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A STUDY ON THE CHEMICAL CONSTITUENTS OF GERANIUM OIL

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Abstract In this paper, the chemical constituents of geranium oil, collected from Rong Jiang, Guizhou, are studied by means of capillary gas chromatography-mass spectrometry. Over 40 constituents are separated, of which 31 components consisting 95.07% of the oil, have been identified. The main ingredients are citronellol (24.73%), garaniol (8.79%), â-guaiene (8.97%), p-menthone (7.18%), and linalool (4.16%).

Keywords geranium oil, capillary gas chromatography-mass spectrometry

Introduction

Pelargonium graveolens is a perennial herb within the Geraniaceue family. It is produced in regions such as France, Egypt, La Reunion, Morrocco, the former USSR, and Japan. It is also grown all over China, with the volume grown in Yunan and Sichuan province being the largest. In Guizhou it is grown in Guiyang, Wangmo, and Rongjiang[1]. Germanium oil is obtained from fresh geraniums, pelaronium graveolens, rose germaniums and their subspecies. The harvesting period is determined by climate conditions in the production location. The processing period is usually from the middle of July to October. The essential oil yield is around 0.1-0.3%. Geranium oil has a rose and germanium aroma and a peppermint tinge. Its color ranges from light yellow to dark yellow. It is mainly used for adding scent to high-grade cosmetics, and for other rose essences. When used this way, it is rather economical[2].

In order to provide a scientific basis for breed selection and essential oil quality evaluation, we used capillary gas chromatography-mass spectrometry (GC-MS) to perform a qualitative and quantitative analysis of of the main components and determine the physical and chemical parameters of the geranium oil obtained from the Rongjiang Region of Guizhou Province. This will have certain significance for the development and utilization of Guizhou's fragrant plant resources, and will help increase the depth of understanding of essential oils.

1. Summary of Principles

Perfume essential oil components are extremely complex. They are compounds formed from organic compounds such as terpene, sesquiterpenes, aromatics, alicylics, and aliphatics. Previously, investigation into scents and essential oils was performed with standard physical and chemical methods. Not only was this slow but it was also difficult to accurately determine the compositions using these methods.

Gas chromatography (GC) uses the matching of volatile substances in high molecular weight liquid and carrier gas to begin chemical separation, and then the spectrum can be determined with a detector. Since perfumes are formed from highly-volatile chemical compounds, gas chromatography is the most suitable method. Furthermore, since each organic compound has its own mass spectrum, mass spectrometry has strong qualitative capacity[3]. This experiment uses a combined capillary gas chromatography-mass spectrometry method. Each component in the mass spectrum will be separately input in order into a spectrograph to undergo mass spectrography analysis. At the same time, this will achieve the quantitative and qualitative objects of this experiment. Furthermore, complex quantitative operations such as spectrum temperature control, collection of spectrum data, data storage and mass spectrum image examination will be performed by a computer. Micro-technology has thus been applied to the process of perfume component analysis, from compound separation to chemical structure determination in a way that is fast and accurate.

2. Samples

Air-dry fresh pelargonium graveolens stem and leaves. Cut, and use the steam distillation method to retrieve the dark-yellow volatile oil, the oil yield is 0.15%, and the denstity is d^{20}_4= 0.895, and the index of refraction is n^{20}_D=1.465-1.473, optical rotation is a^{20}_D= 7°30' ~ –10°16'.

3. Equipment

The HP 5890 Gas Chromatography System Series I HP5989A MS Engine.

The main technological specifications are: mass range 10-1000amu (can be extended to 2000amu); sensitivity, EI hexachlorobenzene s/N >20, CI (chemical source) 100pg = Benzophenone s/N > 10; scan speed: maximum of 2000amu/s, resolution > 2500; ionization energy 10-250eV adjustable; mass stability 0.1amu/8hr.

4. Experimental Conditions

4.1 Gas Spectrometry Conditions

Crosslink 5% benzyl polysiloxane fused silica capillary column 30m x 0.25m; carrier gas: He 50mL/min; column pressure 12.0kPa; temperature of boil room: 240°C; Column temperature starts at 50°C, and raises 25°C/min up to 125°C, than a 10°/min increase to 250°C; stop for 7 minutes; Sample volume: 1ìL (Acetaldehyde solution dilute); diversion ratio 50:1.

