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Chemical Engineering Research and Design

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A new approach to catalytic hydrolysis of ester-bound biphenyl cyclooctene lignans from the fruit of *Schisandra chinensis* Baill by ion exchange resin

Chun-hui Ma^{a,1}, Lei Yang^{a,*,1}, Yuan-gang Zu^{a,**}, Ni-hong Wang^b, Lin Zhang^a, Ying Zhang^a, Xiao-qiang Chen^a, Chun-jian Zhao^a

^a Key Laboratory of Forest Plant Ecology, Ministry of Education, Northeast Forestry University, 150040 Harbin, China

^b College of Information and Computer Engineering, Northeast Forestry University, 150040 Harbin, China

ABSTRACT

In this study, a novel approach was developed to hydrolyze ester-bound biphenyl cyclooctene lignans (EBBCL) from the fruits of *Schisandra chinensis* Baill into free-state biphenyl cyclooctene lignans (FSBCL) using ion exchange resin. The results of static hydrolysis tests showed that SK1B (H-type strongly acidic cation exchange resin) was the best acidic hydrolysis catalyst and 201 × 7 (OH-type strongly basic anion exchange resin) was the best basic hydrolysis catalyst. According to the underlying mechanism for hydrolytic degradation, the hydrolysis effect of basic catalyst is more obviously. The dynamic hydrolysis efficiency of 201 × 7 (146.7 ± 5.0%) was higher than that of SK1B (131.5 ± 4.7%). Compared with the purity of FSBCL (3.52 ± 0.06%) catalytic hydrolysis by traditional catalyst NaOH, the purity of FSBCL (5.85 ± 0.04%) hydrolysis by 201 × 7 resin was much higher, increased 2.94-fold under the optimization hydrolysis conditions.

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Keywords: *Schisandra chinensis* Baill; Biphenyl cyclooctene lignans; Catalytic hydrolysis; Ion exchange resin

1. Introduction

Dried fruits of *Schisandra chinensis* Baill are one of the most famous and frequently used herbal medicines and food additives (Pharmacopoeia of the People's Republic of China, 2010). It has a long history of medical use as a tonic, sedative and astringent agent to treat various diseases in China, Korea and Japan (Park et al., 2009; Chang et al., 2005; Wang, 2002). Various reports suggested that major bioactive constituents of *S. chinensis* were free-state biphenyl cyclooctene lignans (FSBCL), including schizandrin [S], schisantherin A [SA], deoxyschizandrin [DS] and γ -schizandrin [GS] (Kuo et al., 1997; Chen et al., 1998; Choi et al., 2006; Panossian and Wikman, 2008; Ma et al., 2011a). The beneficial biological active effects of *S. chinensis* FSBCL are anti-hepatotoxic, antioxidant

(Chiu et al., 2002; Ko and Lam Brian, 2002), antitumor (Deng et al., 2008; Chen et al., 2002), anti-HIV (Bharate Sandip, 2003; Chen et al., 1996), detoxificant, anticarcinogenic (Fu et al., 2008), activity on circulatory system (Opletal et al., 2001), central nervous system and counteract the fatigue, increase the duration (Peng et al., 2005), anti-inflammatory (Guo et al., 2008) and improve the physical fitness of sportsmen (Peng et al., 2005). It also has other pharmacological effects, such as chronic cough, asthma, spontaneous sweating, palpitation, spermatorrhea, diabetes, insomnia, forgetfulness (Wu, 2005) and antiproliferative effects on cancer cells (Min et al., 2008).

The hydroxyl group in the structure of biphenyl cyclooctene lignans can easily form ester bond with other organic acid in plants. Hydrolysis can increase the content of FSBCL by transformation of ester-bond biphenyl cyclooctene lignans (EBBCL). In the hydrolysis process, cleavage of the

* Corresponding author at: Key Laboratory of Forest Plant Ecology, Ministry of Education, Northeast Forestry University, Box 332, Hexing Road 26, Heilongjiang Province, Harbin 150040, China. Tel.: +86 451 82191387; fax: +86 451 82102082.

** Corresponding author at: Key Laboratory of Forest Plant Ecology, Ministry of Education, Northeast Forestry University, Box 332, Hexing Road 26, Heilongjiang Province, Harbin 150040, China. Tel.: +86 451 82191517; fax: +86 451 82102082.

E-mail addresses: ymanefu@163.com (L. Yang), zygorl@126.com (Y.-g. Zu).

Received 7 August 2011; Received in revised form 19 October 2011; Accepted 29 December 2011

ester bond occurs, but there are no other structural changes (Chen et al., 2001).

Homogeneous acidic or basic catalyst, such as hydrochloric acid and sodium hydroxide, are generally used for hydrolysis of esters in industry (Naomi et al., 2007). However, the aqueous catalyst in solution cannot be recovered after use and have to be neutralized at the end of the hydrolysis reaction, which is usually uneconomical and may result in secondary pollution.

