



Study on the morphology, crystalline structure and thermal properties of yellow ginger starch acetates with different degrees of substitution

Liming Zhang^{a,*}, Weiguang Xie^a, Xi Zhao^c, Ying Liu^b, Wenyuan Gao^c

^a Key Laboratory of Industrial Microbiology, Ministry of Education, Tianjin University of Science and Technology, Tianjin 300457, China

^b College of Bioengineering, Tianjin University of Science and Technology, Tianjin 300457, China

^c School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 30072, China

ARTICLE INFO

Article history:

Received 15 January 2009

Received in revised form 25 May 2009

Accepted 29 May 2009

Available online 12 June 2009

Keywords:

Yellow ginger

Starch acetate

Degrees of substitution

Physicochemical properties

ABSTRACT

Yellow ginger starch acetates with different degrees of substitution (DS) were prepared by reacting native starch with glacial acetic acid/acetic anhydride using sulfuric acid as catalyst. X-ray diffraction (XRD) of acetylated starch revealed that the crystal structure of native starch was disappeared and new crystalline regions were formed. Their formation was confirmed by the presence of the carbonyl signal around 1750 cm^{-1} , as well as the reduced hydroxyl groups, in the Fourier transform infrared spectroscopy (FT-IR). The scanning electron microscopy (SEM) suggested most of the starch granules disintegrated with many visible fragments along with the increasing DS. The thermal behavior of the native starch and starch acetate were investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), it was observed that the thermal stability of acetylated starch depends on the degree of substitution. Thermal stability of high DS acetylated starch is much better than that of the original starch when DS reached to 2.67.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Yellow ginger, whose scientific name is *Dioscorea zingiberensis* C.H. Wright, is a perennial grass vine plant. With its rootstocks containing rich saponins, it is a starting raw material for steroid medicine and is widely applied in medicines for contraception, analgesia and anesthesia, etc. [1]. Yellow ginger is unique to China and it is mainly distributed from the upper reaches of Hanjiang Basin of Wudang Mountain in Hubei province to the northern foot of the Qinling Mountains in Shanxi province. Currently, over 10 provinces and cities in China have developed the yellow ginger industry. The area of yellow ginger bases has been developed to over 166,750 ha, the number of saponins processing enterprises has reached nearly 200 and the production capacity of saponins has reached over 5000 t [2]. In the rhizome of fresh yellow ginger cultivars, starch is the main components making up 13–18% content in the total biomass [3].

The traditional processing technique wastes a large amount of resources. Starch and cellulose are discarded and become the main contents in the water pollutants. The large amount of waste water discharged during yellow ginger processing contained strong acid and the input of treatment is quite high. As for an enterprise with an annual output of 100 t saponins, it will need about Renminbi (RMB)

5–8 million yuan for the disposal work [4]. Therefore, cleaner production is an inevitable choice for extracting saponins from yellow ginger. The ideas of circular economy and cleaner production are consistently implemented in the technique development and application. Under the prerequisite of guaranteeing the saponin recovery rate, physical methods are adopted to separate the starch and cellulose in yellow ginger in order to realize the utilization of wastes as resources and improve economic benefits.

It is well known that extensive research has been conducted on the structure and functional properties of the commercial starches obtained from crops due to their ready availability and their extensive utilization in food and non-food applications [5]. However, the starch derived from medicinal plants has not been paid enough attention by starch researchers. In order to widen the application of these plants which contained plenty of starches and provide a new starch for the food and pharmaceutical industry, the effort should have been made to investigate the physicochemical properties of these starches and their modification.

Native starch has the disadvantages of hydrophilicity, poor mechanical properties and dimensional stability, especially in presence of water and in humid environments [6]. Starch modification can overcome these shortcomings by means of altering the structure and affecting the hydrogen bonding of amylose and amylopectin in a controllable manner to enhance and extend starch application. Following crosslinking, esterification and etherification are the second important modifications in the starch industry [7]. The most typical starch ester is acetylated starch, which is

* Corresponding author. Tel.: +86 22 60601265.

E-mail address: zhanglmd@yahoo.com.cn (L. Zhang).

actively marketed due to the specific properties arising from the substitution groups. The introduction of acetyl groups interrupts the ordered structure of native starch and interferes with the re-association of amylose and amylopectin in gelatinized starch, leading to the change in morphological properties, crystalline properties, gelatinization properties involving transition temperatures and gelatinization enthalpy of the starch [8]. Starches with DS of 0.01–0.2 are of commercial interest because of their usage based on properties with respect to film forming, binding, adhesion, thickening, stabilizing and texturing. Highly acetylated starch with a degree of substitution (DS) of 2–3 was of research interest from 1950 through 1980 for their solubility into acetone and chloroform and for their thermo plasticity [9]. As a biodegradable carbohydrate polymer material, acetylated starch also has many potential uses in pharmaceutical applications [10]. Therefore, acetylated starch could have potential use in food and pharmaceutical industries.

