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硕　士　学　位　论　文

竹叶中黄酮的提取纯化及抗氧化性研究

Study of extraction, purification and antioxidant activity of flavonoidsrecovered from bamboo leaves

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摘要

竹子作为一种重要的自然资源在各行业均有广泛应用，可制成乐器、文具、家具等日常用品。为了满足这些日常需求，每年均有大量的竹子被砍伐而产生大量的竹叶废弃物。竹叶废弃物含有大量的多糖、蛋白质、叶绿素和黄酮类化合物等物质，其中以黄酮类化合物附加值最高，应用前景最广泛。自二十世纪以来，以竹叶为原料提取竹叶黄酮成为高效利用竹叶废弃物的一种有效途径，在研究领域逐渐受到广泛关注。本文以竹叶为原料，系统地研究了竹叶黄酮高效提取、分离和纯化方法，并对所得竹叶黄酮产品进行了抗氧化性能测试，目的是为竹叶黄酮在食品中作为抗氧化剂的应用提供理论依据。

首先，采用表面活性剂协同微波进行了竹叶黄酮的提取。利用单因素法探索了不同类型表面活性剂对竹叶黄酮提取率的影响，结果显示：表面活性剂对微波提取竹叶黄酮有促进作用；且以十二烷基硫酸钠（SDS）的促进效果最佳，竹叶黄酮的提取率可达 68.0%。进一步，采用正交法对表面活性剂协同微波提取竹叶黄酮工艺进行了优化，分别考察表面活性剂浓度、固液比、微波时间和功率对竹叶黄酮提取率的影响。结果表明：表面活性剂 SDS 浓度为 0.90%，固液比 1：50，微波时间 2.0 min，微波功率为 225 W 时效果最佳，竹叶黄酮的提取率可达 98.9%。此外，发现 SDS 浓度对提取率的影响最大。

其次，采用大孔树脂吸附解析法对竹叶黄酮进行分离和纯化研究。分别对竹叶黄酮在大孔树脂上的静态和动态吸附过程进行研究。静态吸附实验结果表明，竹叶黄酮在大孔树脂 AB-8 上有较好的吸附和脱附效果，且吸附量与自身的官能团、溶液中杂质的官能团、树脂的官能团均有一定关系。竹叶黄酮在大孔树脂 AB-8 上的吸附平衡可以用 Frenudlich 方程来描述，吸附过程为一个自发的吸热过程，温度升高有利于吸附的进行；吸附过程的焓变为 29.86kJ/mol，表明竹叶黄酮主要靠氢键在大孔树脂 AB-8 上进行吸附；红外谱图结果显示竹叶黄酮在 AB-8 上的吸附过程为物理吸附过程；动力学研究结果表明，竹叶黄酮在大孔树脂 AB-8 上的吸附过程可用二级动力学模型方程来描述。动态吸附解析实验结果表明，两步解析法明显优于一步解析法，在优化后的解析条件下，所得竹叶黄酮的纯度从 7.0%上升至 50.8%；穿透试验结果表明，在定义 C_t/C_0=0.5，柱高为 2.1

cm 时，柱层的穿透点为 V=8 mL；同时对大孔树脂的循环使用性能进行考察，结果表明大孔树脂 AB-8 具有较好的循环使用性能，具备良好的工业化应用前景。同时，化学显色法表明，所得竹叶黄酮产品主要成分为 5-羟基黄酮，且产品中不含黄酮醇类物质。

最后，分别以 DPPH 自由基清除法、铁氰化钾还原法和 FRAP 法对所得产品进行抗氧化能力测试，并与常用的合成抗氧化剂维生素 B（V_B）、丁基羟基茴香醚（BHT）和特丁基对苯二酚（TBHQ）的抗氧化性能进行了比较。结果表明，所得竹叶黄酮具有较好的抗氧化性能，并明显优于维生素 B（V_B）、丁基羟基茴香醚（BHT）；在 DPPH 自由基清除实验中，特丁基对苯二酚（TBHQ）的抗氧化性能较好，铁氰化钾还原法和 FRAP 实验中，竹叶黄酮产品效果更好。因此，本论文工作所得的竹叶黄酮产品作为天然的抗氧化剂在食品抗氧化剂领域具有广阔的的前景。

