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Application of alkyl polyglycoside surfactant in ultrasonic-assisted extraction followed by macroporous resin enrichment for the separation of vitexin-2″-*O*-rhamnoside and vitexin from *Crataegus pinnatifida* leaves

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A B S T R A C T

An alkyl polyglycoside (APG) surfactant was used in ultrasonic-assisted extraction to effectively extract vitexin-2″-*O*-rhamnoside (VOR) and vitexin (VIT) from *Crataegus pinnatifida* leaves. APG0810 was selected as the surfactant. The extraction process was optimized for ultrasonic power, the APG concentration, ultrasonic time, soaking time, and liquid–solid ratio. The proposed approach showed good recovery (99.80–102.50% for VOR and 98.83–103.19% for VIT) and reproducibility (relative standard deviation, $n = 5$; 3.7% for VOR and 4.2% for VIT) for both components. The proposed sample preparation method is both simple and effective. The use of APG for extraction of key herbal ingredients shows great potential. Ten widely used commercial macroporous resins were evaluated in a screening study to identify a suitable resin for the separation and purification of VOR and VIT. After comparing static and dynamic adsorption and desorption processes, HPD100B was selected as the most suitable resin. After column adsorption and desorption on this resin, the target compounds VOR and VIT can be effectively separated from the APG0810 extraction solution. Recoveries of VOR and VIT were 89.27% ± 0.42% and 85.29% ± 0.36%, respectively. The purity of VOR increased from 35.0% to 58.3% and the purity of VIT increased from 12.5% to 19.9%.

1. Introduction

Medicinally active ingredients extracted from different herbs can improve, prevent, and even cure the disease [1]. To obtain these active ingredients, however, a large number of highly toxic or flammable solvents are used for their extraction from the raw materials. These chemicals pose an increasing environmental burden and a substantial fire risk. In separation science, ionic liquids are new solvents with the potential to replace volatile organic solvents [2]. Widely used ionic liquids include, for example, organic acids [3], alkaloids [4], glycosides [5], proanthocyanidins [6], flavonoids [7], curcuminoids [8], diterpene [9], lignans [10], and coumarins [11]. The high cost and inedibility of ionic liquids, however, limits their further application. Development of a more ecofriendly, economical, and practical extraction method, as well as low-cost solvents is desirable. Most of the active ingredients extracted by organic solvents are hydrophobic so their solubility can be increased by using water and surfactants with non-toxic additives. These aqueous surfactant solutions are non-flammable and are relatively inexpensive as extraction solvents.

Alkyl polyglycosides (APGs, Fig. 1) are novel nonionic surfactants that are eco-friendly, biodegradable, and non-toxic. Under conditions of high temperature, they are usually degraded into fatty alcohols and acids [12]. APGs are composed of renewable hydrophobic and hydrophilic raw materials derived from corn, potato, wheat, and fats such as coconut oil [13]. APG acts as a novel class of surfactants, used as stabilizing agents for beverage products, as thickening and emulsifying agents for food products, and as cleansers for fruits, vegetables, and tableware. It is an effective food-swelling agent and, as a low-caloric sweetener, can be used as fat replacement agent in food [14].

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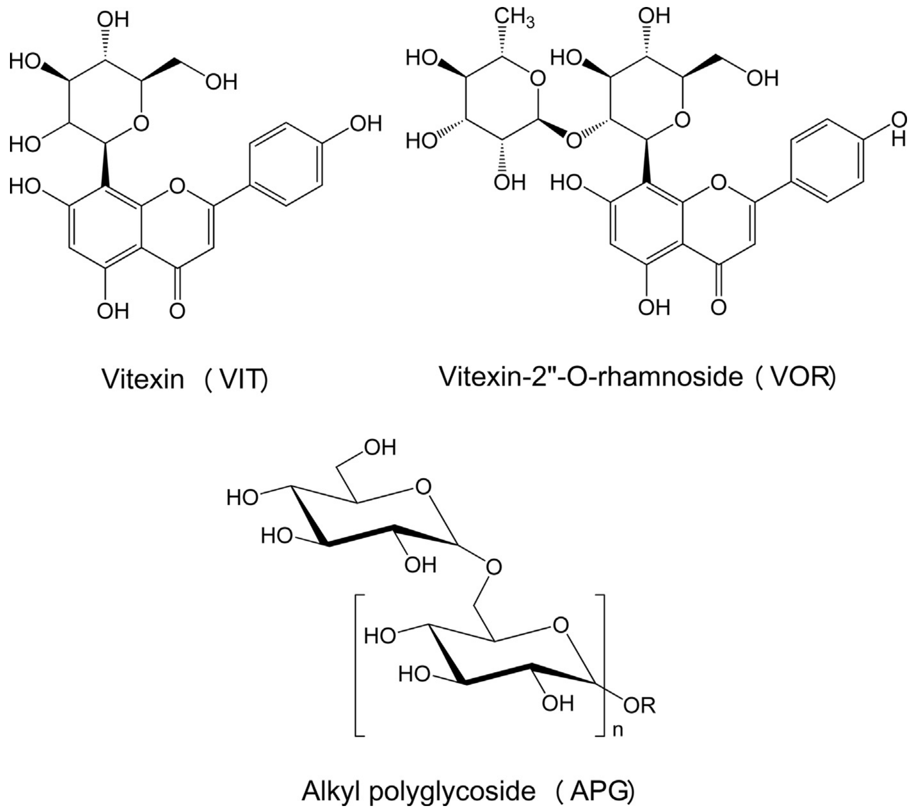