4.2 Mass Spectra Conditions

Ion source temperature 250°C; separation method EI; electric potential 70eV; resolution 2500; connection temperature 280°C; scan speed 0.9s/full process; sweep mass range 40-500amu.

5. Results and Discussion

Using the GC-MS method more than 40 components were separated from the geranium oil. After MS analysis 31 chemical components have been determined as shown in the Figure. Using the surface chemical method to calculate their relative percentage content, the results are shown in Table 1.

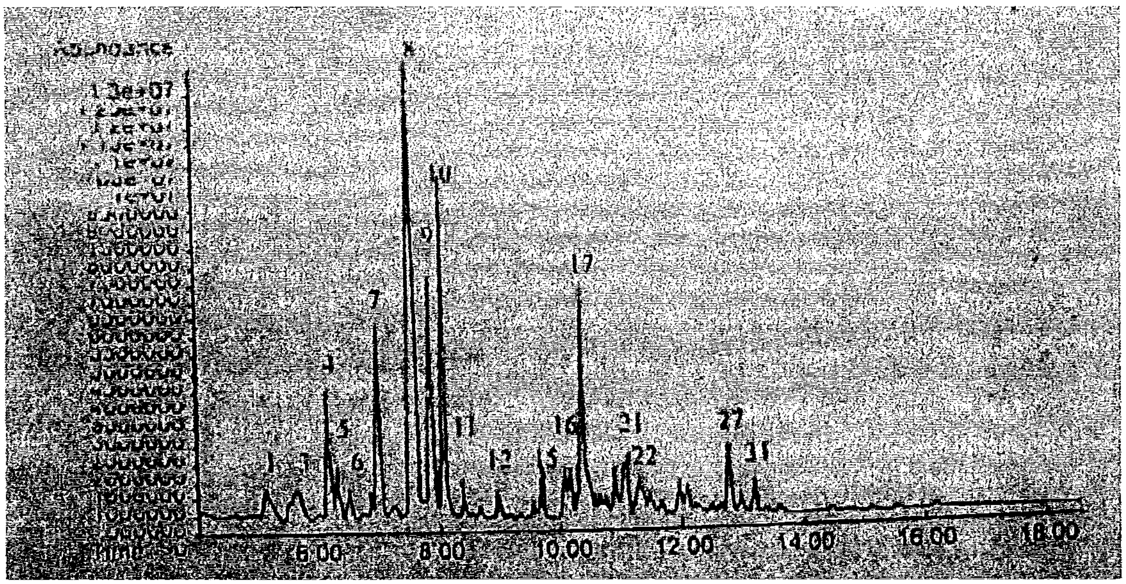

Figure – Geranium oil GC-MS Spectrum

Table 1 – Geranium oil chemical composition

Number/English compound/Chinese name/Molecular formula/Molecular weight/relative content (%)

