

学校编码: 10384

学号: 200433016

分类号__密级__

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厦 门 大 学

硕 士 学 位 论 文

苦楝果实中苦楝素的超临界二氧化碳萃取研究

Study on Extraction of Toosendanin from The Fruit of *Melia Toosendanin* Linn Using Supercritical Carbon Dioxide

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专 业 名 称: 化 学 工 程

论文提交日期: 2 0 0 7 年 6 月

论文答辩时间: 2 0 0 7 年 6 月

学位授予日期:

答辩委员会主席: _____

评 阅 人: _____

2007 年 6 月

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摘要

苦楝 (*Melia azedarach* Linn) 为我国一个乡土树种, 广泛分布于我国南部地区。苦楝中含有多种杀虫活性成分, 其中苦楝素 (toosendanin) 是最主要的活性成分, 它对多种害虫有毒杀作用, 主要表现为使虫忌避、拒食; 抑制昆虫生长发育、触杀、内吸致毒作用等。苦楝素用以制备植物源农药, 与化学农药相比, 具有安全、残效期短、高效、无毒、无污染、杀灭多种农业害虫等优越性, 可以阻止害虫直接为害或抑制种群形成而达到对害虫的可持续控制, 因而具有广泛的应用前景。

超临界 CO₂ 萃取技术是一种新型高效洁净分离技术, 与传统的溶剂萃取方法比较, 具有无溶剂残留、不破坏热敏性和易水解的物质等优点, 在天然产物的提取领域中有良好的应用前景。本文以苦楝果实为原料, 对采用超临界二氧化碳萃取苦楝素工艺的可行性及其适宜条件进行了系统的研究。

采用有机溶剂提取法提取苦楝果实中的天然杀虫活性成分, 考察了固液比、提取时间、提取次数对提取率的影响, 同时成功地分离出萃取物中苦楝素, 并将其纯化。采用差示扫描量热仪 (DSC) 测定苦楝素晶体基本的理化常数熔点。并通过红外吸收光谱 (IR)、紫外吸收光谱 (UV)、有机质谱 (ESI-MS) 对苦楝素晶体进行波谱分析, 其分析结果和文献报道的苦楝素数据基本一致。

研究了以苦楝果实为原料的超临界二氧化碳萃取工艺。实验中采用自行设计的超临界萃取设备, 重点考察了萃取温度、萃取压力对萃取率的影响, 同时也考察了萃取时间、原料颗粒粒度、不同夹带剂及夹带剂用量对萃取率的影响。确定了适宜的萃取工艺条件。研究表明: 萃取温度为 40 °C, 萃取压力为 20 MPa 时, 选择 20% (mol/mol) 乙醇为夹带剂, 苦楝素的萃取得率为 98%。

在超临界 CO₂ 萃取苦楝素过程中, 利用收缩核模型描述溶质的浸出, 溶质首先从收缩核边界层脱附分离出来, 再从固体颗粒的微孔扩散到颗粒表面, 最后跨过液膜, 进入流体主体。该模型结合固相和流体相的质量衡算, 对整个萃取过程进行了模拟, 采用差分法, 求得了模型的数值解, 结果表明模型计算值与实验值基本上吻合。

关键词: 苦楝; 苦楝素; 超临界二氧化碳萃取; 收缩核模型

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ABSTRACT

Melia azadarach Linn belonging to Meliaceae exists broadly in our country. Toosendanin, the main effective ingredient of the fruit of *Melia azadarach Linn*, is a kind of tetracyclic triterpene, which can be made into pesticide. Toosendanin could make pieris rapac antifeed and have stomachtoxic activities, and show high feeding inhibitory effects to *Toxoptera aurantii*. Toosendanin can be put into produce botanical insecticides. This botanical insecticide is a safe and effective and free of toxic residuals and adaptable to controlling pests over crops

With occurring the upsurge of savageness, nutrition and returning natural all over the world, supercritical fluid extraction technology holds prominent status in the domain of extraction of natural products as a kind of high effective and clean separation technology. This thesis mainly explores the feasibility and the optimal conditions of extracting toosendanin from the fruits of *Melia azadarach Linn* with supercritical carbon dioxide.

