

不同地区野生薄荷挥发油的比较

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摘要: 本文采用顶空气相色谱法对广西、云南、河北、江苏四个地区的薄荷 (*Mentha haplocalyx* Briq.) 精油的成分进行分析比较。共检测了 84 种化学成分, 多以烯、醇及酮类物质组成。江苏样品主要由蒎烯 (11.10%)、d-柠檬烯 (42.30%) 和胡薄荷酮 (25.50%) 组成; 广西样品主要有香芹酮 (25.46%)、d-柠檬烯 (28.75%) 和桉油素 (14.91%) 组成; 云南和河北在主要成分上相似, 云南样品主要有蒎烯 (22%)、d-柠檬烯 (18.45%) 和桉油素 (16.96%) 组成; 河北样品主要由蒎烯 (23%) 和 d-柠檬烯 (33.33%) 和桉油素 (12.45%) 组成。研究发现不同地区薄荷精油的组成受环境影响较大, 江苏薄荷胡薄荷酮含量较高, 广西薄荷含香芹酮较高, 云南和河北主要成分相似, 组成比例不同。

关键词: 薄荷; 顶空气相色谱; 挥发油

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Comparative Studies on Volatile Oil Components of *Mentha haplocalyx* from Different Regions in China

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Abstract: In this study the essential oil compositions in *Mentha haplocalyx* Briq. from 4 different regions (Yunnan, Guangxi, Jiangsu and Hebei Province) in China were determined by headspace GC-MS. The results showed that a total of 85 kinds of substances were detected among which alkene, alcohol and ketones are the dominant components. The sample from Jiangsu had a composition of pinene (11.10%), d-limonene (42.30%) and pulegone (25.50%); The sample from Guangxi had a composition of carvone (25.46%), d-limonene (28.75%) and eucalyptol (14.91%); The sample from Yunnan had a composition of pinene (22%), d-limonene (18.45%) and eucalyptol (16.96%) which is similar to the composition of the sample from Hebei with pinene (23%) and d-limonene (33.33%) and eucalyptol (12.45%). Conclusively, the composition of the volatile oil in *M. haplocalyx* was highly dependent on the regional habitat condition. *M. haplocalyx* in Jiangsu had relatively high content of pulegone while that in Guangxi had high content of carvone. Samples from Yunnan and Hebei had similar oil compositions but different proportions of each kind of oil.

Key words: *Mentha haplocalyx* Briq.; Headspace GC-MS; volatile oil

薄荷^[1] (*Mentha haplocalyx* Briq.) 在我国分布广泛, 喜生于水旁潮湿处。薄荷的用途广, 除作为常用中药材^[2] 作驱风、解热、发汗剂使用外, 还作为食品、化妆品添加剂使用。挥发油作为薄荷的有效成分, 是评价薄荷质量的重要标准。

挥发油的组成和在植物体内的积累受环境影响^[3,4] 较大, 与采摘地区及采收时间有密切的联系。

所以不同产地的薄荷, 不同采收季节^[5-10] 不同采收部位^[11-14] 其香型差异比较大。顶空气相色谱是一种成熟的方法, 常用于环境检测, 最早可见于 1939 年 Harger 对水中甲醇的检测。随着技术的进步, 已经成为现代分析的一种有力手段。顶空气相和 MS 的联用, 大大拓宽了顶空技术的应用范围。顶空气相色谱对挥发油检测较传统方法有优势, 特别在小样品的情况下。采用顶空气相色谱法可以最大程度上保持其精油的组成。本实验采集不同地区的鲜活

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样品,通过顶空气相法测其精油的组成,考察不同地区薄荷精油的差别。

1 材料

薄荷于2008年7月,采自云南昆明,广西南宁,河北安国及江苏连云港四个不同地区,均为野生品。经黄璐琦研究员鉴定为唇形科薄荷属植物薄荷(*Mentha haplocalyx* Briq.)。

