JOURNAL OF FOOD AND DRUG ANALYSIS 23 (2015) 442–446

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.jfda-online.com

Original Article

Effective extraction method through alkaline hydrolysis for the detection of starch maleate in foods

Chia-Fen Tsai [a], Guan-Yan Wu [a], Ching-Hao Kuo [a], Yung-Wei Lin [a], Chun-Hsiung Chang [a], Su-Hsiang Tseng [a], Ya-Min Kao [a], Lih-Ching Chiueh [a], Ting-Jang Lu [c], Daniel Yang-Chih Shih [b,*]

[a] Department of Food Chemistry, Food and Drug Administration, Ministry of Health and Welfare, Taipei, Taiwan
[b] Ministry of Health and Welfare, Taipei, Taiwan
[c] Institute of Food Science and Technology, National Taiwan University, Taipei, Taiwan

ARTICLE INFO

Article history:
Received 7 April 2014
Received in revised form
11 August 2014
Accepted 19 September 2014
Available online 2 January 2015

Keywords:
HPLC
LC-MS/MS
maleic acid
starch
starch maleate

ABSTRACT

A high-performance liquid chromatography (HPLC) method was developed for the determination of maleic acid which was released from starch maleate (SM) through the alkaline hydrolysis reaction. The proper alkaline hydrolysis conditions and LC separation are reported in this study. The starch samples were treated with 50% methanol for 30 minutes, and then hydrolyzed by 0.5N KOH for 2 hours to release maleic acid. A C18 column and gradient mobile phase consisting of 0.1% phosphoric acid and methanol at a flow rate of 1.0 mL/minute were used for separation. The method showed a good linearity in the range of 0.01–1.0 ìg/mL, with a limit of quantification (LOQ) at 10 mg/kg in starch. The recoveries in corn starch, noodle, and fish balls were between 93.9% and 108.4%. The relative standard deviation (RSD) of precision was <4.9% ($n = 3$). This valid method was rapid, sensitive, precise, and suitable for routine monitoring of the illegal adulteration of SM in foods.

Copyright © 2014, Food and Drug Administration, Taiwan. Published by Elsevier Taiwan LLC. Open access under CC BY-NC-ND license.

1. Introduction

Starch maleate (SM) is modified starch made of starch and maleic anhydride through the esterification process. It has been used in the paper industry as sealing adhesive [1] and evaluated as a potential drug delivery carrier [2]. Modified starches, in Taiwan, by law are listed in the "Standards for Specification, Scope, Application and Limitation of Food Additives" [3] such as, acid-modified starch, alkaline-treated starch, oxidized hydroxypropyl starch, and starch sodium octenyl succinate allowed to be used in foods.

Although SM is widely manufactured and used in industries, it is not a permitted raw material for foods. However, it has been reported that SM was illegally adulterated into starch and starch food products in Asia to enhance starch

* *Corresponding author*. Ministry of Health and Welfare, 488, Sec. 6, Zhongxiao E. Rd., Taipei, Taiwan.
E-mail address: shihdyc@fda.gov.tw (D.Y.-C. Shih).
http://dx.doi.org/10.1016/j.jfda.2014.09.002
1021-9498/Copyright © 2014, Food and Drug Administration, Taiwan. Published by Elsevier Taiwan LLC. Open access under CC BY-NC-ND license.

properties for the purposes of water keeping, anti-retrogradation, and chewy texture. Hence, there are needs to establish a quantitative and qualitative method for monitoring the prohibited SM in foods.

The monitoring of maleic acid in food products was one of the means for the prevention of SM adulteration in food. Gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE) and LC with tandem-mass spectrometry (LC-MS/MS) [4–6] were reported for the determination of organic acids and/or maleic acid in a wide variety of samples. Among these methods, however, they were limited on the detection of free maleic acid in sample solutions. In SM, maleic acid linked to the hydroxyl group of starch through ester bonding. Therefore, a proper alkaline hydrolysis treatment was necessary in order to release maleic from modified starch. In this study, the proper alkaline hydrolysis conditions, extraction, and LC separation for the determination of maleic in SM and starch products were investigated and are described.

2. Methods

2.1. Materials

Twenty three commercial food starches (1 corn starch, 3 tapioca starches, 3 potato starches, 2 sweet potato starches, and 14 rice flours) and 51 starch foods (4 tapioca starch balls, 15 noodles, 16 fish products, 2 glass vermicelli, 11 rice flour cakes, 2 rice balls, 1 sweet potato, and 1 taros ball) were collected from the retailers and supermarkets in Taipei. These samples were homogenized and stored below −18°C until analysis.

