重庆云阳不同季节种植的青蒿精油成分的 GC-MS分析*

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摘要　目的: 对春、冬两季种植青蒿的精油成分进行分析比较。方法: 水蒸气蒸馏法提取青蒿精油, 乙醚萃取浓缩。用 GC-MS法对 2种青蒿的精油成分进行分析鉴定。结果: 从 2种精油中共鉴定出 41种化合物, 其中蒿酮、樟脑、石竹烯氧化物、α-蛇床烯、桉叶素、香橙烯、表蓝桉醇等 16种化合物是 2种精油所共有的。冬蒿精油的主要成分为蒿酮、樟脑、石竹烯氧化物、α-蛇床烯、桉树脑等; 春蒿精油则为樟脑、石竹烯氧化物、表蓝桉醇、α-蛇床烯等。除蒿酮含量在 2种精油中差别较大外, 另 15种化合物的相对含量之和大致相同, 分别为 59.81%和 63.82%。结论: 结果表明基因型对青蒿精油的组成起决定作用; 气候因素对各成分的相对含量有影响, 尤其对蒿酮和樟脑的积累影响较大。

关键词: 青蒿; 精油; 水蒸气蒸馏法; GC-MS; 组分

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GC-MS analysis of composition of different seasonal essential oil in leaves of *Artemisia annua* L. from Yunyang Chongqing*

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Abstract　**Objective** To study differences between the essential oil of *Artemisia annua* L. sown in spring and in winter by GC-MS. **Methods** The essential oils were extracted with steam distillation method from the two *A. annua* L., respectively. The relative amount of each component was calculated in area normalization. **Results** Forty-one compounds were identified in the two essential oils. The major constituents of winter *A. annua* L. oil were artemisia ketone, camphor, caryophyllene oxide, α-selinene, eucalyptol, *ect*; and the major constituents of spring *A. annua* L. oil were camphor, caryophyllene oxide, epiglobbulol, and α-selinene, *ect*. Sixteen compounds, such as artemisia ketone, camphor, caryophyllene oxide, α-selinene, eucalyptol, aromadendren, epiglobbulol, *ect*. can be found in both of the two essential oils. Except for a greater amount difference of artemisia ketone showed in two essential oils, the relative amounts of the other fifteen compounds summed roughly the same as 59.81% and 63.82% respectively. **Conclusions** Effect of genotype on the composition of essential oils played a decisive role and climate had effected greatly to the relative content of the compositions, especially for the content of artemisia ketone and camphor.

Key words: *Artemisia annua* L.; essential oil; steam distillation method; GC-MS; component

青蒿为菊科一年生草本植物黄花蒿(*Artemisia annua* L.)的干燥地上部分。其性寒、味苦, 主治暑邪发热、阴虚发热、夜热早凉、骨蒸劳热、疟疾寒热、湿热黄疸[1], 主要分布在我国重庆、广西、四川、湖南、云南、贵州、江西等地。现代研究[2~7]已证明青蒿精油具有抗癌、抗菌、抗病毒、抗氧化、杀虫和对中枢神经系统的镇静作用等多种生物活性。青蒿精油中的主要成分为萜类及萜类氧化物, 包括樟脑、石竹烯氧化物、α-蛇床烯、桉叶素、香橙烯等, 此外各地青蒿精油的组成及含量存在着较大的差异[1 8~14]。本文用气相色谱-质谱联用方法对重庆云阳地区春、冬两季种植青蒿的精

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油成分进行分析,以对其组分及含量的不同进行比较,并探讨季节对青蒿精油中物质成分的影响。

1 仪器与材料

GCMS – QP2010(日本岛津),精油提取装置,旋转蒸发仪。

冬季青蒿,采自重庆云阳县,2005年 11月 20日播种,2006年 6月 20日采收,海拔 200~ 300 m;春季青蒿,采自重庆云阳县,2005年 3月 20日播种,2005年 7月 25日采收,海拔 180~ 200 m。经鉴定,为黄花蒿 *Artemisia annua* L。

