

桂郁金茎叶、生品与炮制品挥发油的比较分析

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[摘要] 目的:分析桂郁金茎叶、生品与炮制品的挥发油化学成分。方法:用水蒸气蒸馏法提取挥发油后采用气相色谱-质谱联用法(GC-MS)分析。结果:从桂郁金茎叶中分离得到 57 个化学成分,鉴定了 37 个;桂郁金生品中分离出 45 个化学成分,鉴定了 22 个;从桂郁金炮制品中分离出 44 个化学成分,鉴定了 32 个。结论:3 个样品挥发油的成分及含量均存在较大差异。

[关键词] 桂郁金;挥发油;气相色谱-质谱

[中图分类号] R284.1 [文献标识码] A [文章编号] 1005-9903(2011)21-0107-06

Comparative Analysis of Volatile Oils in Stems and Leaves ,Root Tubers and Its Processed Products of *Curcuma kwangsiensis*

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[Abstract] **Objective:** To analyze constituents in the volatile oils extracted from stems and leaves ,root tubers and its processed products of *Curcuma kwangsiensis*. **Method:** Volatile oils of *C. kwangsiensis* were extracted through steam distillation ,and the constituents were separated and identified by using GC-MS. **Result:** Thirty-seven chemical components were determined in volatile oil from stems and leaves of *curcuma kwangsiensis* ,22 chemical components were determined in volatile oil from root tubers of *C. kwangsiensis* and 32 chemical components were determined in volatile oil from its processed products. **Conclusion:** Chemical components in volatile oils were different in three samples.

[Key words] *Curcuma kwangsiensis*; volatile oil; GC-MS

桂郁金为姜科姜黄属植物广西莪术 *Curcuma kwangsiensis* S. G. Lee et C. F. Liang 的干燥块根,其性味辛、苦、寒,归肝、心、肺经,具有活血止痛、行气解郁、清心凉血、利胆退黄等功效,用于胸胁刺痛、胸痹心痛、经闭痛经、乳房胀痛、热病神昏、癫痫发狂、血热吐衄、黄疸尿赤等症^[1]。姜科姜黄属植物均富含挥发油,现代研究表明,挥发油具有抗肿瘤、抗腹

泻、抗炎、抗旱孕等药理作用。目前对广西莪术挥发油的研究多集中在根茎^[2-3](中药材莪术),对茎叶和块根(中药材桂郁金)目前没有挥发油方面的研究报道。本文采用气质联用方法对桂郁金茎叶、生品与炮制品中的挥发油成分进行了系统分析,并比较了它们所含挥发油成分的差异。

1 材料

1.1 药材 桂郁金茎叶、生品与炮制品均于 2010 年 12 月采购自广西钦州市灵山县陆屋镇,其中桂郁金茎叶为桂郁金干燥的地上部位,桂郁金生品为为自然阴干的块根,桂郁金炮制品为水煮至透心再烘干的块根。样品经广西中医学院何报作教授鉴定为广西莪术 *C. kwangsiensis* 的茎叶、干燥的块根生品和炮制品。

1.2 仪器和试剂 气相色谱-质谱联用仪 HP6890/

[收稿日期] 20110503(002)

[基金项目] 广西科技厅应用基础研究专项(桂科基 0832006)

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HP5973(美国惠普公司);色谱柱为 HP-5MS (0.25 $\mu\text{m} \times 0.25 \text{ mm} \times 30 \text{ m}$) 弹性石英毛细管柱;挥发油提取器;LG16-W 离心机(北京医用离心机厂),无水硫酸钠(分析纯,上海化学试剂公司)。

2 方法与结果

2.1 挥发油提取 分别称取桂郁金茎叶、生品与炮制品各 50 g,用挥发油提取器按常规方法水蒸气蒸馏提取至挥发油量不再增加,得到有浓郁香味的浅黄色油状液体,得率分别为 0.6% 0.4% 0.2%。所得挥发油分别加 1 mL 乙酸乙酯溶解,置 1.5 mL 离心管,加适量无水硫酸钠,离心(10 000 $\text{r} \cdot \text{min}^{-1}$) 10 min,备用。