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1	β-Myrcence	β-香叶烯	$C_{10}H_{16}$	136	1.96
2	δ-4-Carene	δ-4-蒈烯	$C_{10}H_{16}$	136	0.64
3	Linalool	芳樟醇	$C_{10}H_{18}O$	154	4.16
4	Rose- oxidi	玫瑰醚	$C_{10}H_{18}O$	154	2.86
5	2-Propenal, 3-(dimethyl amino)-3-ethon	3-(2-甲胺基)-3-乙氧基-2-丙醇	$C_7H_{13}O_2N$	143	0.82
6	σ-3-Carene	σ-3-蒈烯	$C_{10}H_{16}$	136	1.58
7	P-Menthone	p-薄荷酮	$C_{10}H_{18}O$	154	7.19
8	β-Citronellol	β-香茅醇	$C_{10}H_{20}O$	156	24.73
9	Geraniol	香叶醇	$C_{10}H_{18}O$	154	8.19
10	Citronellyl acetate	香茅醇乙酸酯	$C_{12}H_{22}O_2$	198	9.97
11	1-β-Pinene	1-β-蒎烯	$C_{10}H_{16}$	136	1.08
12	Citronellyl Propionate	香茅醇丙酸酯	$C_{13}H_{24}O_2$	212	2.31
13	α-methyl-Benzeneeth-anarmine	α-甲基-苯乙胺	$C_9H_{13}N$	135	0.19
14	α-Ylangene	α-依兰烯	$C_{15}H_{24}$	204	0.57
15	Calarene	白菖油萜	$C_{15}H_{24}$	204	1.65
16	Caryophyllene	石竹烯	$C_{15}H_{24}$	204	1.62
17	β-Guaiene	β-愈创木烯	$C_{15}H_{24}$	204	8.97
18	α-Humulene	α-葎草烯	$C_{15}H_{24}$	204	0.68
19	N-methyl-Benzen-eethanarmine	N-甲基-苯乙胺	$C_9H_{[illegible]}N$	135	1.59
20	α-Cubebene	α-荜澄茄烯	$C_{15}H_{24}$	204	0.79
21	γ-Cadinen	γ-杜松烯	$C_{15}H_{24}$	204	1.76
22	δ-Elemene	δ-榄香烯	$C_{15}H_{24}$	204	1.75
23	δ-Cadinen	δ-杜松烯	$C_{15}H_{24}$	204	2.17
24	Geranyl acetate	香叶醇乙酸酯	$C_{12}H_{20}O_2$	196	1.13
25	Propanoic acid, 2-phenylethyl ester	丙酸-2-乙酸苯乙酯	$C_{11}H_{14}O_2$	192	1.41
26	[illegible]-2-hydroxyty-ramine	N-甲基-2-羟苯酪胺	$C_9H_{13}NO$	151	1.02
27	Cyclohexene, 1-methyl-4-(1-methylethe)	1-甲基-4-异丙基-环已烯	$C_{10}H_{18}$	138	2.07
28	[illegible]	三环萜	$C_{10}H_{16}$	136	1.03
29	[illegible]-methyl-	5-甲基-2-庚胺	$C_8H_{19}N$	129	0.23
30	[illegible]-4-methyl-	4-甲基-2-己胺	$C_7H_{17}N$	115	0.66
31	Hexanamide, 5-methyl-	5-甲基-2-己胺	$C_8H_{19}N$	129	0.29

Total surface content which is currently determined – 95.07

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香叶油化学成份的研究

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摘 要 采用毛细管气相色谱一质谱一计算机联用法研究了贵州榕江地区香叶油的化学成分。色谱分离出40多个组分，质谱鉴定了31个成分，占该挥发油总量的95.07%。其主要成分是香茅醇(24.73%)、香叶醇(8.19%)、香茅醇乙酸酯(9.97%)、β-愈创木烯(8.97%)、P-薄荷酮(7.19%)和芳樟醇(4.16%)等。

关键词 香叶油；毛细管气相色谱一质谱

中图法分类号 O657.71；TQ 651.2

引 言

香叶天竺葵(*Pelargonium graveolens*)为生牻儿苗科(*Geraniaceue*)植物，多年生草本。原产法国、埃及、留尼旺岛、阿尔及利亚、摩洛哥，前苏联和日本等地。我国各地均有栽培，以云南、四川两省栽培面积最大。我省贵阳、望谟、榕江地区也有栽培[1]。香叶油(*Geranium Oil*)是从新鲜的、整株的香叶植物一香叶天竺葵和玫瑰天竺葵及其亚种中获得。香叶的收割期取决于生长地区的气候条件，加工期一般从每年七月中旬到十月。精油的得率为0.1%～0.3%。香叶油具有玫瑰和香叶的香气以及薄荷气息，颜色自淡黄至深黄色，主要用于高级化妆品加香及其它玫瑰型香精，具有较高的经济价值[2]。为了对香叶植物的品种选育和精油质量的评定工作提供科学依据，我们采用毛细管气相色谱一质谱一计算机联用法对贵州榕江地区的香叶油样进行了主要成分的定性定量分析及理化常数的测定，对贵州芳香植物资源的开发利用及精油的深加工有一定的意义。

1 原理简述

香料精油的成分十分复杂，它是由萜烯、倍半萜烯、芳香族、脂环族和脂肪族等多种有机化合物组成的混合物。过去对香料和精油的检测主要依靠一些常规的理化方法，不但速度慢而且很难弄清其中的组成。气相色谱法(GC)是利用挥发性物质在高分子液体(液相为固定相)和载气之间的分配进行分离、用检测器得到色谱的方法。因为香料是由挥发性强的化合物组成的，所以采用气相色谱法作为分析手段最为合适。又由于每一个有机化合物有它自己的质谱特性，所以质谱法(MS)具有强有力的定性能力[3]。