2 方法

实验仪器: Agilent 气相色谱仪 7694E, Agilent 6973 network, Mass selective Detector Agilent technologies 6890N network GC system。

检测条件: 色谱柱: HP. INNOWAX (Crosslinked polyethylene Glycol) 毛细管柱 (柱长: 30 m, 内径: 0.53 mm, 液膜厚度: 1.0 μm); 载气: N_2 ; 总流量: 54.0 mL/min; 进样口温度: 230 $^{\circ}\text{C}$; 进样口压力: 3 psi (1 psi = 6.895 Kpa); 检测器温度: 250 $^{\circ}\text{C}$; H_2 流量: 30 mL/min; 空气流量: 300 mL/min; 进样方式: 样品在 70 $^{\circ}\text{C}$ 加热 10 min 后直接进样; 程序升温: 60 $^{\circ}\text{C}$ -110 $^{\circ}\text{C}$, 1.5 $^{\circ}\text{C}/\text{min}$, 110 $^{\circ}\text{C}$, 5 min, 110 ~ 200 $^{\circ}\text{C}$, 5 $^{\circ}\text{C}/\text{min}$, 升至 200 $^{\circ}\text{C}$, 保持 2 min。

样品处理: 取盆栽不同地区样品 3 株, 摘取叶片, 采取四分法取样, 取三个平行样。然后称取新鲜薄荷叶 2 g, 叶片剪成 1 \times 1 cm 的小片, 茎剪成 1 cm 长段, 装在 10 mL Agilent 顶空瓶中, 压紧密封。顶空瓶体积: 10 mL; 平衡时间: 10 min; 平衡温度: 70 $^{\circ}\text{C}$; 分析时间: 47.25 min; 样品容积: 20 mL; 进样量: 0.7 mL; 进样方式: 自顶空部分精密抽取顶空气体。

3 结果

经 GC-MS 分析得到薄荷中挥发油组分的总离子流色谱图, 经标准质谱库检索, 确定出 85 个组分。将总离子流色谱图中的各峰面积进行归一化, 得到

四种地区薄荷中各组分的相对含量(表 2)。

河北样品主要由 α -蒎烯 (11.21%)、sabinene (7.72%)、 β -蒎烯 (11.83%)、 β -phellandrene (8.44%) 和 d-柠檬烯 (33.33%) 和 桉油素 (12.45%) 组成; 江苏样品主要由 α -蒎烯 (6.08%)、 β -蒎烯 (5.06%)、 β -phellandrene (3.39%)、d-柠檬烯 (42.30%)、桉油素 (4.75%) 和 胡薄荷酮 (25.50%) 组成; 云南样品主要有 α -蒎烯 (11.46%)、sabinene (7.18%)、 β -蒎烯 (10.63%)、 β -phellandrene (8.52%) 和 d-柠檬烯 (18.45%) 和 桉油素 (16.96%) 组成; 广西样品主要有 α -蒎烯 (4.42%)、香芹酮 (25.46%)、dl-menthol (2.79%)、 β -phellandrene (3.55%)、d-柠檬烯 (28.75%) 和 桉油素 (14.91%) 组成。图 2 可见江苏、云南的主要成分由烯、酮、醇主要组成; 河北、广西主要由烯、酮、氧化物类组成, 烯类成分更加集中。

根据华永丽化学型分类法^[15], 四个不同地区薄荷可划分为四个不同化学型。江苏产薄荷为蒎烯/d-柠檬烯/胡薄荷酮 (11.10%/42.30%/25.50%) 型; 广西产薄荷为香芹酮/d-柠檬烯/桉油素 (25.46%/28.75%/14.91%) 组成; 云南和河北在主要成分上相似, 云南产薄荷为蒎烯/d-柠檬烯/桉油素 (22%/18.45%/16.96%) 型; 河北产薄荷为蒎烯/d-柠檬烯/桉油素 (23%/33.33%/12.45%) 组成。