乙醚、正己烷、无水硫酸钠均为分析纯。

2 精油提取与分析

2.1 精油的提取[15] 将黄花蒿粉碎后,各精确称量粉末 50 g分别置 2000 mL圆底烧瓶中,加水适量,浸泡 12 h。连接精油测定器,自冷凝管上端加水使之充满精油测定器的刻度部分,并溢流入烧瓶时为止。再加适量乙醚浮于水上层。置电热套上缓缓加热至沸,并保持微沸约 6 h,至测定器中的油量不再增加。完毕后,在冷凝管上端加少量乙醚冲洗冷凝管,待充分分层后,打开活塞放出刻度管的水,收取乙醚层,无水硫酸钠干燥后,在室温通风处使乙醚自然挥干,精密称量。其中冬蒿挥发油为 0.15 mL(浅黄色),春蒿挥发油为 0.6 mL(浅黄色);均具有特殊香味。

2.2 GC/MS分析 气相色谱条件:氦气(99.999%),恒流 0.5 mL·min^{-1};色谱柱为 OV – 1701石英毛细管柱(30 m × 0.33 mm × 0.25 μm),进样口温度 260 ℃,出口温度 280 ℃;柱温采取程序升温,起始温度为 50 ℃,10 ℃·min^{-1},20 min后升至 260 ℃。进样量 1 μL,分流比 20∶1。质谱条件:电离方式为 EI,电子能量为 70 eV,电子源温度 230 ℃,接口温度 280 ℃,检测定量为 1.2 kV,质量扫描范围为 10~ 500 amu,扫描速度 1000 amu·s^{-1},扫描周期为 0.5 s,分辨率为 2500。

2.3 实验步骤 取精油 1 μL,加正己烷 5.0 mL溶解。用气相色谱 – 质谱 – 计算机联用仪进行分析鉴定,通过检索 Nist107标准质谱图库,并结合有关文献人工谱图解析,确证精油中的各个化学成分[16-17]。采用峰面积归一化法对精油中的各成分进行定量。

3 结果与讨论

3.1 总离子流图 冬蒿和春蒿挥发油的总离子流图见图 1。

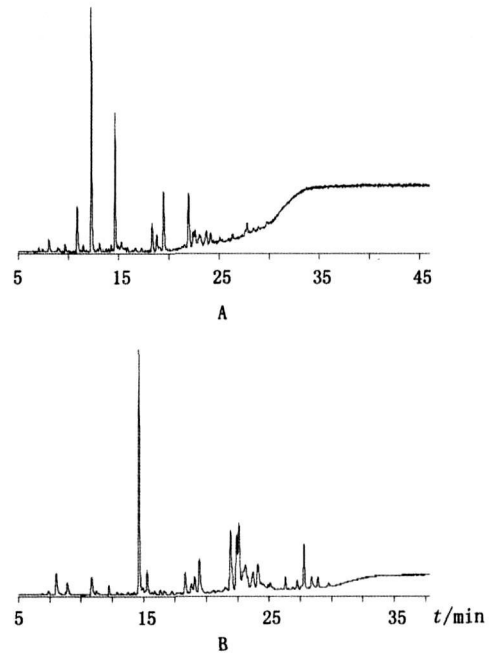

图 1 冬季青蒿(A)与春季青蒿(B)挥发油的总离子流图

Fig 1 GC chromatograms of essential oil from the winter *A. annua* L. (A) and essential oil from the spring *A. annua* L. (B)

3.2 青蒿精油化学成分 青蒿精油组分中主要是萜类化合物。冬蒿精油的主要成分是蒿酮(26.96%)、樟脑(14.29%)、石竹烯氧化物(9.69%)、α – 蛇床烯(9.33%)、桉叶素(6.54%)等。春蒿精油的主要成分是樟脑(23.05%)、石竹烯氧化物(9.36%)、表蓝桉醇(6.86%)、α – 蛇床烯(5.11%)、1,1,7 – 三甲基 – 4 – 亚甲基二苯胺 – 1*H* – 环丙烷[e]甘菊环(4.74%)、蓝桉醇(4.72%)等。冬蒿和春蒿精油的成分见表 1。实验结果表明:冬季青蒿精油和春季青蒿精油的化学成分相差不多,共同含有的化合物有 16种,分别是 α – 蒎烯、莰烯、β – 蒎烯、桉叶素、蒿酮、樟脑、龙脑、桃金娘(烯)醇、香橙烯、(*Z*) – β – 金合欢烯、α – 蛇床烯、石竹烯氧化物、表蓝桉醇、顺 – *Z* – α – 红没药烯环氧化物、异香橙烯环氧化物和反 – *Z* – α – 红没药烯环氧化物。详见图 2。

