研究快报

GAS CHROMATOGRAPHY-MASS SPECTROMETRY DETERMINATION OF FRAGRANT COMPONENTS IN EXTRACT BY SUPERCRITICAL CO_2 FROM FRESH FLOWERS OF CRIMSON GLORY*

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Abstract The Composition of supercritical CO_2 extract from fresh flowers of crimson glory was identified with GC-MS method and was compared with that of organic solvent extracts. The result showed that compounds included in CO_2 extract constitute the main composition of the fragrance of the flowers, and more closely resemble that of the head-space odor of the fresh flowers.

Key words gas chromatography-mass spectrometry, supercritical fluid extraction, essential oil of crimson glory flowers, fragrant components

1 Introduction

In food or perfume production, essential oils of natural spices are generally obtained by steam distillation or organic solvent extraction. During steam distillation, slight change may occur in flavor compounds because of the higher processing temperature. The toxicity of solvent remaining in the product is also a problem for organic solvent extraction. Supercritical carbon dioxide is an inert, non-toxic, non flammable solvent, and leaves no residues. Supercritical CO_2 can be used at temperatures and pressures that are relative safe, convenient and particularly appropriate for the extraction of a range of more volatile or heat-labile compounds, such as food flavor. Therefore, supercritical fluid extraction (SFE) with CO_2 is especially suitable in food industry.

Essential oil or essential oleoresin extracted from fresh flowers of crimson glory (R. Hybrica Hort. crimson glory), is a natural fragrant additive used in food or perfume production. We have studied extraction of essential oil of the flowers with supercritical CO_2. Since many flavor components exist in the sample, each has its selectivity and solubility different from others in SFE and in organic solvent extraction. The extraction method affects not only the yield of production, but also the relative concentrations of flavor compounds in the product, or its flavor quality. The composition of supercritical CO_2 extract was identified with GC-MS method and was compared with that of organic solvent extracts.

2 Experimental

1) Sample for SFE: Fresh flowers of crimson glory were cultivated in the nursery of the Institute. Five gram of flowers was put into a 10mL extraction container.

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2) Apparatus: HP 5890A GC/5970B MSD. Column: 50m× 0.20mm i.d. OV-101. Carrier gas: helium (99.99%). Identification was achieved with a GC/MSD/NBS/EPA standard spectral data system. Supercritical fluid extractor: ISCO-260D, ISCO.

3) Experiment: SFE was conducted at 50℃, 21MPa. Through the outlet of the supercritical fluid extractor CO_2 fluid was conducted to a glass vessel containing 3mL of ethanol, in which the extract was dissolved and collected. The solution was kept at 5℃ before chromatographic analysis. The extract was separated and identified by GC/MS. Chromatographic conditions: split injection, column temperature: 70℃, isothermal for 2 min, then programmed to 250℃ at a rate of 5℃/min.

4) Preparation of organic solvent extract: Extract fresh flowers with petroleum ether for 2 hours. Remove the solvent by reduced pressure distillation and recover petroleum ether for recycling. Dissolve the remained essential oleoresin in ethanol. Dewax by cooling under -10℃ in a refrigerator for 1 week and discardthe solid residue. Remove the solvent by reduced pressure distillation again. Then distill the extract and collect the fraction below 100℃ for analysis.

3 Results and discussion

Identification results of the flavor compounds from the fresh flowers extracted by supercritical CO_2 and by petroleum ether are listed in Table 1 for comparison. Fig. 1 and 2 show the chromatograms of supercritical CO_2 extract and organic solvent extract. The results show that there are signinficant differences in yields and flavor compositions between carbon dioxide-extract and the corresponding traditional organic solvent extract. The components in supercritical CO_2 extract are fewer than those in organic solvent extract, and all the flavor compounds containing in CO_2 extract can be found in the organic solvent extract. Those compounds existing only in organic solvent extract can be regarded as less volatile or higher-molecular weight compounds. Many of them are hydrocarbons as shown in the table, Their concentrations are low in the extract except for 3-nonadecene. It is interesting to notice that there are significant differences in concentrations of compounds 2 and 15(phenylethyl alcohol and 3-nonadecene). Selectivities and solubilities of both extraction solvents, or volatilities of the solvents might play an important role in extraction. It must be mentioned that the selectivity and solubility of supercritical CO_2 are controlled by SFE conditions (such as pressure and temperature) in some degree, but no contrary results were found for these two compounds when SFE condition changed during the experiment.