The purpose of this study was to understand the changes of yellow ginger starch before and after esterification. The morphology and crystalline structure of yellow ginger acetates with different degrees of substitution were investigated by IR, SEM and XRD. The materials were then treated to thermal analysis, using TG–DTG and DTA to examine whether esterification had any effect on the thermal behavior of starch granules. With the obtained result, it is possible to precisely evaluate the availability and provide sufficient parameters to all kinds of uses of yellow ginger starch.

2. Materials and methods

2.1. Materials

The yellow ginger (*D. zingiberensis* C.H. Wright) tubers were provided by Ankang medicine Co., Shanxi, China (November, 2007). These tubers were cultivated (under soil conditions) in the province of Shanxi, China for 2 years cultivation period.

2.2. Starch extraction

In the yellow ginger starch isolation, the tubers were trimmed to get rid of defective parts and washed with water, and then the tubers were sliced into pieces with the thickness between 3 and 5 mm and dried in an oven until weight constancy. The small slices were incubated in 0.2% (w/v) NaOH solution (pH 10–11) for 24 h, in order to macerate the botanical cell wall and to reduce activities of microbes and enzymes that may decompose starches. After the tubers were milled, the slurry was filtered through 150 μm screen. The supernatant was milled for several times and the slurry refiltered through 150 μm screen to keep the cell wall off the starch slurry. Then the residue was amassed and deposited quietly for 6 h. The liquid layer was discarded and the superficial impurity of starch was eradicated. Ethanol (95%) was added to remove the scanty dioscin. Subsequently, the starch fraction was raised several times with distilled water until a neutral pH was reached. The slurry was sieved with 75 μm mesh size several times. The starch suspension obtained was dried in a convection oven at 50 °C until weight constancy. The dried material was milled and sieved with 75 μm screen to get the starch flour [11]. Zhou et al. [12] and Wang et al. [13] have examined the yellow ginger starch for its chemical composition, amylose content and physicochemical properties in paper.

2.3. Preparation of starch acetates

The dry native starch of 10.0 g was stirred with 10.0 mL glacial acetic acid at room temperature for about 2 min. Then 30.0 mL cold acetic anhydride was added over a period of 5 min. Sulfuric acid (98%) of 0.38 mL as the catalyst was diluted with 10.0 mL glacial acetic acid and was added to the reaction system over a period of

10 min. The temperature was controlled at 70 °C, and then held at this temperature for 20, 90, 120, 150 and 180 min to prepare yellow ginger starch acetates with DS of 0.09, 0.50, 1.51, 2.26 and 2.67, respectively. When the reaction was completed, the hot starch acetate solution was added to distilled water to terminate the reaction. The ratio of reaction solution to water was maintained at about 1:10. The precipitated product was collected on a Buchner funnel, washed by distilled water until neutrality, transferred to a glass jar and dried at 50 °C in a vacuum oven overnight [14].

2.4. The determination of the degree of the substitution

Determination of DS by titration involved complete basic hydrolysis of the ester linkages and titration of the excess alkali [15]. The starch acetate grounded sample of 0.5 g was accurately weighted and dissolved with acetone (25 mL), then an exact amount of aqueous solution of sodium hydroxide (0.50 M, 25 mL) was added and the solution was stirred for 1 h at room temperature. After indicator (phenolphthalein) was added, the excess of alkali was titrated with 0.50 M hydrochloride acid. The reference sample and duplicate sample were treated in a similar way.

The acetyl content (A%) was calculated according to following equation [15]:

$$A\% = \frac{(V_0 - V_n) \times N \times 43 \times 10^{-3}}{M} \times 100\% \quad (1)$$

where V_0 (mL) is the volume of 0.5 M HCl used to titrate the blank, V_n (mL) is the volume of 0.5 M HCl used to titrate the sample, N is the concentration of the HCl (M) used, M (g) is the amount of dry starch acetate sample, number 43 is the formular weight of acetyl groups. The acetyl content (A%) was used to calculate the degree of substitution, DS, according to the following equation [15]:

$$DS = \frac{162 \times A}{43 \times 100 - (43 - 1) \times A} \quad (2)$$

where 162 is the molecular weight of anhydroglucose unit, 43 is the formular weight of acetyl groups, and 1 is the atomic mass of hydrogen.

2.5. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of the native starch and starch acetates were recorded with an IR spectrometer (Bruker Vector 22), using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr in the ratio of 1:30.

2.6. Scanning electron microscopy (SEM)

The morphological features of the native starch and starch acetates of different DS were observed with a scanning electron microscope (ESEM Philips XL-30). The dried samples were mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 20 kV. Micrographs were recorded at 500 \times magnification to assure clear images.

2.7. X-ray diffraction

X-ray diffraction patterns of the native yellow ginger starch and starch acetate were analyzed using Rigaku D/max 2500 X-ray powder diffractometer (Rigaku, Tokyo, Japan) with nickel filtered Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at a voltage of 40 kV and a current of 200 mA. The scattered radiation was detected in the angular range of 5–60° (2θ), with a scanning speed of 8° (2θ)/min and a step of 0.06° (2θ).

Download English Version:

<https://daneshyari.com/en/article/674958>

Download Persian Version:

<https://daneshyari.com/article/674958>

[Daneshyari.com](https://daneshyari.com)