3.3 小结 根据上述结果可以推断:(1)同种基因型青蒿的精油组成成分大致相同;(2)生长期的气候条件对青蒿精油中各成分的相对含量有着重要影响,尤其是对蒿酮和樟脑的积累影响较大[18];(3)青蒿精油中樟脑的含量很高,而樟脑是一种用途广泛的物质,要想获得尽可能多的樟脑,应该考虑青蒿的种植季节[18];(4)在冬蒿精油和春蒿精油的 16个相同的化合物中,除蒿酮含量差别较为显著外,其余

表 1　2种青蒿精油的化学成分

Tab 1　Chemical constituent of the essential oils from the two *A. annua* L.

序号(No.)	化合物名称 (identified compounds)	分子式 (molecular formula)	M_r	相对含量(relative content)/%	
				冬蒿精油(essential oil from winter *A. annua* L.)	春蒿精油(essential oil from spring *A. annua* L.)
1	4-蒈烯(4-carene)	$C_{10}H_{16}$	136	0.39	—
2	α-蒎烯(α-pinene)	$C_{10}H_{16}$	136	0.14	0.41
3	莰烯(camphene)	$C_{10}H_{16}$	136	1.76	2.81
4	β-蒎烯(β-pinene)	$C_{10}H_{16}$	136	0.48	1.31
5	香桧烯(sabinene)	$C_{10}H_{16}$	136	0.25	—
6	β-香叶烯(β-myrcene)	$C_{10}H_{16}$	136	0.95	—
7	桉叶素(eucalyptol)	$C_{10}H_{18}O$	154	6.54	2.57
8	艾醇(yomogi alcohol)	$C_{10}H_{18}O$	154	0.79	—
9	蒿酮(artemisia ketone)	$C_{10}H_{16}O$	152	26.96	0.89
10	顺-β-萜品醇(*cis*-β-terpineol)	$C_{10}H_{18}O$	154	—	0.29
11	马鞭草烯酮(verbenone)	$C_{10}H_{14}O$	150	—	0.19
12	蒿醇(artemisia alcohol)	$C_{10}H_{18}O$	154	1.01	—
13	4-丙基-1,6-庚二烯-4-醇(4-propyl-1,6-heptadien-4-ol)	$C_{10}H_{18}O$	154	0.39	—
14	3,7-辛二烯-2-醇,2,6-二甲基-65(3,7-octadien-2-ol,2,6-dimethyl-65)	$C_{10}H_{18}O$	154	0.38	—
15	3,6,6-三甲基二环[3.1.1]-2-庚醇(3,6,6-trimethylbicyclo[3.1.1]heptan-2-ol)	$C_{10}H_{18}O$	154	0.63	—
16	樟脑(camphor)	$C_{10}H_{16}O$	152	14.29	23.05
17	α-柠檬烯二环氧化物(α-limonene diepoxide)	$C_{10}H_{16}O_2$	168	0.49	—
18	异侧柏酮(isothujol)	$C_{10}H_{18}O$	154	—	0.33
19	异香叶醇(isogeraniol)	$C_{10}H_{18}O$	154	—	0.13
20	龙脑(borneol)	$C_{10}H_{18}O$	154	0.98	2.48
21	(1*R*)-(-)-桃金娘烯醛[(1R)-(-)-myrtenal]	$C_{10}H_{14}O$	150	—	0.14
22	桃金娘(烯)醇(myrtenol)	$C_{10}H_{16}O$	152	0.44	0.30
23	反-3(10)-蒎烯-2-醇(*trans*-3(10)-caren-2-ol)	$C_{10}H_{16}O$	152	—	0.57
24	烯(copaene)	$C_{15}H_{24}$	204	—	0.50
25	异香叶烯醇(isomyrcenol)	$C_{10}H_{16}O$	152	0.49	—
26	香橙烯(aromadendrene)	$C_{15}H_{24}$	204	4.43	2.57
27	(*Z*)-β-金合欢烯[(Z)-β-farnesene]	$C_{15}H_{24}$	204	2.63	1.41
28	α-石竹烷(α-caryophyllene)	$C_{15}H_{24}$	204	0.76	—
29	β-恰米烯(β-chamigrene)	$C_{15}H_{24}$	204	—	2.37
30	α-蛇床烯(α-selinene)	$C_{15}H_{24}$	204	9.33	5.11
31	石竹烯氧化物(caryophyllene oxide)	$C_{15}H_{24}O$	204	9.69	9.36
32	表蓝桉醇(epiglobulol)	$C_{15}H_{26}O$	206	2.12	6.86
33	顺-*Z*-α-红没药烯环氧化物(*cis*-*Z*-α-bisabolene epoxide)	$C_{15}H_{24}O$	204	3.21	2.95
34	反-*Z*-α-红没药烯环氧化物(*trans*-*Z*-α-bisabolene epoxide)	$C_{15}H_{24}O$	204	1.03	0.17
35	异香橙烯环氧化物(isoaromadendrene epoxide)	$C_{15}H_{24}O$	204	2.74	2.46
36	绿花白千层醇(viridiflorol)	$C_{15}H_{26}O$	206	3.12	—
37	α-没药醇(α-bisabolol)	$C_{15}H_{26}O$	206	1.76	—
38	蓝桉醇(globulol)	$C_{15}H_{26}O$	222	—	4.72
39	去甲麝香酮(normuscon)	$C_{15}H_{28}O$	224	—	0.43
40	2-丁基-3-甲基-5-(2-甲基-2-丙稀基)环己酮(2-butyl-3-methyl-5-(2-methyl-2-propenyl)cyclohexanone)	$C_{15}H_{26}O$	222	—	1.21
41	1,1,7-三甲基-4-亚甲基二苯胺-1*H*-环丙烷[e]甘菊环(1,1,7-trimethyl-4-methylenedecahydro-1*H*-cyclopropa[e]azulene)	$C_{15}H_{24}$	204	—	4.74