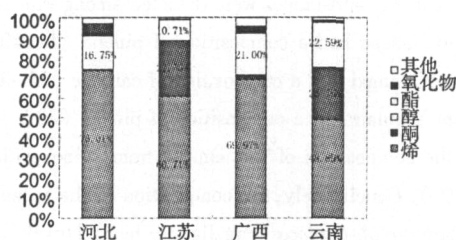


图 1 不同地区薄荷挥发油的成分分析

Fig. 1 The volatile oils of peppermint of different regions

表 1 四种不同地区薄荷精油的组成

Table 1 The composition of peppermint essential oil of four different regions

化合物 Compounds	分子式 Mol. form.	保留时间 t_R	河北 Hebei	江苏 Jiangsu	广西 Guangxi	云南 Yunnan
1# Methyl 2-methylbutanoate	$\text{C}_6\text{H}_{12}\text{O}_2$	10.089	-	-	-	0.05%
2# Ethyl 2-methylbutyrate	$\text{C}_7\text{H}_{14}\text{O}_2$	12.784	-	-	-	0.02%
3# Leaf alcohol	$\text{C}_6\text{H}_{12}\text{O}$	14.111	-	-	-	0.50%

4# Styrene	C ₈ H ₈	14.588	-	0.01%	0.01%	-
5# α -Thujene	C ₁₀ H ₁₆	15.151	0.37%	1.33%	0.38%	0.12%
6# α -Pinene	C ₁₀ H ₁₆	15.503	11.21%	6.08%	11.46%	4.42%
7# Camphene	C ₁₀ H ₁₆	16.278	0.32%	0.30%	1.10%	0.35%
8# Sabinene	C ₁₀ H ₁₆	17.438	7.72%	0.00%	7.18%	2.45%
9# β -Pinene	C ₁₀ H ₁₆	17.604	11.83%	5.06%	10.63%	3.84%
10# β -Phellandrene	C ₁₀ H ₁₆	17.975	8.44%	3.39%	8.52%	3.55%
11# β -Terpinene	C ₁₀ H ₁₆	18.980	0.35%	0.55%	-	0.37%
12# 3-Octanone	C ₈ H ₁₆ O	19.268	0.26%	0.07%	0.40%	-
13# 1-Octen-3-ol	C ₈ H ₁₆ O	19.178	-	-	-	0.45%
14# α -Terpinene	C ₁₀ H ₁₆	19.604	0.03%	0.14%	-	0.01%
15# (+)-4-Carene	C ₁₀ H ₁₆	19.614	-	-	-	2.68%
16# 3-Octanol	C ₈ H ₁₈ O	19.857	1.78%	0.72%	0.41%	0.59%
17# d-Limonene	C ₁₀ H ₁₆	20.180	33.33%	42.30%	18.45%	28.75%
18# trans -beta-ocimene	C ₁₀ H ₁₆	20.395	1.60%	0.00%	4.33%	1.45%
19# eucalyptol	C ₈ H ₁₈ O	20.755	12.45%	4.75%	16.96%	14.91%
