

云南使君子仁油中挥发性成分的 GC-MS 分析

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摘 要:采用醇提和乙酸乙酯萃取使君子仁油, 用固相微萃取技术对油中的挥发性成分进行 GC-MS 定性和定量分析。结果表明:使君子仁油的挥发性成分中含有 52 种精油成分, 鉴定出 29 种化合物, 其中蚁酸、乙酸、柠檬烯、甲苯的含量较高, 分别为 1.65%、6.51%、2.41%、2.75%。使君子仁油中所含挥发性成分大多为有毒和刺激性化合物, 为保证用药的安全性, 在直接食用种仁驱虫时必须熟食, 禁止生食, 避免发生中毒现象。

关键词:使君子仁油; 固相微萃取; 挥发性成分; 气相色谱-质谱

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Analysis of the Volatile Constituents of *Fructus quisqualis* kernel Oil from Yunnan by GC-MS

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Abstract: The *Fructus quisqualis* kernel oil was extracted by ethanol and ethyl acetate. The volatile components of *Fructus quisqualis* kernel oil were qualitatively and quantitatively analyzed by GC-MS with solid-phase microextraction. The results indicated that fifty-two volatile constituents were examined from the volatile components of *Fructus quisqualis* kernel oil, and twenty-nine compounds were identified, in which the contents of formic acid, acetic acid, Toluene and D-Limonene are relatively high, the relative contents of them were 1.65%, 6.51%, 2.41% and 2.75%, respectively. The volatile components of *Fructus quisqualis* kernel oil were most toxicant and stimulative compounds, when repelling parasites with *Fructus quisqualis* kernel, we must eat cooked *Fructus quisqualis* kernel and prohibit eating uncooked medicine, so that we can guarantee the safety of applying medicine and avoid taking place phenomenon of toxicosis.

Key words: *Fructus quisqualis* kernel oil; solid-phase microextraction; the volatile components; GC-MS-Compute.

中药使君子 (*Fructus quisqualis*) 为使君子科植物使君子 (*Quisqualis indica* L.) 的干燥成熟果实, 生于平地、山坡、路旁等向阳灌木丛中, 有栽培。分布于福建、台湾、广西、江西、湖南、四川、贵州、贵州、台湾、云南及广东海南岛等地^[1]。云南以德宏地区、孟腊、景洪、华坪、景东、景谷、普洱、保山、巧家等县分布最多。具有杀虫消积、健脾的功能, 用于虫积腹痛、疳积等症。使君子主要含有使君子酸 (Quisqualic acid)、使君子酸钾 (Potassium Quisqualate)、植物甾醇 (Phytosterol)、糖类、苹果酸、柠檬酸、琥珀酸、

胡芦巴碱 (Trigonelline)、吡啶 (Pyridine) 及其同类物等化合物^[2,3]。目前使君子发生中毒现象时有发生, 如金光虎等 (2004) 报道生食使君子肉引起过敏性紫癜 1 例^[4]; 何丽芸 (2004)^[5] 报道 2 例儿童口服过量使君子致膈肌痉挛。为了解使君子中毒成分是否与种仁所含的挥发性成分有关, 在研究使君子杀家畜寄生虫的同时, 本文首次采用固相微萃取技术对使君子油中挥发性成分进行气相色谱-质谱 (GC-MS) 联用技术分析。

1 材料与方 法

1.1 材料

中草药使君子在云南省各地均有分布, 所研究的中药来源于云南省西双版纳州, 经云南农业大学

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中兽医实验室崔汝正副教授鉴定为使君子科植物使君子 *Quisqualis indica* L. 的干燥成熟果实。

1.2 方法

1.2.1 仪器与条件

气相色谱-质谱仪: Agilent technologies 6890N/5973N。色谱柱: HP-5 毛细管石英柱 (30 m × 0.25 mm × 0.25 μm) 弹性石英毛细管柱。载气 He; 进样口温度 250 °C; 接口温度 280 °C; 恒定柱流量 1 mL/min。分流比 30:1, 进样量: 2 μL。采用升温程序: 50 °C (1 min) → 180 °C (5 °C/min) → 260 °C (15 °C/min, 15 min)。

1.2.2 萃取提取与 GC-MS 分析

采用醇提和乙酸乙酯萃取使君子仁油, 采用 85 μm 固相微萃取膜, 在温度 60 °C 条件下进行顶空萃取 10 min; 然后在 250 °C 解吸附 1 min, 再进行 GC-MS 分析, 重复两次。质谱经计算机检索, 并核对标准图谱, 最后用面积归一化法测出各成分的相对含量。

2 结果与讨论

2.1 利用 GC-MS 联用仪对使君子仁油中挥发性成分分析的总离子流图见图 1

从使君子仁油中共检出挥发性成分 52 种, 鉴定出 29 种化合物, 其中蚁酸、乙酸、柠檬烯、甲苯的含量较高, 分别为 1.65%、6.51%、2.41%、2.75%, 在上述条件下挥发性成分及相对含量见表 1。

