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Influence of Organic Acids on a Non-Conventional Starch from *Corypha umbraculifera* L. to Improve Its Functionality and Resistant Starch Content †

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Abstract: Talipot starch isolated from the stem of talipot palm is an underutilized and non-conventional source of starch with a high yield (76%). Resistant starch (RS) possesses varied physiological benefits by acting as a dietary fiber and reduces the risk of many degenerative diseases. The process of starch esterification considerably increases the RS and improves other starch characteristics like reducing gelatinization temperature and retrogradation tendency. In the present study, talipot starch was esterified with two organic acids; acetic acid and lactic acid. By introducing the ester group (C=O), the modified starches exhibited a significant decrease ($p \leq 0.05$) in amylose content, relative crystallinity, swelling index, gelatinization temperature and peak viscosity of starch. Lactic acid showed a higher impact on starch depolymerization and RS formation than acetic acid between the organic acids. Esterified talipot starch with a comparatively high yield can be utilized in the preparation of low-calorie foods.

Keywords: non-conventional starch; acetic acid; lactic acid; resistant starch; retrogradation tendency; ester groups; low-calorie foods

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1. Introduction

Starch is a natural polymer possessing widened application in food and non-food industries owing to its technological properties, biodegradability, and safety [1]. According to the rate of in-vitro starch digestibility, starch can be categorized into resistant starch (RS), slowly digestible starch (SDS), and rapidly digestible starch (RDS) [2]. The RS is the starch that is not hydrolyzed in the small intestine and hence converted into short-chain fatty acids by colon microflora. RS is alike dietary fiber and helps control or prevent diabetes and other degenerative diseases [3]. The RS content of starch is improved by modifications such as hydrothermal, chemical and enzymatic treatments. A feasible method to chemically modify starch is through esterification with nutritionally harmless organic acids like lactic acid, citric acid and acetic acid. Organic acids decrease starch digestibility and affect the functional and pasting properties of starch [3]. However, from studies, it is observed that each organic acid differs in the action of starch depolymerization, and the reaction is determined by the origin and properties of organic acids and crystalline type of starches [4]. Since organic acids and starches are cost-effective and readily available materials, modification of starch with organic acids or with its derivatives is a promising technique to utilize starch for food industrial applications.

Corypha umbraculifera L. widely known as talipot palm from the *Arecaceae* family is a tropical monocarpic palm. Talipot palms are native to Myanmar, Malaysia, Sri Lanka, and India and inhabit the moist climate. The stem pith of mature talipot palms stores abound

quantity of starch of light brown color. The non-conventional starch obtained from talipot palm has approx. 76% yield and mere protein and lipid content. This study aims to examine the crystalline, thermal, and pasting properties and in vitro digestibility of starch from talipot palm esterified with generally recognized as safe (GRAS) organic acids, acetic acid and lactic acid.

2. Materials and Methods

2.1. Materials

From a fully matured talipot palm stem pith, starch is isolated by the alkali method with the help of the procedure described by Navaf et al. [5]. The obtained talipot starch was finely ground, sieved, and stored in an air-tight container under refrigeration conditions (4 ± 2 °C). The native talipot starch was considered as control and referred to as NS. Analytical grade chemicals were used for the study.

2.2. Modification with Organic Acids

The native talipot starch was esterified with acetic acid and lactic acid, and the degree of substitution was determined by employing the procedure detailed in Shaikh et al. [3]. The obtained talipot starch was finely ground and sieved for analyses. The esterified starches with acetic acid and lactic acid were referred to as AES and LES, respectively.

2.3. FT-IR, XRD, and RC

FT-IR spectra were performed in the scanning range, 400–4000 cm^{-1} in an FT-IR spectrophotometer (Thermo Fisher Scientific, Nicolet 6700, Waltham, MA, USA). The crystalline pattern was analyzed in an X-ray diffractometer (XRD) (BRUKER, D2 PHASER, Karlsruhe, Germany). The relative crystallinity (RC) of the starch granules was estimated with the formula:

$$\text{RC}\ (\%) = \frac{\text{Crystalline Area}}{\text{Total Area}} \times 100 \quad (1)$$

2.4. Amylose Content, Swelling Index and In Vitro Digestibility

Amylose content was estimated with the method of Williams et al. [6], and swelling index was performed by following the procedure detailed in Sudheesh et al. [7]. The in vitro digestibility of esterified talipot starch was analyzed by the technique of Englyst et al. [8].