2.2. Chemicals and reagents

Maleic acid (99%), oxolic acid, malic acid, succinic acid, and maleic anhydride were purchased from Sigma-Aldrich (St. Louis, MO, USA). Citric acid was purchased from JT Baker Chemical Co. (Phillipsburg, NJ, USA). Fumaric acid was from Nacalai Tesque Inc. (Kyoto, Japan). HPLC grade methanol, glacial acetic acid (100%), ascorbic acid, potassium hydroxide, phosphoric acid (85%), and hydrochloric acid were from E. Merck (Darmstadt, Germany).

2.3. Preparation of SM

A mixture of corn starch (10 g) and glacial acetic acid (10 mL) was stirred at 95°C, and then maleic anhydride (10 g) was added. This dispersed starch slurry gradually turned a pale yellow color while stirring and heating. Sulfuric acid (0.98 mmole) was slowly added to the mixture, and it was stirred continuously for a further 30 minutes at the same temperature. Upon completion of the reaction, the mixture was cooled to room temperature, and then the SM product was precipitated by absolute ethanol (50 mL) at room temperature. MS was collected by vacuum filtration, and then rinsed three times with 95% ethanol to remove excess maleic anhydride. The product was then dried overnight at 45°C in a conventional oven. The major pathway of the esterification is shown in Fig. 1 [7]. The bound maleic acid can be released form SM through alkaline hydrolysis reaction (Fig. 1).

2.4. Instrumentation and HPLC-DAD, LC-MS/MS analytical conditions

The separation of target analytes was carried out using an UltiMate3000 Standard LC System with a detector DAD-3000RS (diode array detector, Dionex Corporation Sunnyvale, CA, USA) which equipped with an InertSustain C18 (4.6 mm × 250 mm, 5 μm) column (GL Sciences, Tokyo, Japan). The mobile phase was a mixed solution of 0.1% phosphoric acid/methanol (98:2, v/v). Isocratic elution chromatography was at a flow rate of 1 mL/minute. The target analytes were detected at the wavelength of 214 nm. The injection volume was 20 μL.

LC-MS/MS chromatographic separation was performed using an HPLC system including an ekspert ultraLC 100 system (Eksigent Technologies, Livermore, CA, USA), a triple quadrupole mass spectrometer QTRAP 5500 LC-MS/MS system (Applied Biosystems, Foster City, CA, USA), a Turbo V ion source, and a GL Sciences InertSustain C18 column (2.1 mm × 150 mm, 3 μm). Gas nitrogen was supplied by a nitrogen generator (Peak Scientific Instruments Ltd., Chicago, IL, USA). Nitrogen was employed as curtain gas, nebulizer gas, and collision gas on the MS. The mobile phase consisted of 0.1% formic acid/methanol (98:2, v/v) at a flow rate of 0.3 mL/minute. The electrospray ionization mass spectra (ESI-MS) were acquired in the negative ion (ESI^-) mode. The other MS parameters were: ion spray voltage: −4.5 kV, curtain gas: 20 psi, collision gas: high, turbo gas: 55 psi, nebulizer gas: 55 psi, declustering potential: 15V, collision energy: 11 and 30V for m/z 115 > 71 and m/z 115 > 27, respectively.

2.5. Fourier transform infrared spectrometer

Infrared spectra of SM and starches were recorded using Smiths Identify IR (Smiths Detection Inc., Watford, UK) with attenuated total reflectance (ATR) accessory (resolution = 4 cm^{-1}, 32 scans/

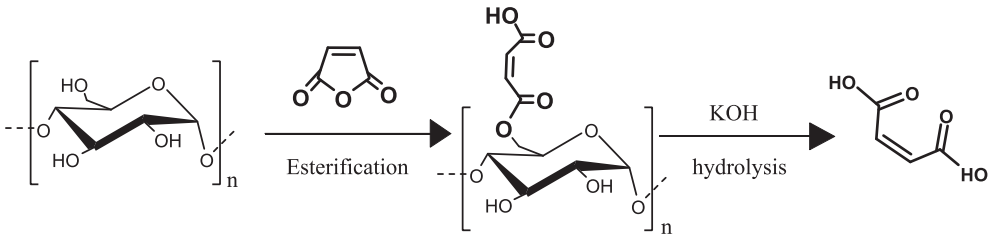

Fig. 1 – Pathway of the esterification and hydrolysis of starch maleate.

Download English Version:

https://daneshyari.com/en/article/2507443

Download Persian Version:

https://daneshyari.com/article/2507443

Daneshyari.com