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Chromatographic analysis and preparation of L-arabinose from corncob by acid hydrolysis

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ABSTRACT

L-arabinose, a kind of rare sugar, which has already become newly developed functional saccharide with many beneficial biomedical and health effects. In this study, we carried out several experiments to analyze the component of hydrolyzed corncob. Components in the hydrolysate were detected by the methods of ultraviolet spectrogram, HPLC, TLC and High-efficient Thin Layer scanning analysis. The hydrolysis temperature, holding time, concentration of oxalic acid and solid-liquid ratio were investigated as objects by single factor experiments. The results showed that the content of saccharides in the hydrolysate of corncob was up to 72.70%. Three kinds of monosaccharide (D-xylose, L-arabinose, D-glucose) were detected by HPLC analysis and the relative amount of the above three saccharides were 32.8%, 31.4% and 35.7%, respectively. The optimum conditions were: temperature 90 °C, holding time 5 h, concentration of oxalic acid 6%, solid-liquid ratio 1:12, and the highest L-arabinose yield was 14.89%.

1. Introduction

L-arabinose is a kind of rare sugar, which can significantly decrease bodies' blood sugar (Kaats et al., 2011). The sweet taste of L-arabinose is similar to that of sucrose, but approximately equivalent to half of the sweetness of sucrose (Loeza-Corte et al., 2007). It can be used as a starting material in the synthesis of non-ionic surfactants (Bouquillon, 2011), as pharmaceutical intermediates for the synthesis of anti-AIDS, anti-virus and anti-cancer drugs (Helanto et al., 2009). It can also inhibit sucrase activity (Krog-Mikkelsen et al., 2011) and has very peculiar physiological functions. Nowadays L-arabinose is obtained mainly from maize bran, wheat bran, begass pith and beets by the methods of enzymatic hydrolysis, chemical synthesis, microbiological fermentation and acid hydrolysis. However the products prepared by those methods usually contain other components. Content of L-arabinose in the mixture is unknown (Liu et al., 2013). Corncob, as another important source, contains lots of nutritional ingredients such as saccharides, crude fiber, alkaloids and so on (Wang et al., 2014). Usually, corncob is treated with burning, which not only leads to pollution but also resource-wasting (Cheng et al., 2012; Fang et al., 2010). A small part of corncob is used in production of xylo-oligosaccharides (Kawee et al., 2016; Katapodis and Christakopoulos, 2008) or furfuraldehyde. However, there are not enough works dealing with the preparation of L-arabinose from corncob. Limited by its production method, L-arabinose is expensive in present international market, which limits its application and popularity in the food and pharmaceutical industry. Therefore, reducing the preparation cost and improving the yield are necessary.

Compared to former researches, preparation method in this study was less expensive and much easier in practice; content of each component was elucidated clearly; furthermore, the highest yield of L-arabinose and the optimal preparation conditions were obtained.

2. Materials and methods

2.1. Materials and reagents

Corncob was provided by Shandong Long Li Biotechnology Co. Ltd. Basic components in it were water, ash, crude fiber and lignin, and content of them were 12.06%, 1.87%, 43.34% and 28.47%, respectively. Standard monosaccharides (D-glucose, D-xylose and

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Table 1
Data analyses of the high-efficient thin layer scanning curve.

NO.	Location	Rf	Height(mm)	Width (mm)	Integral value	Area percentage (%)
Sample 1	1	0.37 ± 0.27	29.64 ± 0.83	2.30 ± 0.48	1030 ± 0.59	32.80 ± 1.54
Sample 2	2	0.51 ± 0.54	29.53 ± 1.44	2.30 ± 0.69	985 ± 0.67	31.40 ± 1.40
Sample 3	3	0.59 ± 0.19	38.47 ± 0.95	2.35 ± 1.21	1120 ± 0.82	35.70 ± 0.63

L-arabinose) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All other chemicals and solvents used in this study were of analytical grade.

2.2. Acid hydrolysis of corncob

Corncob was heated with dilute oxalic acid to extract L-arabinose by controlling ratio (90 °C, 5 h, 6%, 1:12). The reaction mixture was cooled to room temperature, then the suspension was filtrated in vacuum with centrifugation at 4000r/min for 15 min. Filtrate was freeze-dried in vacuum (Sjoman et al., 2007).

2.3. Determination of saccharides

The content of saccharides in hydrolysate was determinated by phenol-sulfuric acid method using D-glucose as standards (Zhang et al., 2013). 0.01, 0.02, 0.04, 0.08 and 0.1 ml of glucose standard solution (0.1 mg/ml) were put into separate tubes, and diluted with water till 1.0 ml. Then 1 ml of 6% phenol and 5 ml of concentrate H_2SO_4 were added into each tube. After fully mixing for 15 min, the tubes were heated on the boiling water bath for 15 min. After cooling to room temperature, OD value of each tube was examined in 490 nm (Masuko et al., 2005; Hou and Chen, 2008).