2.5. Thermal and Pasting Properties

The onset temperature (T_o), peak temperature (T_P), conclusion temperature (T_c) and gelatinization enthalpy (ΔH) were estimated in differential scanning calorimetry (DSC) (TA Instruments, Q20, New Castle, DE, USA). The pasting viscosities and pasting temperature were analyzed in Rapid Visco Analyzer (Newport Scientific, RVA StarchMaster 2, Warriewood, NSW, Australia). Thermal and pasting properties were performed by following the method described elsewhere [9].

2.6. Statistical Analysis

The experimental data are shown as mean ± standard deviation (SD) and SDs are noted at a significant difference of $p \leq 0.05$. The data from each experiment were put through one-way analysis of variance (ANOVA) and Duncan's multiple range test (DMRT) employing the software, IBM SPSS Statistics 23.

3. Results and Discussions

3.1. FT-IR, XRD and RC

The major peaks observed in all the talipot starch samples, at 3427 cm^{-1}, 2927 cm^{-1}, and 1640 cm^{-1} represents O-H stretching vibration, C-H_2 asymmetric stretching vibration and H-O-H bending vibration, and the extent of peaks reduced in esterified starches because of covalent bond development between the carbonyl and hydroxyl groups of organic acids and starch molecules (Figure 1a). A new peak in the modified starches was observed at 1724 cm^{-1} representing C=O stretching group and it confirms the esterification modification by two organic acids. However, by the esterification with organic acids, it is observed that acetic acid had a DS of 0.091%, whereas lactic acid has a higher DS of 0.107%.

Native talipot starch possessed A-type crystallinity comprising a minor peak at an angle (2θ) 11.2° and major peaks 15.1°, 17.2°, 18.1°, 23.2° (Figure 1b). The crystalline pattern did not change with organic acid treatment; however peaks intensity and RC exhibited a significant reduction ($p \leq 0.05$) (Table. 1). The crystalline structure of starch was destroyed to a reasonable extent by esterification resulting in the destruction of hydrogen bond between the molecules in that region, thus reducing the RC by depolymerization [10].

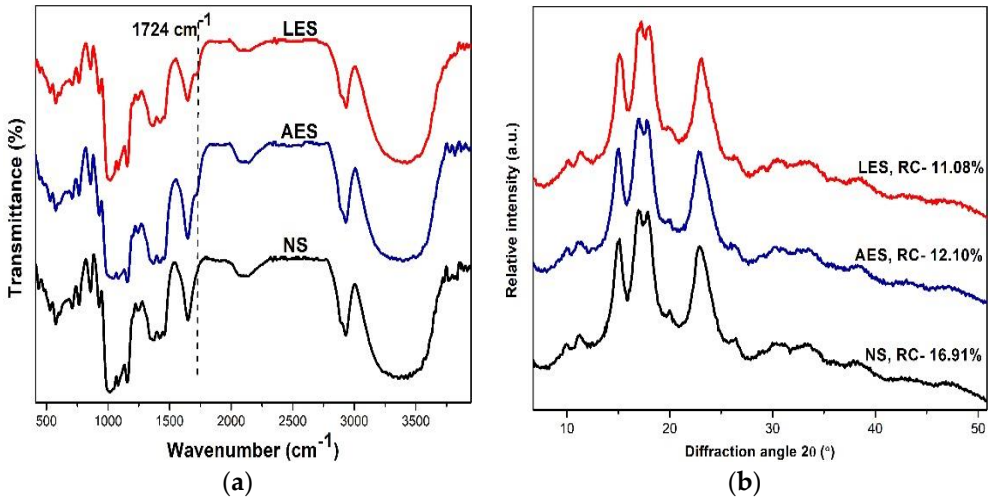

Figure 1. (**a**) FT-IR spectra and; (**b**) XRD of native and organic acid treated talipot starches.