2.2 气相色谱分析条件 HP-5MS(0.25 $\text{mm} \times 0.25 \mu\text{m} \times 30 \text{ m}$) 弹性石英毛细管柱;载气为氮气,流速为 1 $\text{mL} \cdot \text{min}^{-1}$,进样量 0.5 μL ,分流比 50:1,气化室温度 250 $^{\circ}\text{C}$,离子流温度 230 $^{\circ}\text{C}$,电离方式 EI,电子能量 70 eV,扫描质量范围为 15 ~ 550。谱图采用 NIST98 和 NIST05 进行检索。桂郁金茎叶挥发油的升温程序为起始温度 70 $^{\circ}\text{C}$,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 160 $^{\circ}\text{C}$,保持 1 min,以 0.5 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 170 $^{\circ}\text{C}$,以 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 180 $^{\circ}\text{C}$ 。桂郁金生品挥发油

的升温程序为起始温度 70 $^{\circ}\text{C}$,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 160 $^{\circ}\text{C}$,保持 1 min,以 0.5 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 165 $^{\circ}\text{C}$,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 180 $^{\circ}\text{C}$ 。桂郁金炮制品挥发油的升温程序为:起始温度 70 $^{\circ}\text{C}$,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 130 $^{\circ}\text{C}$,保持 1 min,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 160 $^{\circ}\text{C}$,保持 1 min,以 0.5 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 165 $^{\circ}\text{C}$,以 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ 升温至 180 $^{\circ}\text{C}$ 。

2.3 结果 桂郁金茎叶共检出 57 个成分,已鉴定成分 37 个,占挥发油总量的 69.78%,其中含量最高的 3 个化合物为(*E,E*)-4-(1-甲乙烯基)-3,7-环壬二烯酮(7.09%)、莜术呋喃烯(6.96%)、石竹烯氧化物(4.73%);桂郁生品共检出 45 个成分,已鉴定成分 22 个,占挥发油总量的 68.31%,其中含量最高的 3 个化合物为莜术呋喃烯(25.23%)、吉马酮(11.13%)、 β -榄香烯(6.53%);桂郁金炮制品共检出 44 个成分,已鉴定成分 32 个,占挥发油总量的 79.06%,其中含量最高的 3 个化合物为吉马酮(20.68%)、香橙烯(9.05%)、莜术呋喃烯(7.27%)。各样品挥发油成分差异较大,相同成分相对含量差异也较大。各样品挥发油中已鉴定成分及共有成分见表 1~4。

表 1 桂郁金茎叶挥发油化学成分分析

No.	t_R / min	桂郁金茎叶挥发油所含化学成分	分子式	相对含量 / %
1	3.48	(1 <i>S</i>)-6- β -dimethyl-2-methylene-bicyclo[3.1.1]heptane (1 <i>S</i>)-(-)- β -蒎烯	$\text{C}_{10}\text{H}_{16}$	0.28
2	3.89	eucalyptol 桉叶素	$\text{C}_{10}\text{H}_{18}\text{O}$	0.87
3	4.40	3,7-Dimethyl-1- β -octadien-3-ol 芳樟醇	$\text{C}_{10}\text{H}_{18}\text{O}$	0.52
4	4.82	camphor 樟脑	$\text{C}_{10}\text{H}_{16}\text{O}$	2.81
5	5.00	isoborneol 异龙脑	$\text{C}_{10}\text{H}_{18}\text{O}$	3.61
6	5.25	α -terpineol (<i>p</i> -menth-1-en-8-ol) α -松油醇	$\text{C}_{10}\text{H}_{18}\text{O}$	0.82
7	5.57	cis-2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol 顺式-2-甲基-5-(1-甲乙烯基)-2-环乙烯醇-1	$\text{C}_{10}\text{H}_{16}\text{O}$	0.19
8	5.86	3,7-dimethyl-2- β -octadienal 柠檬醛	$\text{C}_{20}\text{H}_{32}\text{O}_2$	0.05
9	6.16	isobornyl acetate 乙酸异龙脑酯	$\text{C}_{12}\text{H}_{20}\text{O}_2$	0.33
10	6.80	(3 <i>R</i> -trans)-4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)-cyclohexene (3 <i>R</i> -反式)-4-甲基-4-乙烯基-3-(1-甲乙烯基)-1-(1-甲基乙基)-环己烯	$\text{C}_{15}\text{H}_{24}$	0.31
11	6.95	α -cubebene α -荜澄茄油萜	$\text{C}_{15}\text{H}_{24}$	0.06
12	7.31	copaene 胡椒烯	$\text{C}_{15}\text{H}_{24}$	0.47
13	7.43	[1 <i>S</i> -(1 <i>α</i> 2 <i>β</i> 4 <i>β</i>)]-1-ethenyl-1-methyl-2- β -bis(1-methylethenyl)-cyclohexane β -榄香烯	$\text{C}_{15}\text{H}_{24}$	3.82
14	7.85	caryophyllene 石竹烯	$\text{C}_{14}\text{H}_{22}$	2.71
15	8.20	(1 <i>α</i> ,4 <i>$\alpha\alpha$</i> ,8 <i>$\alpha\alpha$</i>)-1,2,3,4,4 <i>α</i> ,5,6,8 <i>α</i> -octahydro-7-methyl-4-methylene-1-(1-methylethyl)-naphthalene (1 <i>α</i> 4 <i>$\alpha\alpha$</i> 8 <i>$\alpha\alpha$</i>)-1,2,3,4,4 <i>α</i> ,5,6,8 <i>α</i> -八氢-7-甲基-4-亚甲基-1-(1-甲基乙基)-萜	$\text{C}_{15}\text{H}_{24}$	0.72