Fig. 1. Chemical structures of vitexin, vitexin-2″-*O*-rhamnoside, and alkyl polyglucosides. *n*: degree of polymerization; *R*: alkyl chain (for APG0810, $R = C_{8/10}$; for APG1214, $R = C_{12/14}$).

Crataegus, commonly known as hawthorn, is a genus of Rosaceae [15,16], and is widely distributed in Europe, North America, and Asia [17]. *Crataegus pinnatifida* is cultivated in China for its significant economic and market value. The fruits of *C. pinnatifida* are used to prepare several Chinese snacks, including haw flakes, haw rolls, and tanghulu, as well as jams, jellies, and juices. The leaves of *C. pinnatifida* are well known in traditional Chinese medicine, as documented by the Chinese Pharmacopoeia Commission [18]. Pharmacology studies show that *C. pinnatifida* manifests anti-inflammatory [19], antioxidant [20], anti-cataract [21], anti-thrombotic [22], and cardiovascular activities [23]. Studies suggest that vitexin and its glycoside are the major components underlying the pharmacological effects of the leaves of *C. pinnatifida*.

Vitexin (VIT), 5,7,4′-trihydroxyflavone-8-glucoside, is a *C*-glycosylated flavone found in certain herbs, including bamboo, pigeon pea, mung bean, and hawthorn [24]. Vitexin-2″-*O*-rhamnoside (VOR) is a derivative of VIT with an α-L-rhamnosyl residue attached at the 2′-position of the glucitol moiety (Fig. 1). VIT shows anti-spasmodic [25], antioxidant [26], anti-*Helicobacter pylori* [27], anti-viral [28], anti-inflammatory [29], and anti-tumor [30] activities. It inhibits adipogenesis [31], platelet aggregation [32], urease [33], and α-glucosidase [34]. VOR has been widely used for the treatment of cardiovascular diseases [35]. It inhibits the synthesis of dinucleic acid [36].

Flavonoids were the important plant secondary metabolites and widely distributed in plants [37], they were previously extracted from medicinal plants using Soxhlet and homogenate extraction. However, these extraction methods entail condensation, degradation, isomerization, or oxidation, resulting in diminished glycoside content. These methods are inefficient, requiring large amounts of high-purity organic solvents. Because of the toxicity of organic solvents, which are volatile and flammable, their use in flavanoid extraction from medicinal plants is undesirable. Ultrasonic-assisted as a simple, fast and efficient extraction method has been widely used [38]. It can not only to accelerate the reaction processes [39], but also saves time and solvents compared with the traditional extraction methods [40].

We therefore sought to use a safe, eco-friendly, and efficient ultrasonic-assisted approach to extract the VOR and VIT from *C. pinnatifida* leaves using APG surfactants. APG chain length and concentration, ultrasonic power and time, soaking time, and liquid–solid ratio were optimized. Macroporous resins, an organic polymer adsorbent, have good adsorption performance and are used in medicine, food, chemistry, and other fields. Use of these resins is effective, simple, has a low production cost, is not affected by the presence of inorganic materials, and are easily regenerated [41]. In recent years, macroporous resins have been widely used for the separation and purification of effective components of herbal medicines. Therefore, in this study, we also chose ten different types of resins to evaluate the adsorption and desorption performance of VOR and VIT from the APG extract solution. Based on the experimental results, the most suitable resin was selected and used to develop a process for the separation and purification of VOR and VIT.

2. Experimental

2.1. Materials and chemicals

Fresh leaves of *C. pinnatifida* were harvested manually in September 2014 from the Botanical Garden of Northeast Forestry University (Heilongjiang, Harbin, China) and dried naturally indoors. After filtering through a 60-mesh stainless steel sieve, all samples were stored at 4 °C until use. All samples used for the experiments originated from the same batch. The VOR and VIT reference standards were purchased from Sigma-Aldrich Corporation