The process of extracting toosendanin from the fruits of *Melia azadarach Linn* using ethanol extraction and crystallization method was firstly studied. And effects of extraction time, extraction times and the ratio of liquid to solid on the yield of toosendanin were investigated. Two melting points of the crystal obtained were determined by using differential scanning calorimetric (DSC). Its structure was elucidated by spectroscopic means (ultra violet spectroscopy, electrospray ioniazation mass spectroscopy and infrared spectroscopy). All the results of qualitative analysis agreed roughly well with the results in the related references.

The process of extracting toosendanin was further studied from the fruits of *Melia azadarach Linn* with supercritical CO₂ using the supercritical fluid extraction apparatus. which was made by ourselves. And effects of extraction temperature and pressure on the extraction yield were investigated. Effects of extraction time, the size of material and the concentration and dosage of modifiers on the extraction yield of toosendanin were studied. The optimal extraction conditions were obtained experimentally. It is found that the yield of toosendanin is up to 98% when using 20 % ethonal modifier at pressure 20 Mpa and temperature 40 °C.

Moreover, the shrinking model was used to simulate the mass transfer process of toosendanin in supercritical fluid. A simplex method was used to fit and optimize the model parameters. The numerical solution of yields vs. extraction time was obtained by differential method. The simulating results show that the model fits the experimental data well.

Key words: *Melia azadarach Linn*; Toosendanin; Supercritical carbon dioxide extraction; Shrinking core model

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目录

第一章 文献综述	1
1.1 植物源农药的发展	1
1.1.1 农药的发展.....	1
1.1.2 植物源农药的研究进展.....	1
1.1.3 植物源农药作用机理的研究.....	2
1.1.4 植物源农药的特点.....	4
1.1.5 植物源农药的发展前景及展望.....	5
1.2 楝科植物杀虫物质的研究情况	6
1.2.1 化学成分.....	7
1.2.2 苦楝杀虫机理及其应用.....	8
1.2.3 苦楝素的提取方法.....	9
1.3 超临界流体萃取技术	11
1.3.1 超临界流体的性质及萃取原理.....	12
1.3.2 超临界流体萃取技术的特点.....	15
1.3.3 超临界流体萃取中各操作参数的影响.....	16
1.4 超临界流体萃取过程中的传质	18
1.4.1 经验模型.....	19
1.4.2 基于传热分析的模型.....	19
1.4.3 基于微分物料衡算方程的模型.....	19
1.5 本文的研究工作	20
第二章 苦楝素的溶剂提取与鉴定	21
2.1 引言.....	21
2.2 实验部分	22
2.2.1 实验原料与试剂.....	22
2.2.2 实验仪器.....	22

2.2.3 实验方法.....	22
2.3 结果与讨论.....	23
2.3.1 苦楝素鉴定.....	23
2.3.2 有机溶剂提取苦楝素.....	28
2.4 小结.....	31
第三章 超临界CO₂ 萃取苦楝果实中的苦楝素.....	32
3.1 引言.....	32
3.2 实验部分.....	32
3.2.1 原料与试剂.....	32
3.2.2 试验仪器与设备.....	32
3.2.3 超临界流体萃取实验.....	33
3.3 萃取物中苦楝素含量的检测.....	34
3.3.1 苦楝素的检测方法.....	34
3.3.2 苦楝素的检测实验.....	35
3.3.3 检测结果及讨论.....	35
3.4 苦楝果实中苦楝素的总含量.....	38
3.5 实验结果与讨论.....	39
3.5.1 萃取时间的确定.....	39
3.5.2 萃取温度的影响.....	40
3.5.3 萃取压力的影响.....	41
3.5.4 颗粒粒径的影响.....	42
3.5.5 夹带剂的确定.....	43
3.5.6 夹带剂的影响.....	44
3.6 小结.....	45
第四章 超临界CO₂萃取过程数值计算.....	46
4.1 引言.....	46