续表 1

No.	t_R / min	化学成分	分子式	相对含量 / %
16	8.31	<i>cis</i> -1,1,4,8-tetramethyl-4,7,10-cycloundecatriene 顺式-1,1,4,8-四甲基-4,7,10-环十一三烯	$C_{15}H_{24}$	2.61
17	8.58	(4 <i>aR</i> - <i>trans</i>)-decahydro-4 <i>a</i> -methyl-1-methylene-7-(1-methylethylidene)-naphthalene (4 <i>aR</i> -反式)-十氢-4 <i>a</i> -甲基-1-亚甲基-7-(1-甲基亚乙基)-萘	$C_{15}H_{24}$	1.21
18	8.68	germacrene D 大根香叶烯 D	$C_{15}H_{24}$	1.23
19	8.80	<i>trans</i> -6-ethenyl-4,5,6,7-tetrahydro-3,6-dimethyl-5-isopropenyl-benzofuran 莪术呋喃烯	$C_{15}H_{20}O$	6.96
20	8.95	[2 <i>R</i> -(2 <i>α</i> ,4 <i>αα</i> ,8 <i>αβ</i>)]-1,2,3,4,4 <i>a</i> ,5,6,8 <i>a</i> -Octahydro-4 <i>a</i> ,8-dimethyl-2-(1-methylethenyl)-naphthalene [2 <i>R</i> -(2 <i>α</i> ,4 <i>αα</i> ,8 <i>αβ</i>)]-1,2,3,4,4 <i>a</i> ,5,6,8 <i>a</i> -八氢-4 <i>a</i> ,8-二甲基-2-(1-甲乙烯基)-萘	$C_{15}H_{24}$	4.36
21	9.29	(1 <i>S</i> - <i>cis</i>)-1,2,3,5,6,8 <i>a</i> -hexahydro-4,7-dimethyl-1-(1-methylethyl)-naphthalene (1 <i>S</i> -顺式)-1,2,3,5,6,8 <i>a</i> -六氢-4,7-双甲基-1-(1-甲基乙基)-萘	$C_{15}H_{24}$	2.40
22	9.77	(4 <i>aR</i> - <i>trans</i>)-1,2,3,4,4 <i>a</i> ,5,6,8 <i>a</i> -octahydro-4 <i>a</i> ,8-dimethyl-2-(1-methylethylidene)-naphthalene (4 <i>aR</i> -反式)-1,2,3,4,4 <i>a</i> ,5,6,8 <i>a</i> -八氢-4 <i>a</i> ,8-二甲基-2-(1-甲基亚乙基)-萘	$C_{15}H_{24}$	1.29
23	10.04	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-cyclohexane 1-甲基-1-乙烯基-2-(1-甲乙烯基)-4-(1-甲基亚乙基)环己烷	$C_{15}H_{24}$	2.15
24	10.34	1,7,7-trimethyl-2-vinylbicyclo[2.2.1]hept-2-ene 1,7,7-三甲基-2-乙烯基双环[2.2.1]庚烯-2	$C_{12}H_{18}$	1.17
25	10.45	caryophyllene oxide 石竹烯氧化物	$C_{15}H_{24}O$	4.73
