski, 1986) or largely due to molecular structures of the starch samples (Ishiwu *et al.*, 2017).

The swelling capacity of the native and modified starches was presented in Figure 5. The result revealed that there was no ($p > 0.05$) significant difference in the % swelling capacity of both the native and modified starches. The swelling power between the native and modified starches which ranged between 1.97 ± 0.05 g/g and 2.19 ± 0.54 g/g correlates with the results obtained for cocoyam at 60 °C by Ishiwu *et al.*, (2017) ranging from 1.51 – 2.32 g/g. Okunade and Arinola (2021) also reported a similar result for native and cocoyam starches ranging between 1.80 and 2.18 g/g. Lawal (2004) argued that acetylation reduces intermolecular associations in the starch granules and this reduces structural limitations against swelling. Enzyme hydrolysis of starch further reduces the swelling capacity. It could also be argued that the

sufficient temperature was not provided to allow high swelling and solubility in the modified starches.

Table 1: Starch Yield from Native Cocoyam Roots

Sample	Amount (g)
Initial weight	4843.00
Final weight	1079.99
Yield (%)	22.30

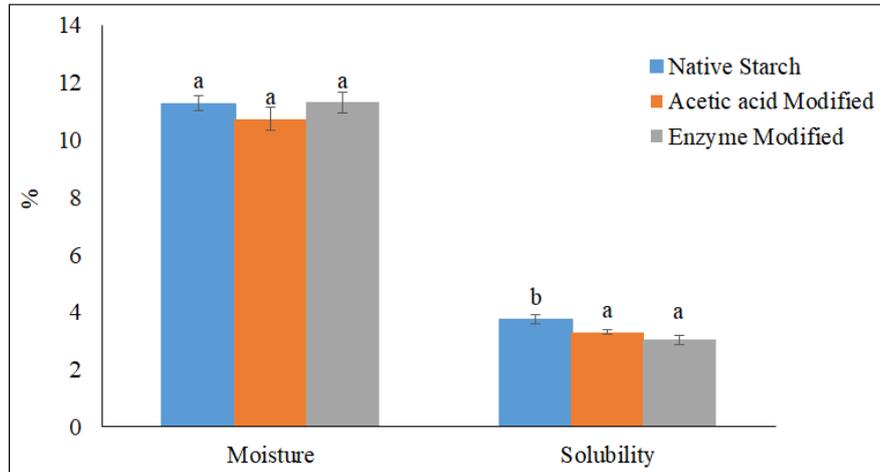


Figure 2: Moisture Content and Solubility of Native and Modified Cocoyam Starches