3.2. Amylose Content, Swelling Index, and In Vitro Digestibility

On esterification with acetic acid and lactic acid, amylose showed a significant decrease ($p \leq 0.05$) (Table 1). The organic acids attack the deftly available amorphous regions of the granules and hydrolyze the glycosidic linkages, reducing the amylose content. A similar trend was perceived when talipot starch was treated with another organic acid (citric acid) [10]. The hydration property of starch under different temperatures is determined by its swelling index. As indicated in Figure 2. as the temperature increases from 60 to 90 °C, the swelling index of native and modified starches significantly increased ($p \leq 0.05$). However, treatment with organic acid significantly reduced ($p \leq 0.05$) the swelling index of esterified starches. Starch degradation by partial acid hydrolysis of amylopectin and amylose in both amorphous and crystalline regions reduces the swelling index of modified talipot starches [11]. Shaikh et al. [3] in their study with lactic acid and citric acid-modified sorghum and corn starches reported a similar decrease in swelling index.

Upon esterification with acetic acid and lactic acid, in vitro digestibility decreased with a significant increase ($p \leq 0.05$) in RS content (Table 1). When treated with organic acids, the hydroxyl groups in all positions of starch were substituted with the ester group to form bulky chains. This reaction enhanced stearic hindrance, which resists starch's enzymatic hydrolysis increasing the RS contents [3]. A consistent trend in RS content was

observed when rice starches were dual modified with organic acid and heat-moisture treatment [11]. Hence, esterified talipot starch with organic acids can be used for preparing low-glycemic index food products.

Table 1. Relative crystallinity, amylose content and in vitro digestibility of native and organic acid-treated talipot starches.

Samples	RC (%)	Amylose Content (%)	RDS (%)	SDS (%)	RS (%)
NS	16.91 ± 0.06 ^{c}	28.13 ± 0.07 ^{c}	29.45 ± 0.35 ^{c}	33.84 ± 0.14 ^{a}	36.71 ± 0.02 ^{a}
AES	12.10 ± 0.17 ^{b}	25.14 ± 0.18 ^{b}	22.66 ± 0.64 ^{b}	36.12 ± 0.23 ^{b}	41.22 ± 0.11 ^{b}
LES	11.08 ± 0.02 ^{a}	23.99 ± 0.12 ^{a}	17.28 ± 0.21 ^{a}	38.02 ± 0.71 ^{c}	44.70 ± 0.54 ^{c}

[1] Values articulated are the mean of triplicate measurements ± SD. The values within the same column having different superscript alphabets indicate a significant difference at $p \leq 0.05$.

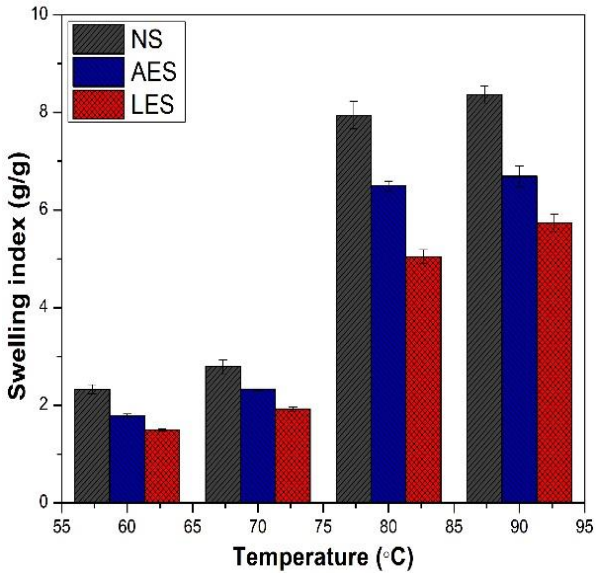

Figure 2. Swelling index of native and organic acid-treated talipot starches.

3.3. Thermal Properties

The gelatinization temperatures (T_o, T_p, and T_c) significantly decreased ($p \leq 0.05$) with organic acid treatment by partial esterification due to the incorporation of new functional groups into starch granules (Table 2). ΔH is the energy needed to melt the crystalline region of starch and it exhibited a significant decrease ($p \leq 0.05$) in organic acid modified talipot starches due to degradation of double helices and reduction of RC. The crystalline region of starch molecules was attacked by the organic acids and in turn, increases the amorphous region [10]. Hence less energy and temperature were required to melt the crystalline structure of esterified starches. The results were on par with the gelatinization parameters of lactic acid and acetic acid modified wheat starch [4].

Table 2. Thermal parameters of native and organic acid treated talipot starches.

