研 究 快 报

STUDY ON EXTRACTING CITRAL FROM *LITSEA CUBEBA* FRUITS BY MICROWAVE RADIATION AND DETERMINATION OF CITRAL*

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Abstract: Citral is extracted from *Litsea cubeba* with microwave radiation. Content of essential oil extracted from *L. cubeba* fruit using microwave radiation is on an average 2.48% higher than that using traditional direct steam distillation. Adopting gas chromatography with temperature programming, citral content in the oil was determined to be 68.46%, at recovery 101.3%, relative standard deviation 0.28%, linear relative coefficient 0.9997, which are in good agreement with those measured by internal standard method, but the operation is simpler than both the internal standard and GB 11424–89 methods.

Key words: *Litsea cubeba*; citral

CLC number: S 573.8; TQ 655 **Document code:** A **Article ID:** 0253-2417(2001)03-0087-04

Litsea cubeba is grown as deciduous shrub or small arbor. Citral and other volatile aromatic elements exist in its leaves, flowers and fruits to exhibit pleasant fragrance. Essential oil of *L. cubeba*, in which the major component is citral, is a traditional product in forestry industry in China extracted by steam distillation from the fruits at 4%~6% yield, for individuals up to 10%. High pure citral can be obtained from essential oil of *L. cubeba* through chemical method.

A preliminary exploration of extracting and producing citral from *L. cubeba* with microwave radiation were examined in this study.

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* **Received date:** 2000–05–30
Foundation item: 江西省科委 1996 年重点科技计划资助项目(0514)
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1 Materials and methods

1.1 Materials

L. cubeba fruit gathered from Xiajiang County and Jinggangshan City, the essential oil of *L. cubeba* and self-produced citral; Sodium hydrogen sulphite and standard reagent of citral (AR); acetone and acetophenone (chromatographic reagent).

GG-14A gas chromatograph(Shimadzu), ZFA rotary esteamator, microwave oven(Xianhua E70T-2/J220, 850 W, 2450 MHz), thermometer(no adjustment).

1.2 Methods

1.2.1 Methods of extracting and producing citral from fruits of *L. cubeba* Fresh fruits of *L. cubeba*, in a round-bottomed flask and added with 45 ℃ distilled water, was set in a microwave oven to extract citral for a certain time, taken out of microwave oven, steam-distilled to collect the distillate. Repeat this procedure twice to three times. Essential oil was collected from separating funnel by salting-out of distillate with NaCl overnight, dried. Add a certain sodium chloride to distilled substances that have been gathered, standing overnight, and then isolate them. The content of citral was determined.

A certain amount of essential oil in a reactor was put in microwave oven, added with supersaturated solution of sodium hydrogen sulphite under stirring, and run in the microwave oven at temperature not over 10 ℃ (controlled with ice-salt water), until citral in the material liquids have been transformed completely into product. The reactor taken out from the microwave oven was kept stood to isolate crystallized materials, rinsed with ether, and 0.1 mol/L resolved crystallized sodium hydrogen sulphite was added, run in microwave oven until the hydrolysis is completely finished. Then citral was isolated.

1.2.2 Determination methods Chromatographic column: SE-54 quartz capillary, 25 m, internal diameter 0.2 mm; FID (hydrogen flame ionization detector); 80~ 230 ℃, 10 ℃/min programmed temperature, sample was added at 240 ℃, detected at 250 ℃; nitrogen flow 20 mL/min; air flow 50 mL/min; sample injection 0.5 μL. Results are shown in Fig. 1.