26	10.69	γ -elemene γ -榄香烯	$C_{15}H_{24}$	3.51
27	11.19	[1 <i>aR</i> -(1 <i>αα</i> ,7 <i>α</i> ,7 <i>αβ</i> ,7 <i>bα</i>)]-1 <i>a</i> ,2,3,5,6,7,7 <i>a</i> ,7 <i>b</i> -octahydro-1,1,4,7-tetramethyl-1 <i>H</i> -cycloprop[<i>e</i>]azulene [1 <i>aR</i> -(1 <i>αα</i> ,7 <i>α</i> ,7 <i>αβ</i> ,7 <i>bα</i>)]-1 <i>a</i> ,2,3,5,6,7,7 <i>a</i> ,7 <i>b</i> -八氢-1,1,4,7-四甲基-1 <i>H</i> -环丙烷[<i>e</i>]甘菊环烃	$C_{15}H_{24}$	1.05
28	11.52	(1 <i>S</i> - <i>cis</i>)-1,2,3,4,5,6,7,8-Octahydro-1,4-dimethyl-7-(1-methylethylidene)-azulene 愈创木烯	$C_{15}H_{24}$	1.99
29	11.71	2-isopropyl-5-methyl-9-methylen-bicyclo[4.4.0]dec-1-ene 5-甲基-9-亚甲基-2-异丙基双环[4.4.0]十烯-1	$C_{15}H_{24}$	2.49
30	12.29	(<i>E</i> , <i>E</i>)-3,7-dimethyl-10-(1-methylethylidene)-3,7-cyclodecadien-1-one 吉马酮	$C_{15}H_{22}O$	1.16
31	12.60	(-)-spathulenol (-)-匙叶桉油烯醇	$C_{15}H_{24}O$	0.39
32	13.14	(<i>E</i> , <i>E</i>)-10-(1-methylethenyl)-3,7-cyclodecadien-1-one (<i>E</i> , <i>E</i>)-10-(1-甲乙烯基)-3,7-环奎二烯酮-1	$C_{13}H_{18}O$	7.09
33	13.59	6,10-dimethyl-3-(1-methylethyl)-6-cyclodecene-1,4-dione 莪二酮	$C_{15}H_{24}O_2$	3.65
34	13.93	6-isopropenyl-4,8 <i>a</i> -dimethyl-1,2,3,5,6,7,8,8 <i>a</i> -octahydro-naphthalen-2-ol 6-异丙烯基-4,8 <i>a</i> -二甲基-1,2,3,5,6,7,8,8 <i>a</i> -八氢-萘醇-2	$C_{15}H_{24}O$	1.89
35	18.95	bis(2-methylpropyl) ester-1,2-benzenedicarboxylic acid 邻苯二甲酸二异丁酯	$C_{16}H_{20}O_4$	0.27
36	19.31	6,10,14-Trimethyl-2-pentadecanone 植酮	$C_{18}H_{36}O$	0.47
37	22.71	(<i>E</i> , <i>E</i>)-6,10,14-trimethyl-5,9,13-pentadecatrien-2-one 法尼基丙酮	$C_{18}H_{30}O$	0.14