2.4. Ultraviolet spectrogram analysis

1 mg hydrolysate was put into tube and dissolved with 10 ml of distilled water. After being fully mixed the solution was added slowly into quartz colorimetric utensil (Be careful not to over three-quarters of the capacity). It was treated by G10S UV–vis spectrophotometer with full wave scanning within 200nm–400 nm waves, scanning speed medium and interval being 1.0 nm.

2.5. Thin-layer chromatography analysis (David et al., 2009)

Thin-layer chromatography (TLC) was performed on 10 × 20 cm silica gel 60F254 plates (Darmstadt, Merck, Germany). All standards and samples were applied by means of capillary tube (Simonovska et al., 2003). Plates were developed in horizontal trough developing chamber using a solvent system consisted of glacial acetic acid–chloroform–absolute ethyl alcohol–distilled water (3:11:11:1, v/v/v/v). 2.5 g of diphenylamine was used as detection reagent which was added to 5 ml of aniline and 25 ml of 85% (v/v) phosphoric acid and diluted to 250 ml by acetone (Zhu et al., 2015).

2.6. High-efficient thin layer chromatography scanning analysis

The above silica gel plate was put into the KH-3000 Thin Layer Chromatographic Scanner. In the scanning system, setting the testing type was single-wavelength testing and sample point spacing was unequal interval scanning. Under the conditions of 560 nm wavelength, 25mm–35 mm vertical test range and 5 mm horizontal position, the fingerprint chromatography and related data analysis were obtained.

2.7. High-pressure liquid chromatography analysis

Qualitative and quantitative analyses of monosaccharides were carried out by high-pressure liquid chromatography (HPLC) using an Agilent 1200 chromatograph (Agilent Technologies) (Yoshihiro et al., 2010). Sample was dissolved in 2 ml of acetonitrile/water (75:25, v/v) and filtered through a 0.22-μm Millipore filter, applied to a HPLC system equipped with APS-2 Hypersil column (4.6 × 250 mm, column temperature 30 °C, refractive index detector,detecting temperature 35 °C). A sample solution (20 μl) was injected with acetonitrile/water (75:25, v/v) at a flow rate of 0.2 ml/min.

Method for preparing the L-arabinose standard curve: Weighing accurately L-arabinose: 5 mg, 10 mg, 20 mg, 30 mg, 40 mg, 50 mg, which was dissolved in 10 ml of acetonitrile/water (75:25, v/v) respectively. Horizontal ordinate means the concentration of L-arabinose (mg/ml) and vertical ordinate is lgA and A means peak area. Therefore, if the peak area of L-arabinose in the hydrolysate was detected, then we would obtain its actual content based on the standard curve. The yield of L-arabinose was then calculated using the following equation:

$$\text{yieldofl-arabinose}(\%) = (m \cdot c)/M \times 100$$

In the equation: m is the weight of hydrolysate (g), c is the content of L-arabinose (%) and M is the weight of corncob (10 g).

2.8. Single factor experiment

2.8.1. Hydrolysis temperature

Corncob was crushed and sifted through 60 meshes sieves. 10 g of corncob powder was added into 6% oxalic acid solution. The solid-liquid ratio was 1:12, holding time 5 h with continuous stirring. The temperature was set as 60 °C, 70 °C, 80 °C, 90 °C and 100 °C, respectively. The reaction mixture was cooled to room temperature, then the suspension was filtrated in vacuum with centrifugation at 4000r/min for 15 min. Filtrate was freeze-dried in vacuum.

Table 2
Influence of single factor to the yield of L-arabinose.

Temperature/C	yield(%)	Holding time/h	yield(%)	Concentration of acid	yield(%)	Solid-liquid ratio	yield(%)
60 °C	3.42 ± 0.14	1	3.33 ± 0.22	2%	4.78 ± 0.52	01:08	4.59 ± 0.25
70 °C	6.49 ± 0.81	2	4.36 ± 0.28	3%	6.21 ± 0.29	01:10	6.84 ± 0.76
80 °C	8.01 ± 0.20	3	6.01 ± 0.35	4%	7.46 ± 0.37	01:12	7.52 ± 0.82
90 °C	9.11 ± 0.32	4	7.89 ± 0.19	5%	8.21 ± 0.09	01:14	7.13 ± 0.48
100 °C	8.32 ± 0.17	5	7.41 ± 0.42	6%	7.74 ± 0.74	01:16	6.43 ± 0.73