20# cis- β -octatriene	C ₁₀ H ₁₆	21.042	0.45%	0.56%	3.78%	0.33%
21# γ -Terpinene	C ₁₀ H ₁₆	21.609	0.08%	0.57%	0.09%	0.03%
22# 2-Ethylhexanol	C ₈ H ₁₈ O	21.792	-	0.02%	0.02%	0.02%
23# Terpinolene	C ₁₀ H ₁₆	22.992	0.29%	0.15%	0.44%	0.09%
24# (Z)-Linalool oxide	C ₁₀ H ₁₈ O ₂	23.529	0.02%	-	0.11%	-
25# Linalool	C ₁₀ H ₁₈ O	24.741	1.82%	0.80%	1.37%	0.55%
26# Ocimene. allo. (e μ)	C ₁₀ H ₁₆	24.927	2.25%	0.38%	3.90%	1.41%
27# Fenchene	C ₁₀ H ₁₆	25.188	-	0.02%	0.10%	0.03%
28# 1 β β -p-Menthatriene	C ₁₀ H ₁₄	25.371	0.01%	-	0.11%	-
29# Trimethyl(2-methyl-1-propenylidene)-cyclopropane	C ₁₀ H ₁₆	25.555	0.02%	-	0.09%	-
30# α β -Thujone	C ₁₀ H ₁₆ O	25.991	-	-	0.06%	-
31# (+)-Limonene oxide	C ₁₀ H ₁₆ O	25.997	-	-	0.00%	0.01%
32# (+)-cis-Limonene 1,2-epoxide	C ₁₀ H ₁₆ O	25.989	-	0.02%	0.04%	-
33# (+)-(E)-Limonene oxide	C ₁₀ H ₁₆ O	26.173	-	0.02%	-	0.06%
34# 2 β -Dimethylhydroquinone	C ₈ H ₁₀ O ₂	26.453	-	-	0.11%	-
35# (3Z 5E)-1 β 5-undecatriene	C ₁₁ H ₁₈	26.665	-	-	-	0.05%
36# Menthofuran	C ₁₀ H ₁₄ O	26.862	-	0.04%	-	-
37# Isopulegol	C ₁₀ H ₁₈ O	26.887	0.02%	-	0.12%	-
38# (-)-Camphor	C ₁₀ H ₁₆ O	27.343	0.00%	-	0.01%	-
39# Menthone	C ₁₀ H ₁₈ O	27.355	0.02%	-	-	0.10%
40# (-)-Lavandulol	C ₁₀ H ₁₈ O	27.587	-	-	0.45%	-
41# Terpinen-4-ol	C ₁₀ H ₁₈ O	27.869	-	0.15%	0.18%	-
42# Isopulegol	C ₁₀ H ₁₈ O	27.858	0.08%	0.00%	-	0.02%
43# dl-Menthol	C ₁₀ H ₂₀ O	28.005	0.22%	0.01%	0.09%	2.79%
44# Borneol	C ₁₀ H ₁₈ O	28.143	0.02%	0.11%	0.43%	0.05%