表 2 桂郁金生品挥发油化学成分分析结果

序号	t_R / min	桂郁金生品挥发油所含化学成分	分子式	相对含量 / %
1	3.25	camphene 莰烯	$C_{10}H_{16}$	0.28
2	3.46	β -pinene β -蒎烯	$C_{10}H_{16}$	0.40
3	3.73	3-carene 3-萜烯	$C_{10}H_{16}$	0.35
4	4.38	(+)-4-carene (+)-4-萜烯	$C_{10}H_{16}$	0.30
5	4.80	camphor 樟脑	$C_{10}H_{16}O$	1.23
6	4.98	borneol 龙脑	$C_{10}H_{16}O$	0.90
7	6.14	(1S-endo)-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol-acetate 左旋乙酸冰片酯	$C_{12}H_{20}O_2$	0.91
8	6.80	(3R-trans)-4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)-cyclohexene(3R-反式)-4-甲基-4-乙烯基-3-(1-甲基烯基)-1-(1-甲基烯基)-环己烯	$C_{15}H_{24}$	0.79
9	7.43	[1S-(1 α ,2 β ,4 β)]-1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-cyclohexane β -榄香烯	$C_{15}H_{24}$	6.53
10	7.84	caryophyllene 石竹烯	$C_{14}H_{22}$	2.05
11	8.29	α -Caryophyllene α -石竹烯	$C_{14}H_{22}$	1.50
12	8.81	trans-6-ethenyl-4,5,6,7-tetrahydro-3,6-dimethyl-5-isopropenyl-benzofuran 莜术呋喃烯	$C_{15}H_{20}O$	25.23
13	8.95	(4aR-trans)-decahydro-4a-methyl-1-methylene-7-(1-methylethylidene)-naphthalene(4aR-反式)-10-氢-4a-甲基-1-亚甲基-7-(1-甲基亚乙基)-萘	$C_{15}H_{24}$	2.01
14	10.04	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-cyclohexane 1-甲基-1-乙烯基-2-(1-甲基烯基)-4-(1-甲基亚乙基)-环己烷	$C_{15}H_{24}$	3.47
15	10.65	β -elemenone β -榄香烯酮	$C_{15}H_{22}O$	2.97
16	11.49	[1S-(1 α ,7 α ,8 α)]-1,2,3,5,6,7,8,8a-Octahydro-1,8a-dimethyl-7-(1-methylethenyl)-naphthalene 佛术烯	$C_{15}H_{24}$	1.15
17	12.00	β -humulene β -蛇麻烯	$C_{14}H_{22}$	2.22
18	12.13	[1S-(1 α ,7 α ,8 α)]-1,2,3,5,6,7,8,8a-Octahydro-1,4-dimethyl-7-(1-methylethenyl)-azulene [1S-(1 α ,7 α ,8 α)]-1,2,3,5,6,7,8,8a-八氢-1,4-双甲基-7-(1-甲基烯基)-甘菊环烯	$C_{15}H_{24}$	1.58
19	12.41	isoaromadendrene epoxide 异香橙烯环氧化物	$C_{15}H_{24}O$	1.27
20	13.13	(E,E)-3,7-dimethyl-10-(1-methylethylidene)-3,7-cyclodecadien-1-one 吉马酮	$C_{15}H_{22}O$	11.13
21	13.49	neocurdiol 新郁金二酮	$C_{15}H_{24}O_2$	0.80
22	13.69	6-isopropenyl-4,8a-dimethyl-1,2,3,5,6,7,8,8a-octahydro-naphthalen-2-ol 6-异丙烯基-4,8a-双甲基-1,2,3,5,6,7,8,8a-八氢-萘醇-2	$C_{15}H_{24}O$	1.24

表 3 桂郁金炮制品挥发油化学成分分析

序号	t_R / min	桂郁金生品挥发油所含化学成分	分子式	相对含量 / %
1	3.20	2-methyl-5-(1-methylethyl)-bicyclo[3.1.0]hex-2-ene 2-甲基-5-(1-甲基乙基)-二环[3.1.0]六烯-2	$C_{10}H_{16}$	0.22
2	3.28	(1R)- α -pinene (1R)- α -蒎烯	$C_{10}H_{16}$	1.86
3	3.42	camphene 莰烯	$C_{10}H_{16}$	4.62
4	3.65	β -pinene β -蒎烯	$C_{10}H_{16}$	2.39
5	4.02	1-methyl-2-(1-methylethyl)-benzene 邻异丙基甲苯	$C_{10}H_{14}$	0.23
6	4.06	D-limonene 右旋萜二烯	$C_{10}H_{16}$	1.47
7	4.11	eucalyptol 桉叶素	$C_{10}H_{18}O$	5.21
8	4.69	3,7-dimethyl-1,6-octadien-3-ol 芳樟醇	$C_{10}H_{18}O$	0.19
9	5.38	camphor 樟脑	$C_{10}H_{16}O$	4.46