注(note): -未检出(not detected)

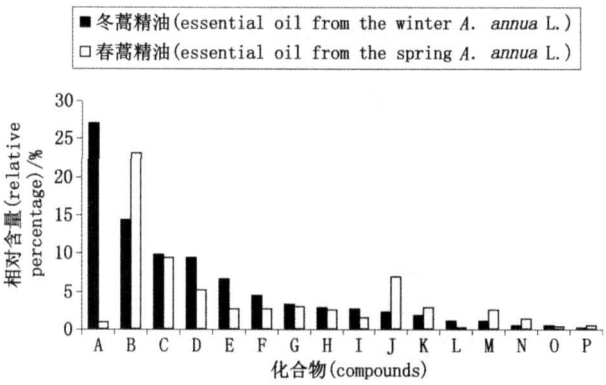

图 2 2种青蒿精油中所含共同化合物含量对比

Fig. 2 Content comparison of the common compounds in the essential oils from two *A. annua* L.

A. 蒿酮(artemisia ketone) B. 樟脑(camphor) C. 石竹烯氧化物(caryophyllene oxide) D. α-蛇床烯(α-selinene) E. 桉叶素(eucalyptol) F. 香橙烯(aromadendrene) G. 顺-*Z*-α-红没药烯环氧化物(*cis*-*Z*-α-bisabolene epoxide) H. 异香橙烯环氧化物(isoaromadendrene epoxide) I. (*Z*)-β-金合欢烯[(*Z*)-β-farnesene] J. 表蓝桉醇(epiglobulol) K. 莰烯(camphene) L. 反-*Z*-α-红没药烯环氧化物(*trans*-*Z*-α-bisabolene epoxide) M. 龙脑(borneol) N. β-蒎烯(β-Pinene) O. 桃金娘(烯)醇(myrtenol) P. α-蒎烯(α-pinene)

15种化合物的相对含量之和大致相同, 分别为59.81%和63.82%。

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