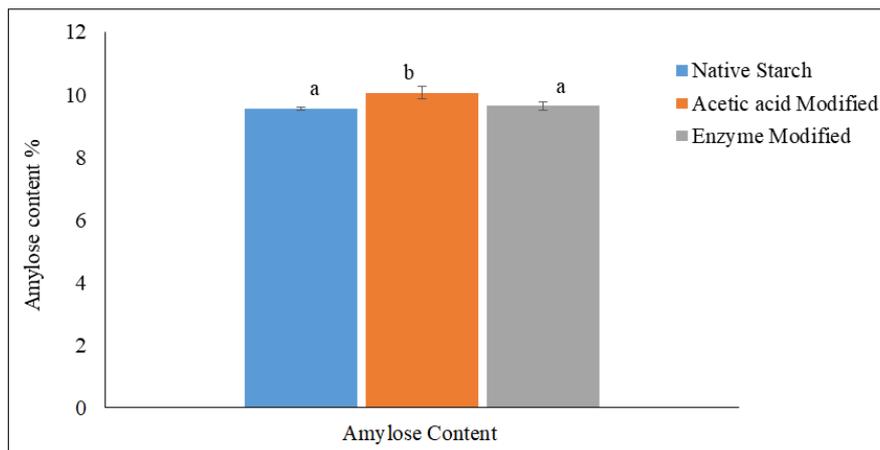


Figure 3: Amylose Content of Native and Modified Cocoyam Starches

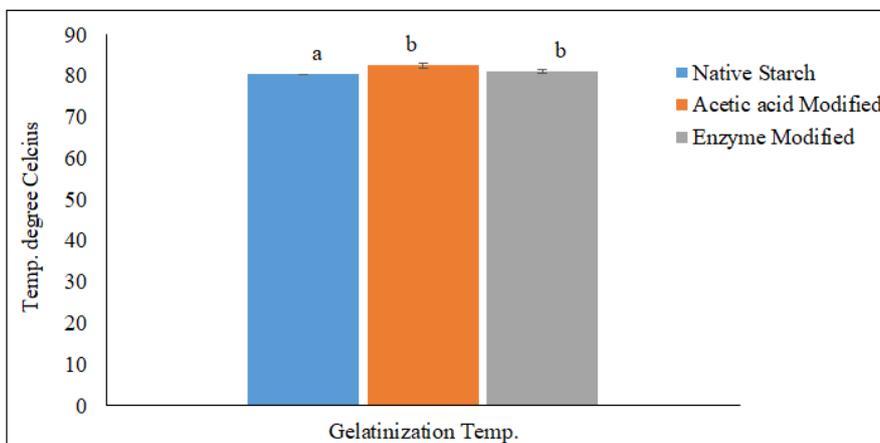


Figure 4: Gelatinization Temperature of Native and Modified Cocoyam Starches

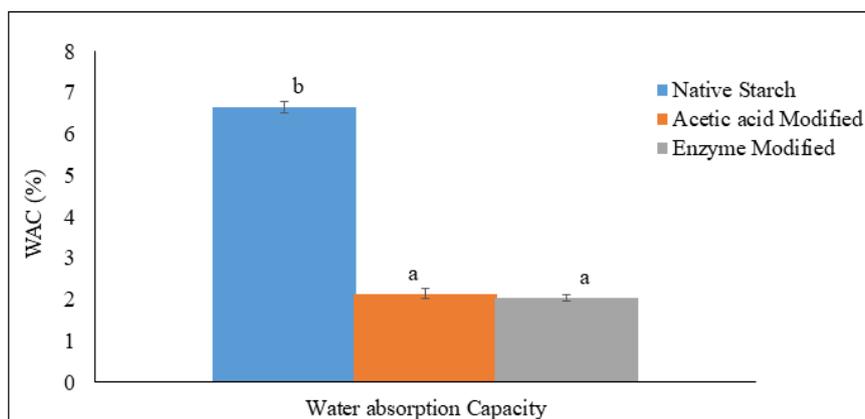


Figure 5: Water Adsorption Capacity of Native and Modified Cocoyam Starches

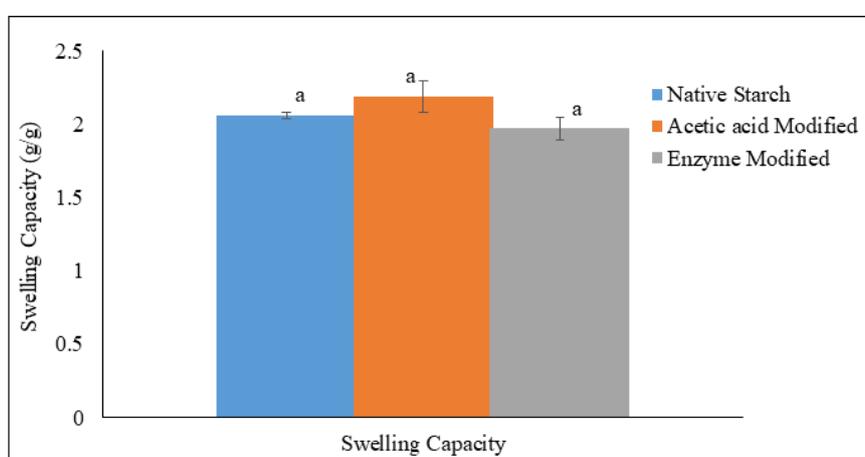


Figure 6: Swelling Capacity of Native and Modified Cocoyam Starches

4. CONCLUSION

The study showed that some physicochemical features of starch was altered by modification. Solubility as well as water absorption capacity were significantly lowered in modified cocoyam starch while gelatinization was elevated. These alterations from native starch will open up diverse route for the industrial application of this starch.

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Conflict of Interest: There was no conflict of interest amongst the authors

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