续表 3

No.	t_R / min	桂郁金生品挥发油所含化学成分	分子式	相对含量 / %
10	5.51	borneol 龙脑	$C_{10}H_{16}O$	2.56
11	5.60	isoborneol 异龙脑	$C_{10}H_{18}O$	0.70
12	5.71	(<i>R</i>)-4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol (-)-4-萜品醇	$C_{10}H_{18}O$	0.24
13	5.85	α -terpineol (<i>p</i> -menth-1-en-8-ol) α -松油醇	$C_{10}H_{18}O$	0.56
14	6.95	(1 <i>S</i> -endo)-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol-acetate 左旋乙酸冰片酯	$C_{12}H_{20}O_2$	1.75
15	7.56	(3 <i>R</i> -trans)-4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)-cyclohexene (3 <i>R</i> -反式)-4-甲基-4-乙基-3-(1-甲乙烯基)-1-(1-甲基乙基)-环己烯	$C_{15}H_{24}$	2.30
16	8.19	[1 <i>S</i> -(1 α ,2 β ,4 β)]-1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-cyclohexane β -榄香烯	$C_{15}H_{24}$	0.22
17	8.31	[1 <i>R</i> -(1 α ,4 α ,7 α ,7 β ,7 α)]-decahydro-1,1,7-trimethyl-4-methylene-1 <i>H</i> -cycloprop[<i>e</i>]azulene 香橙烯	$C_{15}H_{24}$	9.05
18	8.80	caryophyllene 石竹烯	$C_{14}H_{22}$	0.81
19	8.90	γ -elemene γ -榄香烯	$C_{15}H_{24}$	0.42
20	9.22	β -panasinsene β -人参烯		0.29
21	9.35	α -caryophyllene α -石竹烯	$C_{14}H_{22}$	0.61
22	9.66	[1 <i>S</i> -(1 α ,4 α ,7 α)]-1,2,3,4,5,6,7,8-octahydro-1,4,9,9-tetramethyl-4,7-methanoazulene [1 <i>S</i> -(1 α ,4 α ,7 α)]-1,2,3,4,5,6,7,8-八氢-1,4,9,9-四甲基-4,7-亚甲基奥	$C_{15}H_{24}$	0.24
23	9.81	[<i>s</i> -(<i>E</i> , <i>E</i>)]-1-methyl-5-methylene-8-(1-methylethyl)-1,6-cyclodecadiene [<i>s</i> -(<i>E</i> , <i>E</i>)]-1-甲基-亚甲基-8-(1-甲基乙基)-1,6-环癸二烯	$C_{15}H_{24}$	1.59
24	9.93	(4 <i>aR</i> -trans)-decahydro-4 <i>a</i> -methyl-1-methylene-7-(1-methylethenyl)-naphthalene (4 <i>aR</i> -反式)-十氢-4 <i>a</i> -甲基-1-亚甲基-7-(1-甲基亚乙基)-萘	$C_{15}H_{24}$	0.83
25	10.05	trans-6-ethenyl-4,5,6,7-tetrahydro-3,6-dimethyl-5-isopropenyl-benzofuran 莪术呋喃烯	$C_{15}H_{20}O$	7.27
26	11.09	[1 <i>R</i> -(1 α ,3 α ,4 β)]-4-ethenyl- α , α ,4-trimethyl-3-(1-methylethenyl)-cyclohexanemethanol [1 <i>R</i> -(1 α ,3 α ,4 β)]-4-乙烯基- α , α ,4-三甲基-3-(1-甲乙烯基)-环己甲醇	$C_{15}H_{26}O$	0.23
27	11.43	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-cyclohexane 1-甲基-1-乙烯基-2-(1-甲乙烯基)-4-(1-甲基亚乙基)-环己烷	$C_{15}H_{24}$	1.67
28	12.11	[1 <i>aR</i> -(1 α ,7 α ,7 α ,7 β)]-1 <i>a</i> ,2,3,5,6,7,7 <i>a</i> ,7 <i>b</i> -octahydro-1,1,7,7 <i>a</i> -tetramethyl-1 <i>H</i> -cyclopropa[<i>a</i>]naphthalene, [1 <i>aR</i> -(1 α ,7 α ,7 α ,7 β)]-1 <i>a</i> ,2,3,5,6,7,7 <i>a</i> ,7 <i>b</i> -八氢-1,1,7,7 <i>a</i> -四甲基-1 <i>H</i> -环丙烷[<i>a</i>]萘	$C_{15}H_{24}$	2.11
29	12.25	[2 <i>R</i> -(2 α ,4 α ,8 α)]-decahydro- α , α ,4 <i>a</i> -trimethyl-8-methylene-2-naphthalenemethanol α -桉叶醇	$C_{15}H_{26}O$	1.59
30	12.49	β -elemenone β -榄香烯酮	$C_{15}H_{22}O$	1.90
31	14.24	[1 <i>S</i> -(1 α ,3 α ,4 α ,8 α)]-decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene 长叶烯	$C_{15}H_{24}$	0.79
32	15.63	(<i>E</i> , <i>E</i>)-3,7-dimethyl-10-(1-methylethylidene)-3,7-cyclodecadien-1-one 吉马酮	$C_{15}H_{22}O$	20.68