Samples	T_o (°C)	T_P (°C)	T_c (°C)	ΔH (J/g)
NS	79.70 ± 0.10 ^{c}	82.31 ± 0.03 ^{c}	87.51 ± 0.20 ^{c}	11.29 ± 0.05 ^{c}
AES	71.05 ± 0.11 ^{b}	75.89 ± 0.12 ^{b}	82.12 ± 0.17 ^{b}	6.72 ± 0.04 ^{b}
LES	66.52 ± 0.21 ^{a}	72.64 ± 0.15 ^{a}	80.23 ± 0.08 ^{a}	5.87 ± 0.20 ^{a}

[1] Values articulated are the mean of triplicate measurements ± SD. The values within the same column having different superscript alphabets indicate a significant difference at $p \leq 0.05$.

3.4. Pasting Properties

The pasting temperature (PT), peak viscosity (PV), breakdown viscosity (BDV), final viscosity (FV), and setback viscosity (SBV) of native talipot starch is 86.46 °C, 3642 cP, 1882 cP, 2560 cP and 800 cP (Figure 3). Upon esterification with an organic acid, PT did not show a significant change in PT of modified talipot starches. On the other hand, the PV, BDV, FV, and SBV significantly reduced ($p \leq 0.05$) with acetic acid and lactic acid treatment when compared to native talipot starch. The reduction in RC and swelling index reduced the pasting viscosity of the organic acid-treated talipot starches. The reduction in the pasting viscosities of modified starch resulted from reduced swelling caused by partial depolymerization of amylose or amylopectin in the amorphous region of starch granules [12]. The significant reduction in FV and SBV indicated a reduced rate of retrogradation tendency of starch by the depolymerization action of acetic acid and lactic acid on talipot starches [13]. Organic acid-treated talipot starches with low pasting viscosity can be utilized as a texturizer in dairy and baked products.

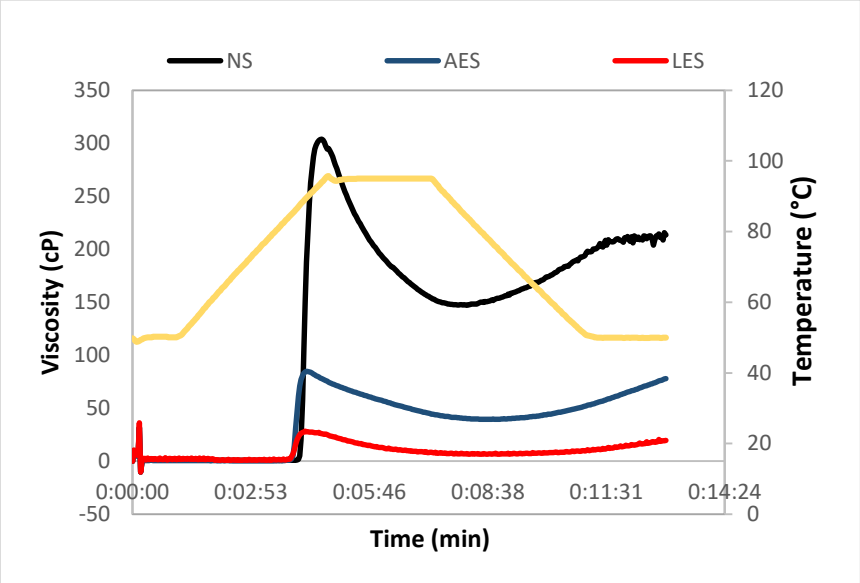

Figure 3. RVA viscogram of native and organic acid-treated talipot starches.

4. Conclusions

The talipot starch is an underutilized source of starch that has the potential to substitute commercially exploited starch sources that are of comparatively low starch yield. Esterification with lactic acid showed a higher impact on starch depolymerization and resistant starch formation than acetic acid. Hence, esterified talipot starches with organic acids are suitable for developing low-glycemic index food products. Besides, organic acid-treated talipot starches exhibiting low pasting viscosity and low retrogradation tendency can be utilized as a texturizer in dairy and baked products.