45# Azulene	C ₁₀ H ₈	28.431	0.10%	-	-	0.03%
46# Isopulegone	C ₁₀ H ₁₆ O	28.450	-	0.20%	0.90%	-
47# α -Terpineol	C ₁₀ H ₁₈ O	28.630	0.01%	-	0.51%	0.02%
48# Dihydrocarveol	C ₁₀ H ₁₈ O	28.988	-	-	-	1.00%
49# 2-Allyl-6-methylphenol	C ₁₀ H ₁₂ O	29.151	-	-	0.46%	-
50# (E)-Dihydrocarvone	C ₁₀ H ₁₆ O	29.182	-	1.37%	-	1.10%
51# (Z)-3-Hexenyl valerate	C ₁₁ H ₂₀ O ₂	29.205	0.09%	-	-	-
52# 4,7-Dimethylbenzofuran	C ₁₀ H ₁₀ O	29.279	0.13%	-	-	-
53# Trans-2-carene-4-ol	C ₁₀ H ₁₆ O	29.805	-	3.60%	-	0.98%
54# 1-Ethyl-3-iso-propylbenzene	C ₁₁ H ₁₆	30.006	0.12%	-	-	-
55# (E)-carveol	C ₁₀ H ₁₆ O	30.241	-	-	-	0.26%
56# Carvone	C ₁₀ H ₁₄ O	30.782	0.42%	0.02%	0.17%	25.46%
57# Pulegone	C ₁₀ H ₁₆ O	30.879	-	25.50%	-	-
58# Piperitone	C ₁₂ H ₂₀ O ₂	31.091	-	0.01%	0.43%	0.05%
59# Piperitone oxide	C ₁₀ H ₁₄	31.365	3.23%	-	1.46%	0.02%
60# Thymol	C ₁₀ H ₁₄ O	31.448	-	0.34%	0.00%	-
61# Lavandulyl acetate	C ₉ H ₁₆	31.908	0.40%	-	0.51%	-
62# 2-Methylnaphthalene	C ₁₁ H ₁₀	32.170	-	-	0.03%	-
63# Isophorone	C ₉ H ₁₄ O	32.276	-	-	0.31%	-
64# Dihydrocarvyl acetate	C ₁₂ H ₂ O ₂	32.616	-	-	-	0.29%
65# (Z)-Carveyl acetate	C ₁₂ H ₁₈ O ₂	32.820	-	0.02%	-	0.29%
66# n-Tetradecane	C ₁₄ H ₃ O	33.372	0.20%	-	0.13%	0.02%
67# α -Cubebene	C ₁₅ H ₂₄	33.546	-	0.01%	-	-
68# (1r)-(+) -Trans-isolimonene	C ₁₀ H ₁₆	33.629	-	0.01%	-	-
69# β -Bourbonene	C ₁₅ H ₂₄	33.970	-	0.04%	-	0.02%
70# β -Elemene	C ₁₅ H ₂₄	34.120	-	0.02%	-	-
71# Piperitenone	C ₁₀ H ₁₈ O	34.284	0.06%	0.36%	0.08%	0.04%
72# α -Gurjunene	C ₁₅ H ₂₄	34.608	0.00%	0.03%	0.06%	0.04%
73# Caryophyllene	C ₁₅ H ₂₄	35.230	0.09%	0.18%	1.88%	0.26%
74# β -Cubebene	C ₁₅ H ₂₄	35.304	-	0.02%	-	-
75# (Z)- β -Farnesene	C ₁₅ H ₂₄	35.444	-	0.02%	-	-
76# β -Farnesene	C ₁₅ H ₂₄	35.451	-	-	0.22%	-
77# β -Sesquiphellandrene	C ₁₅ H ₂₄	35.445	-	-	-	0.03%
78# δ -Cadinene	C ₁₅ H ₂₄	35.734	-	-	0.18%	0.11%
79# α -Fenchene	C ₁₀ H ₁₆	36.224	-	0.01%	0.15%	0.02%
80# Bicyclosesquiphellandrene	C ₁₅ H ₂₄	36.367	-	0.09%	0.29%	0.09%
81# β -Cubebene	C ₁₅ H ₂₄	36.368	0.05%	0.36%	0.60%	0.19%
82# α -Amorphene	C ₁₅ H ₂₄	37.413	-	0.01%	-	-
83# Calamenene	C ₁₅ H ₂₂	38.032	-	0.05%	0.05%	0.02%
84# Hexadecane	C ₁₆ H ₃₄	38.859	0.09%	0.04%	0.07%	0.02%

注 “-”表示微量或痕量物质,或不含。Noté “-” means trace or not detected

4 讨论

本文提供了不同地区薄荷的精油组成特点, 四种薄荷因地理气候不同而呈现差异性。云南野生薄荷为香芹酮型, 其挥发油均以香芹酮为主要成分, 并伴有一定的苜烯; 江苏薄荷精油为薄荷酮/胡薄荷酮型, 与周荣汉^[15]所研究相一致。河北与广西的化学成分相似, 富含蒎烯、柠檬烯及桉油素, 但广西样品含香芹酮含量较高。

不同地区样品中, α -蒎烯(4.42% ~ 11.46%)、 β -蒎烯(3.84% ~ 11.83%) 都是主要组成成分。在魏兴国^[10]、安秋容^[9]的研究中 α -蒎烯(4.42% ~ 11.46%)、 β -蒎烯(3.84% ~ 11.83%) 都是微量成分, 在夏季采收的样品中属于痕量成分。薄荷酮含量在俞桂新的研究中属主要成分, 而在本实验中却是少量成分, 可能与采集时间有关。

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