本实验采用气相色谱一质谱一计算机联用法，把色谱分离出来的每个成份按次序连续通进质谱仪中进行质谱分析，同时达到定性、定量的目的。且色谱程序升温控制，质谱离子碎片信

* 1995—09—25 收稿。

息的采集，数据的贮存和质谱图的自动检索，定量计算等复杂的操作均由计算机按指令自动地进行工作。它使香料精油的成份分析从组分的分离到化学结构的鉴定真正实现了微量、快速、精确。

2 样　品

将新鲜的香叶天竺葵枝和叶略为风干，剪碎，用水蒸汽蒸馏法提取得到淡黄色挥发油，出油率为 0.15%，密度 $d_4^{20}=0.895$，折光率 $n_D^{20}=1.465\sim1.473$，旋光度 $\alpha_D^{20}=-7°30'\sim-10°16'$。

3 仪　器

美国惠普公司 HP5890 Ⅱ 型气相色谱—HP5989A 型质谱联用仪。其主要技术指标为：质量范围 10～1000 amu（可扩大到 2000 amu）；灵敏度：EI（电子轰击）50Pg 六氯苯 s/N＞20，CI（化学源）100 pg＝苯甲酮 s/N＞10；扫描速度：最大到 2000 amu/s；分辨率＞2500；电离能：10～250 eV 可调，质量稳定性 0.1 amu/8hr。

4 实验条件

4.1 气相色谱条件

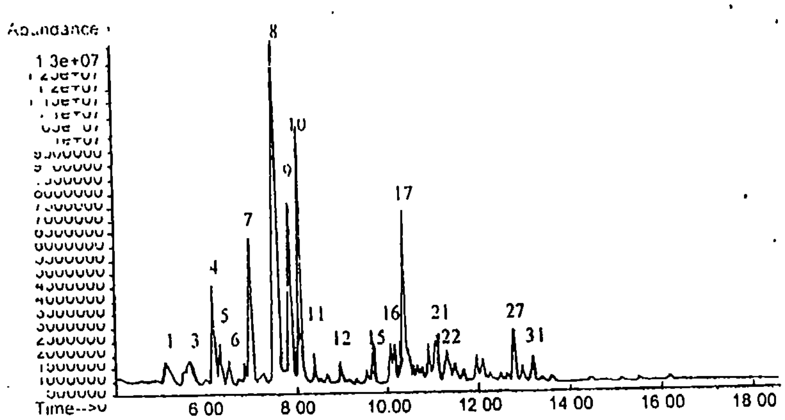
交联 5%苯甲基聚硅氧烷弹性石英毛细管柱，30 m×0.25 mm；载气：氦气 He，50 mL/min；柱前压12.0 kPa；汽化室温度 240 ℃；柱温从初温 50 ℃以 25 ℃/min 升到 125 ℃，再以 10 ℃/min 升至 250 ℃，停留 7 分钟；进样量：1 μL（无水乙醇稀释）；分流比 50:1。

4.2 质谱条件

离子源温度 250℃；电离方式 EI；电子能量 70 eV；分辨率 2500；接口温度 280 ℃；扫描速度 0.9 s/全程；扫描质量范围 40～500 amu。