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References

1. Aaliya, B.; Sunooj, K.V.; Lackner, M. Biopolymer composites : A review. *Int. J. Biobased Plast.* **2021**, *3*, 40–84. https://doi.org/10.1080/24759651.2021.1881214.
2. Sudheesh, C.; Sunooj, K.V.; Anjali, K.U.; Aaliya, B.; Navaf, M.; Kumar, S.; Sajeevkumar, V.A.; George, J. Effect of lysine incorporation, annealing and heat moisture treatment alone and in combination on the physico-chemical, retrogradation, rheological properties and in vitro digestibility of kithul (*Caryota urens* L.) starch. *Int. J. Food Sci. Technol.* **2020**, *55*, 2391–2398. https://doi.org/10.1111/ijfs.14488.
3. Shaikh, F.; Ali, T.M.; Mustafa, G.; Hasnain, A. Comparative study on effects of citric and lactic acid treatment on morphological, functional, resistant starch fraction and glycemic index of corn and sorghum starches. *Int. J. Biol. Macromol.* **2019**, *135*, 314–327. https://doi.org/10.1016/j.ijbiomac.2019.05.115.
4. Majzoobi, M.; Beparva, P.; Farahnaky, A.; Badii, F. Effects of malic acid and citric acid on the functional properties of native and cross-linked wheat starches. *Starch/Staerke* **2014**, *66*, 491–495. https://doi.org/10.1002/star.201300188.
5. Navaf, M.; Sunooj, K.V.; Aaliya, B.; Sudheesh, C.; George, J. Physico-chemical, functional, morphological, thermal properties and digestibility of Talipot palm (*Corypha umbraculifera* L.) flour and starch grown in Malabar region of South India. *J. Food Meas. Charact.* **2020**, *14*, 1601–1613. https://doi.org/10.1007/s11694-020-00408-1.
6. Williams, P.C.; Kuzina, F.D.; Hlynka, I. Rapid colorimetric procedure for estimating the amylose content of starches and flours. *Cereal Chem.* **1970**, *47*, 411–420.
7. Sudheesh, C.; Sunooj, K.V.; Bhavani, B.; Aaliya, B.; Navaf, M.; Akhila, P.P.; Sabu, S.; Sasidharan, A.; Sinha, K.S.; Kumar, S.; et al. Energetic neutral atoms assisted development of kithul (*Caryota urens*) starch–lauric acid complexes : A characterisation study. *Carbohydr. Polym.* **2020**, *250*, 116991. https://doi.org/10.1016/j.carbpol.2020.116991.
8. Englyst, H.N.; Kingman, S.M.; Cummings, J.H. Classification and measurement of nutritionally important starch fractions. *Eur. J. Clin. Nutr.* **1992**, *46*, S33–S50.
9. George, J.; Nair, S.G.; Kumar, R.; Semwal, A.D.; Sudheesh, C.; Basheer, A.; Sunooj, K.V. A new insight into the effect of starch nanocrystals in the retrogradation properties of starch. *Food Hydrocoll. Health* **2021**, *1*, 100009. https://doi.org/10.1016/j.fhfh.2021.100009.
10. Navaf, M.; Sunooj, K.V.; Aaliya, B.; Sudheesh, C.; Akhila, P.P.; Sabu, S.; Sasidharan, A.; George, J. Talipot palm (Corypha umbraculifera L.) a nonconventional source of starch: Effect of citric acid on structural, rheological, thermal properties and in vitro digestibility. *Int. J. Biol. Macromol.* **2021**, *182*, 554–563. https://doi.org/10.1016/j.ijbiomac.2021.04.035.
11. Van Hung, P.; Vien, N.L.; Phi, N.T.L. Resistant starch improvement of rice starches under a combination of acid and heat-moisture treatments. *Food Chem.* **2016**, *191*, 67–73. https://doi.org/10.1016/j.foodchem.2015.02.002.
12. Haros, M.; Blaszczak, W.; Perez, O.E.; Sadowska, J.; Rosell, C.M. Effect of ground corn steeping on starch properties. *Eur. Food Res. Technol.* **2006**, *222*, 194–200. https://doi.org/10.1007/s00217-005-0102-2.
13. Tavares, A.C.K.; Zanatta, E.; Da Rosa Zavareze, E.; Helbig, E.; Dias, A.R.G. The effects of acid and oxidative modification on the expansion properties of rice flours with varying levels of amylose. *LWT—Food Sci. Technol.* **2010**, *43*, 1213–1219. https://doi.org/10.1016/j.lwt.2010.04.007.