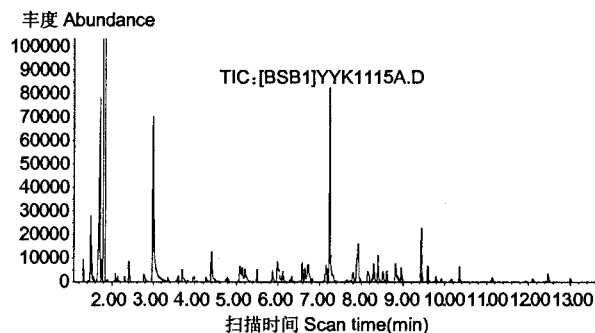


图 1 使君子仁油中精油成分 GC-MS 分析的总离子流图
Fig. 1 Total ion beam drawing of GC-MS analysis of the volatile components from *Fructus quisqualis* kernel oil

表 1 使君子仁精油成分的 GC-MS 分析结果

Table 1 The result of GC-MS analysis of the volatile components from *Fructus quisqualis* kernel oil

峰号 Peak No.	化合物名称 Compound	分子式 Molecular formula	分子量 M	相对含量 (%) Relative content
1	蚁酸 Formic acid	CH ₂ O ₂	46	1.65
2	二氯甲烷 Methylene chloride	CH ₂ Cl ₂	84	0.31
3	乙酸 Acetic acid	C ₂ H ₄ O ₂	60	6.51
4	己烷 Hexane	C ₆ H ₁₂	84	0.43
5	苯 Benzene	C ₆ H ₆	78	0.46
6	庚烷 Heptane	C ₇ H ₁₆	100	0.28
7	丙酸乙酯 Propanoic acid, ethyl ester	C ₅ H ₁₀ O ₂	126	0.48
8	吡啶 Pyridine	C ₅ H ₅ N	79	0.30
9	甲苯 Toluene	C ₇ H ₈	92	2.75
10	N,N-二甲基吡啶 4-Pyridinamine	C ₇ H ₁₀ N ₂	122	0.22
11	2-甲基丁酸 2-Methyl-butanoic acid	C ₅ H ₁₀ O ₂	102	0.20
12	1,2-二甲基苯 1,2-Dimethyl-benzene	C ₈ H ₁₀	106	0.42
13	α-蒎烯 α-Pinene	C ₁₀ H ₁₆	136	0.12
14	1-乙基-2-甲基苯 1-Ethyl-2-methyl-benzene	C ₉ H ₁₂	120	0.34
15	1,3,5-三甲基苯 1,3,5-Trimethylbenzene	C ₉ H ₁₂	120	0.33
16	三甲基胡椒嗪 Trimethyl-pyrazine	C ₇ H ₁₀ N ₂	122	0.42
17	4-乙基-1,2-二甲基苯 4-Ethyl-1,2-dimethyl-benzene	C ₁₀ H ₁₄	134	0.35
18	D-柠檬烯 D-Limonene	C ₁₀ H ₁₆	136	2.41
19	1-乙基-3,5-二甲基苯 1-Ethyl-3,5-dimethyl-benzene	C ₁₀ H ₁₄	143	0.31
20	十一烷 Undecane	C ₁₁ H ₂₄	132	0.37
21	2-壬烯-1-醇 2-Nonen-1-ol	C ₉ H ₁₈ O	142	0.28

22	苯乙醇 Phenylethyl Alcohol	C ₇ H ₈ O	108	0.28
23	1,2,4,5-四甲基苯 1,2,4,5-Tetramethyl-benzene	C ₁₀ H ₁₄	122	0.26
24	樟脑 Camphor	C ₁₀ H ₁₆ O	152	0.68
25	5-甲基-2-异丙基环己酮 5-Methyl-2-1-methyl-cyclohexanone	C ₉ H ₁₆ O	140	0.34
26	5-甲基-2-异丙基环己醇 5-Methyl-2-1-methyl-cyclohexanol	C ₉ H ₁₈ O	142	0.08
27	十二烷 Dodecane	C ₁₂ H ₂₆	170	0.45
28	二十八烷 Octacosane	C ₂₈ H ₅₈	394	0.13
29	新烟碱 DL-Anabesine	C ₁₀ H ₁₄ N ₂	162	0.12

分析数据表明,使君子仁油中挥发性成分主要以蚁酸、乙酸、柠檬烯、甲苯为主,其它组分有甲苯及衍生物如1,2-二甲基苯,1,3,5-三甲基苯;烷萜类如庚烷、十一烷、二十八烷、十六烷等。大多数化合物为有毒和具刺激性物质,使君子仁用药时产生中毒可能与这些成分有关。因此,为保证用药的安全性,在直接食用使君子种仁驱虫时必须熟食,禁止生食,避免发生中毒现象。

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