Ion exchange resins have been widely used as catalyst in organic synthesis. Conventional strongly basic anion exchange resin or those which carry other functional group were used as phase-transfer catalyst in preparations of cyanide or ether. Sometimes, they are used as substitute for small basic molecule to catalyze aldol condensation, addition, rearrangement, etc. (Zhang and Ye, 2008; Chen et al., 1999; Heidekum et al., 1999; Liu and Tan, 2001). Ion exchange resins are commonly used for esterification (Yadav and Thathagar, 2002) and transesterification reactions (Reis et al., 2005), and their catalytic role in ester hydrolysis (e.g., ethyl acetate, ethyl n-hexanoate, ethyl phenylacetate and dimethyl phthalate) has been well demonstrated (Samelson and Hammett, 1956; Miyazaki et al., 1996; Xu et al., 2010). More recently, Basu used Dowex-50 (Basu et al., 1989), a solid acid polymer catalyst, to selectively catalyze the hydrolysis in an aqueous suspension. As compared to the traditional aqueous acid/base catalyst, one advantage of ion exchange resin is that it can be readily separated from the reaction system for reusability. Nevertheless, high operation temperature renders such solid-acid-induced hydrolysis and removal from contaminated water phase. Another advantage, a strong economic driver to use a solid catalyst instead of a liquid is reduced equipment corrosion (Harmer and Sun, 2001). Hence, it is of interest to investigate the hydrolysis effect of EBBCL using solid polymer acid or basic catalyst.

In this report, a novel hydrolysis method of EBBCL from *S. chinensis* crude extract was developed by catalytic transformation using ion exchange resin. The hydrolysis parameters are optimized and then a dynamic hydrolytic degradation process of EBBCL is established.

2. Material and methods

2.1. Material

2.1.1. Chemicals and reagents

S, SA, DS, GS standards (98% purity) were purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China) respectively. The standards (S, SA, DS and GS) were dissolved in methanol. Deionized water was prepared by a Milli-Q water purification system (Millipore, MA, USA). All solution prepared for HPLC were filtered through 0.45 μm membranes (GuangFu Chemical Reagents Co., Tianjin, China) before using. Acetonitrile and acetic acid of HPLC grade were purchased from J&K Chemical Ltd. (USA), and all of other solvents and chemicals used in this study were of analytical grade from Beijing Chemical Reagents Co. (Beijing, China).

2.1.2. Ion exchange resins

Ion exchange resins SK1B and WK11 were purchased from Mitsubishi Chemical Corporation (Tokyo, Japan), other 14 ion exchange resins were purchased from Cangzhou Bon Adsorber Technology Co., Ltd. (Hebei, China), and the physical properties of ion exchange resins were summarized in Table 1. Prior to the hydrolysis experiments, weighed amounts of resins

were soaked in ethanol and subsequently washed by deionized water thoroughly. Then the resins were pretreated by 1 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH) solution successively to remove the monomers and porogenic agents trapped inside the pores during the synthesis process and washed by deionized water until neutral. Three parallel samples for each resin were accurately weighed, placed in an oven and dried at $105 \pm 2^\circ\text{C}$ until the mass was constant. The moisture contents are shown in Table 1.

2.2. Methods

2.2.1. LC-ESI-MS qualitative analysis and HPLC-UV quantitative analysis method

The structure of biphenyl cyclooctene lignans is determined by LC-ESI-MS, in order to prove that whether the base core structure of biphenyl cyclooctene lignans change or not in hydrolysis process. Agilent 1100 series HPLC system equipped with G1312A Bin pump and G1379A Degasser (Agilent, San Jose, CA, USA) and G1316A automatic column temperature control box. Chromatographic separation was performed on a HiQ sil-C18 reversed-phase column (4.6 mm \times 250 mm, 5 μm , KYA TECH). The following elution program was used for separation: acetonitrile–water–acetic acid (60:40:0.1, v/v/v); the flow rate was 1.0 ml/min; the run time was 65 min. The injection volume was 10 μl ; the column temperature was maintained at 25°C .

An API3000 Triple tandem quadrupole mass spectrometry with a Turbolon-Spray interface from Applied Biosystems (USA) was operated in positive electrospray ionization (ESI+) source mode. All mass spectra were acquired in multiple reaction monitoring transitions. The analytical conditions were as follows: the ion source was operated at a temperature of 250°C . The nebulizing gas, curtain gas and collision gas were set at 12, 10 and 6 a.u., respectively. The ion spray voltage was 5500 V. The entrance potential and focusing potential were set at 10 and 400 V. The declustering potential were 10 V for S, 15 V for SA, 80 V for DS and G. The collision energy was 18 V for S and SA, 35 V for DS and 33 V for G. Analyst software (version 1.4) installed on a Dell computer was used for data acquisition and processing.

The quantification analysis method is according with Ma et al. (2011b).

2.2.2. Preparation method of *S. chinensis* extracts

S. chinensis fruits were purchased from San Keshu Trading (Heilongjiang, China) and identified by professor Shao-quan Nie from Key Laboratory of Forest Plant Ecology, Northeast Forestry University. 100 g fruits were refluxed with 1000 ml an ethanol–water (80:20, v/v) solution at 90°C for 2 h and then filtered. The residue was refluxed with 800 ml of ethanol–water (80:20, v/v) solution for 1.5 h, and then filtered and concentrated to dryness in a rotary evaporator. This residue was reconstituted in ethanol–water (90:10, v/v) with 1:10 solid–liquid ratio, and the concentration of S, SA, DS and GS were 369.22, 40.61, 23.85 and 31.06 $\mu\text{g}/\text{ml}$ (464.74 $\mu\text{g}/\text{ml}$ total FSBL).

2.2.3. Static hydrolysis method

In the static hydrolysis experiment, six factors would be investigated, including the types of ion exchange resin, the hydrolysis kinetics of EBBCL with ion exchange resin, the hydrolysis temperature, the mass of ion exchange resin, the moisture content in solution and the types of solvents. The

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