4.2 收缩核模型	46
4.3 方程相关参数的计算	49
4.3.1 颗粒表面与流体间的对流传质系数 k_f	49
4.3.2 轴向扩散系数 D_L	50
4.3.3 多孔壳层中有效扩散系数 De	50
4.3.4 床层孔隙率的计算.....	51
4.3.5 颗粒密度的测量.....	51
4.3.6 苦楝素在超临界 CO_2 中的平衡溶度.....	51
4.4 结果与讨论	51
4.5 小结.....	53
第五章 结论.....	54
符号说明.....	55
参考文献.....	56
附录.....	61
致谢.....	69

Contents

CHAPTER ONE	INTRODUCTION	1
1.1	The Devepment of Plant Pesticide	1
1.1.1	The Devepment of Pesticide.....	1
1.1.2	The Devepment of Plant Pesticide	1
1.1.3	Insecticidal Activity of Plant Pesticide.....	2
1.1.4	The Properties of Plant Pesticide.....	4
1.1.5	The Devepment Foreground of Plant Pesticide.....	5
1.2	Present Status of The Study of Insecticidal Component from Meliaceae	6
1.2.1	Chemical Component.....	7
1.2.2	Insecticidal Activity and Application of Melia Toosendanin	8
1.2.3	The Extraction Methods of Toosendanin	9
1.3	Supercritical Fluid Extraction Technology	11
1.3.1	The Properties of Supercritical Fluid and Fundamental of Extraction.	12
1.3.2	The Properties of Supercritical Fluid Extraction.....	15
1.3.3	The Effects of Parameter on Supercritical Fluid Extraction	16
1.4	Mass Transfer Process of supercritical fluid extraction	18
1.4.1	The Empirical Model.....	19
1.4.2	The Model on Heat Transfer	19
1.4.3	The Model on Mass Equilibrium.....	19
1.5	The Content of This Thesis.....	20
CHAPTER TWO	ORGANIC SOLVENTS EXTRACTION AND IDENTIFY OF TOOSENDANIN	21
2.1	Introduction	21
2.2	Materials and Methods	22

2.2.1 Materials	22
2.2.2 Equipments	22
2.2.3 Methods.....	22
2.3 Results and Discussion	23
2.3.1 Identify of Toosendanin	23
2.3.2 Extraction of Toosendanin by Organic Solvents.....	28
2.4 Concluction.....	31
CHAPTER THREE EXTRACTION OF TOSENDANIN	
FROM THE FRUIT OF MELIA TOSENDANIN USING	
SUPERCritical CO₂.....	32
3.1 Introduction.....	32
3.2 Materials	32
3.2.1 Materials	32
3.2.2 Equipments	32
3.2.3 Supercritical Fluid Extraction	33
3.3 Toosendanin Evaluation	34
3.3.1 Evaluation Method of Toosendanin	34
3.3.2 Toosendanin Evaluation Experiment of Toosendanin.....	35
3.3.3 Results and Discussion of Evaluation.....	35
3.4 The Total Content of Toosendanin from The Fruit of Melia	
Toosendanin.....	38
3.5 Results and Discussion	39
3.5.1 Effect of Extraction Time.....	39
3.5.2 Effect of Extraction Temperature.....	40
3.5.3 Effect of Extraction Pressure	41
3.5.4 Effect of Particle Size	42

3.5.5 Effect of Modifiers	43
3.5.6 Effect of The Ratio of Modifier to CO ₂	44
3.6 Conclution	45
CHAPTER FOUR MATHEMATICAL MODEL OF SUPERCRITICAL EXTRACTION	46
4.1 Introduction	46
4.2 Shrinking Core Model	46
4.3 Parameters for Model	49
4.3.1 The Mass Transfer Coefficient in Fluid Phase k_f	49
4.3.2 The Axial Dispersion Coefficient D_L	50
4.3.3 The Effective Diffusivity in The Particle D_e	50
4.3.4 Void Fraction in Bed ϵ	51
4.3.5 The Density of Particle ρ_s	51
4.3.6 Solubility of Toosendanin in Supercritical Carbon Dioxide	51
4.4 Results and Discussion	51
4.5 Conclution	53
CHAPTER FIVE CONCLUSIONS.....	54
NOTATION.....	55
REFERENCES.....	56
APPENDIX	61
ACKNOWLEDGMENT	69

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