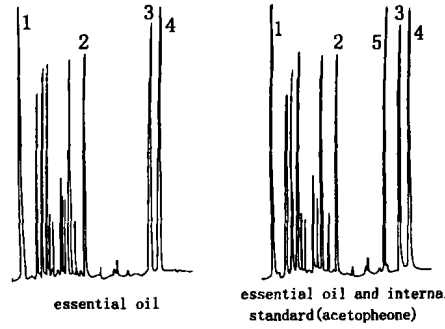

Fig. 1 GC spectra of essential oil from *L. cubeba*

1. solvent; 2. impurities; 3. neral; 4. geranial; 5. acetophenone

2 Results and discussions

2.1 The conditions where essential oil of fruits of *L. cubeba* is extracted with microwave radiation and steam distillation according to orthogonal experiment are as follows: microwave radiation time 5~ 20 min, temperature 60 ~ 80 ℃, distillation temperature 80~ 100 ℃, extracted for 3 times. Results of extracting with microwave radiation plus steam distillation and traditional steam distillation are showed in Table 1.

Table 1　Influence of extracting essential oil of *L. cubeba* with microwave radiation and traditional steam distillation　%

items	yield*	average yield*	extracting time(min)	content of citral*	average content
microwave method	5.5~ 8.6	8.38	90~ 120	68.3~ 75.9	74.78
traditional method	4.0~ 6.3	5.86	380~ 480	63.3~ 70.4	68.64

* Results from eight batches, twenty-four samples.

It is obvious from Table 1 that comparing microwave radiation with traditional methods, the time of extracting is 4 times shorter, the content of essential oil is 36.5% ~ 37.5% higher, and content of citral of essential oil is more than 5% higher. These could be explained by that essential oil of *L. cubeba* can infiltrate, diffuse and exchange more effectively and quickly from the cells of fruits tissue during microwave radiation, so that essential oil can be extracted quickly and completely. These operations are quite complicated.

2.2　Citral can be obtained from the oil of *L. cubeba* by using sodium hydrogen sulphite. The reaction between sodium hydrogen sulphite and aldehyde is very fast and can be completed in three minutes. Temperature of reaction can be controlled easily. There are few side reactions with microwave radiation so that the process of isolating and extracting citral can be simplified and the loss of citral could be decreased steeply. The loss of citral is less than 0.8% with microwave radiation, compared with 1.2% without microwave radiation.

2.3　Contents of essential oil of *L. cubeba* and self-produced citral are showed in Table 2.

Table 2　Quantitative analysis result of essential oil of *L. cubeba* and self-produced citral　%

samples	analysis methods	content of citral					average	standard deviation	relative standard deviation
essential oil of *L. cubeba*	reduction-to-one	68.7	68.8	68.4	68.5	68.8	68.64	0.19	0.28
	internal standard	68.5	68.8	68.2	68.4	68.6	68.52	0.19	0.28
	GB 11424-89	68.5	68.9	68.4	68.6	68.9	68.66	0.23	0.34
citral	reduction-to-one	99.3	99.6	99.4	99.5	99.5	99.46	0.11	0.11
	internal standard	99.2	99.6	99.3	99.5	99.4	99.40	0.18	0.18

From Table 2 and Fig. 1, the results determined by reduction-to-one method are basically in accordance to those internal standard method. We have got the results that the relative coefficient of reduction-to-one method of capillary chromatographic column and internal standard was separately 0.9997 and 0.9998, the content of their recoveries was 101.3% and 101.0%. Therefore reduction-to-one method and internal standard method used to determine citral have the same accuracy. However, the content of citral determined with reduction-to-one method is a slightly higher than that with internal standard method. The request of quantitative analysis of citral in essential oil of *L. cubeba* can be completely satisfied with reduction-to-one of capillary column gas chromatography.

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微波法从山苍子中提取柠檬醛及其测定研究

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摘 要: 讨论了采用微波辐照从山苍子中提取制备柠檬醛, 精油的得率较传统的直接水蒸气蒸馏法平均提高 2. 48% 以上。用程序升温毛细管柱气相色谱归一化法测定山苍子精油中的柠檬醛, 获得了山苍子精油中柠檬醛含量为 68. 64% , 回收率为 101. 3% , 相对标准偏差为 0. 28% , 线性相关系数为 0. 9997, 准确性与内标法相一致的实验结果, 而且操作较内标法和 GB 11424- 89 法更为方便。

关键词: 山苍子; 柠檬醛

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