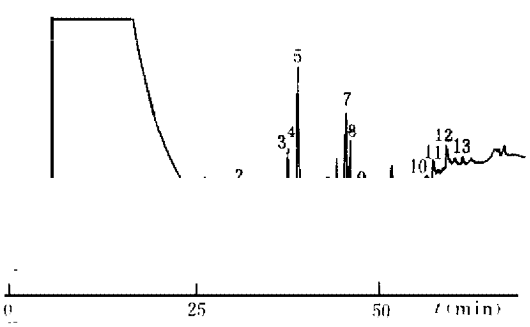

Fig. 1 Chromatogram of supercritical CO_2 extract from crimson glory

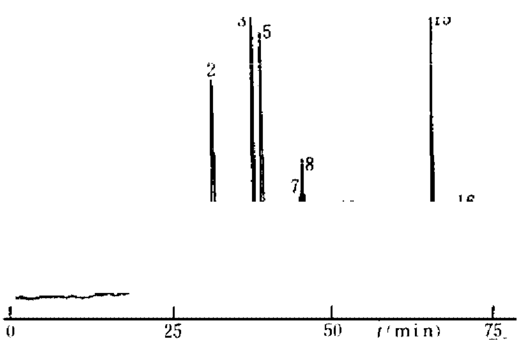

Fig. 2 Chromatogram of organic solvent extract from crimson glory

In spite of the absence of less volatile components, supercritical CO_2 extracts still smell of the fragrance of the fresh flowers. It means that the compounds included in CO_2 extract constitute the main composition of the fragrance of the flowers, and more closely resemble that of the head-space odor of the fresh flowers. Therefore, the supercritical CO_2 extract is not only superior in purity to the organic solvent, but also a product of quality.

Table 1　Compositions of supercritical CO_2 extract and organic solvent extract identified by GC/MS method

No.	Compounds	Retention time(min)	CO_2 extract(%)	Petroleum ether extact(%)
1	benzyl alcohol	26.9	1.5	3.7
2	phenylethyl alcohol	31.8	2.8	18.0
3	citronellol	38.1	12.5	13.9
4	2-phenylethyl acetate	38.7	1.6	0.7
5	geraniol	39.5	17.7	15.3
6	isoeugenol	43.9	2.6	1.9
7	eugenyl methyl ether	45.7	12.9	7.0
8	1, 2, 3-trimethoxy benzene	46.0	8.4	5.7
9	1, 5-divinyl-3-methyl-2-isopropylenyl cyclohexane	48.0	2.6	0.6
10	4-vinyl-α, α, 4-trimethyl-3(1-methylvinyl)-cyclohexylmethanol	57.0	1.2	0.7
11	1-heptadecene	57.6	5.2	1.5
12	3, 7, 10-trimethyl-2, 6, 10-undecene-1-ol	59.7	5.1	0.8
13	benzyl benzoate	60.8	1.8	0.4
14	4a, 8-dimethyl-1, 2, 3, 4, 4a, 5, 6, 8a-octahydronaphthalene	63.4	-	1.0
15	3-nonadecene	66.1	-	13.0
16	3-icosene	72.9	-	0.6
17	5-icosene	73.5	-	0.5

* the ratio(%) of individual chromatographic peak area to the total peak areas

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墨红花超临界二氧化碳香味萃取成分的色谱-质谱法测定

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提要　由墨红花提取的精油或油树脂是优质的天然香料, 被广泛用于化妆品和食品工业。超临界 CO_2 萃取墨红花精油, 既可保持很好的香气, 又能克服传统的有机溶剂萃取时有残余溶剂的缺点。用气相色谱-质谱联用法对超临界 CO_2 萃取物与石油醚萃取物中的组成进行了分析比较。色谱条件为: OV-101 固定相, 氦气, 0.2mm× 50m 石英毛细管柱, 柱温 70℃ 2min, 然后以 5℃/min 程序升温至 250℃。超临界萃取条件为 50℃, 21MPa, CO_2 流量为 10mL。发现超临界萃取物中的成分包括了石油醚萃取物中的多数主要香味成分, 但对香味影响较小的、分子量较大的烷烃和烯烃的含量较少。超临界二氧化碳萃取物的香气与鲜花相近。

关键词　气相色谱-质谱法, 超临界萃取, 墨红花精油, 香味成分