5 结果与讨论

用气相色谱—质谱法从香叶油中分离出 40 多个组分，经质谱分析确定了 31 个化学成份，如附图所示。用面积归一化法计算其相对百分含量，分析结果列于表 1。



附图　香叶油 GC/MS 总离子流色谱图

表 1 香叶油化学成份

峰号	化合物英文名称	中文名称	分子式	分子量	相对含量(%)
1	β-Myrcence	β-香叶烯	$C_{10}H_{16}$	136	1.96
2	δ-4-Carene	δ-4-蒈烯	$C_{10}H_{16}$	136	0.64
3	Linaluol	芳樟醇	$C_{10}H_{18}O$	154	4.16
4	Rose oxidi	玫瑰醚	$C_{10}H_{18}O$	154	2.86
5	2-Propenal,3-(dimethyl -mino)-3-ethon	3-(2-甲胺基)-3-乙氧基-2-丙醇	$C_7H_{13}O_2N$	143	0.82
6	σ-3-Carene	σ-3-蒈烯	$C_{10}H_{16}$	136	1.58
7	P-Menthone	p-薄荷酮	$C_{10}H_{18}O$	154	7.19
8	β-Citronellol	β-香茅醇	$C_{10}H_{20}O$	156	24.73
9	Geraniol	香叶醇	$C_{10}H_{18}O$	154	8.19
10	Citronellyl acetate	香茅醇乙酸酯	$C_{12}H_{22}O_2$	198	9.97
11	1-β-Pinene	1-β-蒎烯	$C_{10}H_{16}$	136	1.08
12	Citronellyl Propionate	香茅醇丙酸酯	$C_{13}H_{24}O_2$	212	2.31
13	α-methyl-Benzeneeth-anarmine	α-甲基-苯乙胺	$C_9H_{13}N$	135	0.19
14	α-Ylangene	α-依兰烯	$C_{15}H_{24}$	204	0.57
15	Calarene	白菖油萜	$C_{15}H_{24}$	204	1.65
16	Caryophyllene	石竹烯	$C_{15}H_{24}$	204	1.62
17	β-Guaiene	β-愈创木烯	$C_{15}H_{24}$	204	8.97
18	α-Humulene	α-葎草烯	$C_{15}H_{24}$	204	0.68
19	N-methyl-Benzen-eethanarmine	N-甲基-苯乙胺	$C_9H_{13}N$	135	1.59
20	α-Cubebene	α-荜澄茄烯	$C_{15}H_{24}$	204	0.79
21	γ-Cadinen	γ-杜松烯	$C_{15}H_{24}$	204	1.76
22	α-Elemene	α-榄香烯	$C_{15}H_{24}$	204	1.75
23	δ-Cadinen	δ-杜松烯	$C_{15}H_{24}$	204	2.17
24	Geranyl acetate	香叶醇乙酸酯	$C_{12}H_{20}O_2$	196	1.13
25	Propanoic acid, 2-pheny-lethyl ester	丙酸-2-乙酸苯乙酯	$C_{13}H_{16}O_2$	192	1.41
26	N-methyl-2-hydro-xyty-ramine	N-甲基-2-羟基酪胺	$C_9H_{13}NO$	151	1.02
27	Cyclohexame, 1-methyl-4(1-methylethe)	1-甲基-4-异丙基-环已烯	$C_{10}H_{18}$	138	2.07
28	Tricyclene	三环萜	$C_{10}H_{16}$	136	1.03
29	2-Heptanamine,5-methyl-	5-甲基-2-庚胺	$C_8H_{19}N$	129	0.23
30	2-Hexanamide,4-methyl-	4-甲基-2-已胺	$C_7H_{17}N$	115	0.66
31	2-Hexanamide,5-methyl-	5-甲基-2-已胺	$C_7H_{19}N$	129	0.29
	已定性的组分占色谱总流出峰面积的百分数				95.07

结果表明，其主要成分为香茅醇、香叶醇、香茅醇乙酸酯、β-愈创木烯、P-薄荷酮和芳樟醇，其它成分含量低。据资料报道[4,5]，香叶油的醇部分主要以香叶醇和香茅醇为主，分别为 10%～20%和 30%～40%，酯部分以香茅醇和香叶醇的甲酸酯为主。贵州榕江地区香叶油中香茅醇和香叶醇的含量比国外同类产品稍低一些，但所含 β-愈创木烯，P-薄荷酮、芳樟醇和玫瑰醚的含量都较高，具有浓郁的橙花、玫瑰花香气和薄荷气息。酯部分是以香茅醇乙酸酯、丙酸酯和香叶醇乙酸酯的形式存在，而不是以甲酸酯的形式存在。另外，还有一定量的香叶烯、蒎烯、白菖油萜、杜松烯、榄香烯和石竹烯等萜类芳香物质，在化学组成上具有它的特点。这些物质虽然含量较低，但对于精油香气的贡献是十分重要的，它们赋于精油一种圆浑的天然香气。所以该香叶油具有良好的开发价值。

作为天然香料植物，由于其部位、产地、气候、栽培及管理方法、收割时间和提取方法的不同，其成份和比例也发生变化。本文采用色质谱计算机联用技术测定香叶油的化学成份，为进一步开发利用贵州野生香料资源及天然香料品种改良，加工工艺的改进，质量监控和成分分析提供了科学依据，具有一定的实用价值和参考意义。

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Key Words　geranium oil, capillary gas chromatography-mass spectrometry