关键词：竹叶黄酮表面活性剂微波提取大孔树脂抗氧化性

Abstract

As an important resource, bamboo is widely used and can be made into various products, such as musical instruments, stationery, furniture and other daily necessities. In order to meet those demands, a large amount of bamboos were cut down and a lot of bamboo leave wastes were generated every year. Bamboo leaves contain polysaccharides, proteins, chlorophyll, flavonoids and some other components, and flavonoids are the highest value-added productswhichhave a lot of applications. Since the 20th century, bamboo leaves were used to extract flavonoids, which has become an efficient method for the utilization of bamboo leavesand has attracted a lotof attentions. In this work, a series of studies were carried out includingthe finding of efficient extraction method,separation and purification of flavonoids, and the validation of antioxidant activity of flavonoids. All these studies could provide a theoretical basis for the applications of flavonoids as an antioxidant in food industry.

In Chapter 2, the single-factor test method was performed to find the influence of different surfactants on the extraction yield of flavonoids. The surfactants showed a positive impact on the microwave extraction, and the best result was obtained with sodium dodecyl sulfate (SDS) added, which reached an extraction yield of 68.0%. Operation parametersfor the surfactant-assistant microwave extraction, such as surfactant concentration, solid-liquid ratio, microwave time and power, were examined and optimized with theorthogonal method. Based on the analysis of the experimental results, the optimized extraction conditions were found to be: surfactant SDS concentration of 0.90%, solid-liquid ratio of 1:50, microwave time of 2.0 min and power of 225 W, which had arecovery rate of 98.9% for flavonoids.It was also found that the concentration of surfactant was the most important factor influencing the extraction process.

In Chapter 3, macroporous resin was used for the separation and purification of flavonoids. The static and dynamic adsorption processes were studied respectively, and AB-8 was found to have the best adsorption and desorption capability. In the static adsorption process, the adsorbing capacity of flavonoids on AB-8 hadsomething to do with the functional groups of impurities and resin. The adsorption equilibrium could be described by the FrenudlichEquation, and the adsorption process is a spontaneously endothermic process, thusthe temperature rise will be favorableto the adsorption process. The value of ΔH was 29.86kJ/mol,which indicates that the force between flavonoids and AB-8 was hydrogen force. The infrared spectra of FT-IR showed the adsorption process is a physical adsorption process. Moreover, the adsorption process could be described by the second-order kinetic model equation which is indicated by the study of kinetics. In the dynamic adsorption process, two-step elution process indicates higher purity than one-step elution process. Under the optimized conditions, the purity of flavonoids increased from 7.0% to 50.8%. As definition of C_t/C_0=0.5, the breakthrough curve indicated that the breakthrough point of column was 8 mL, while the column height was 2.1 cm. What's more, the study of macroporous resin recycling performance demonstrated that the AB-8 has a good recycling performance, which suggested the AB-8 have good prospects for industrial application. Finally, the color test showed that the main components in the flavonoids were 5-hydroxy-flavones, and no flavonols.

In Chapter 4, the DPPH radical scavenging assay, ferricyanide reduction assay and ferric reducing antioxidant power (FRAP) assay were investigated to measure the antioxidant activity of flavonoids respectively. And some synthetic antioxidants, such as vitamin B, butylated hydroxytoluene, tertiary butylhydroquinone, were used for comparing the antioxidant activity with flavonoids. The resultsdemonstrate that the flavonoids have better antioxidant activity than vitamin B and butylated hydroxytoluene. However, in the DPPH radical scavenging assay, tertiary butylhydroquinone showed better results, but in the other two assay,flavonoidswere better. Therefore,as a kind of natural antioxidant, flavonoids obtained in this work have great prospects in food application.

Keywords: flavonoids of bamboo leaves; surfactants; microwave extraction; macroporous resin; antioxidant activity

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