3 讨论

桂郁金茎叶和块根之间的挥发油差异较大。桂郁金每年都是在冬季茎叶枯萎后采挖地下部位,所以桂郁金产地会遗弃大量废弃茎叶。因茎叶含有丰富的挥发油,具有刺激气味不适合作为动物饲料和生活燃料,故通常是用燃烧的方法将其焚毁,这样就

造成了空气污染和资源浪费。本研究表明桂郁金茎叶总挥发油含量较高(0.6%),其中樟脑、 β -榄香烯、莪术呋喃烯、石竹烯、石竹烯氧化物、异龙脑等化学成分含量较高,可考虑将茎叶“变废为宝”,将其挥发油开发用于日化产品。

表 4 3 种样品挥发油中含有相同化学成分

No.	化学成分	相对含量 / %		
		桂郁金茎叶	桂郁金生品	桂郁金炮制品
1	camphor 樟脑	2. 81	1. 23	4. 46
2	(3 <i>R</i> -trans) -4-ethenyl-4-methyl-3-(1-methylethenyl) -1-(1-methylethyl) -cyclohexene (3 <i>R</i> -反式) -4-甲基-4-乙烯基-3-(1-甲乙烯基) -1-(1-甲基乙基) -环己烯	0. 31	0. 79	2. 30
3	[1 <i>S</i> -(1 <i>α</i> 2 <i>β</i> 4 <i>β</i>)]-1-ethenyl-1-methyl-2-4-bis(1-methylethenyl) -cyclohexane <i>β</i> -榄香烯	3. 82	6. 53	0. 22
4	(4 <i>aR</i> -trans) -decahydro-4 <i>a</i> -methyl-1-methylene-7-(1-methylethylidene) -naphthalene (4 <i>aR</i> -反式) -十氢-4 <i>a</i> -甲基-1-亚甲基-7-(1-甲基亚乙基) -萘	1. 21	2. 01	0. 83
5	trans-6-ethenyl-4, 5, 6, 7-tetrahydro-3, 6-dimethyl-5-isopropenyl-benzofuran 莪术呋喃烯	6. 96	25. 23	7. 27
6	1-ethenyl-1-methyl-2-(1-methylethenyl) -4-(1-methylethylidene) -cyclohexane 1-甲基-1-乙烯基-2-(1-甲乙烯基) -4-(1-甲基亚乙基) 环己烷	2. 15	3. 47	1. 67
7	(<i>E, E</i>)-3, 7-dimethyl-10-(1-methylethylidene) -3, 7-cyclodecadien-1-one 吉马酮	1. 16	11. 13	20. 68
8	caryophyllene 石竹烯	2. 71	2. 05	0. 81
9	6-isopropenyl-4, 8 <i>a</i> -dimethyl-1, 2, 3, 5, 6, 7, 8, 8 <i>a</i> -octahydro-naphthalen-2-ol 6-异丙烯基-4, 8 <i>a</i> -双甲基-1, 2, 3, 5, 6, 7, 8, 8 <i>a</i> -八氢-萘醇-2	1. 89	1. 24	-
10	eucalyptol 桉叶素	0. 87	-	5. 21
11	3, 7-dimethyl-1, 6-octadien-3-ol 芳樟醇	0. 52	-	0. 19
12	isoborneol 异龙脑	3. 61	-	0. 70
13	<i>α</i> -terpineol (<i>p</i> -menth-1-en-8-ol) <i>α</i> -松油醇	0. 82	-	0. 56
14	<i>γ</i> -elemene <i>γ</i> -榄香烯	3. 51	-	0. 42
15	camphene 茨烯	-	0. 28	4. 62
16	<i>β</i> -pinene <i>β</i> -蒎烯	-	0. 40	2. 39
17	borneol 龙脑	-	0. 90	2. 56
18	(1 <i>S</i> -endo) -1, 7, 7-trimethyl-bicyclo[2. 2. 1]heptan-2-ol-acetate 左旋乙酸冰片酯	-	0. 91	1. 75
19	<i>α</i> -caryophyllene <i>α</i> -石竹烯	-	1. 50	0. 61
20	<i>β</i> -elemenone <i>β</i> -榄香烯酮	-	2. 97	1. 90

桂郁金生品和炮制品的挥发油差异较大,可见不同的加工方法对挥发油化学成分有很大的影响。至于挥发油之间的差异是否会影响药理作用,还有待进一步研究阐明。

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