

## 药对川芎 羌活与其单味药挥发油共有组分的分析

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**摘要:** 利用气相色谱-质谱法分离检测药对川芎 羌活、单味药川芎和羌活的挥发油成分,再采用交互移动窗口因子分析法对药对川芎 羌活与单味药川芎 羌活挥发油成分的共有组分进行了分析,并采用总体积分法定量。药对川芎 羌活、川芎和羌活的挥发油分别定性了 79、65和 71个成分,占总含量的 95.39%、83.69%和 96.04%。药对川芎 羌活分别与川芎 羌活的共有组分为 45和 63个,三者共有的挥发油组分为 31个。药对川芎 羌活挥发油种类基本为两个单味药的加和,挥发油组分主要来自羌活。

**关键词:** 药对川芎 羌活; 气相色谱-质谱; 交互移动窗口因子分析法; 挥发油; 共有组分

中图分类号: O657; R917 文献标识码: A 文章编号: 0513 - 4870(2007)10 - 1082 - 05

## Analysis of common volatile constituents in herbal pair *Chuanxiong Rhizome-Notoperygium Root and its single herb*

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**Abstract:** Analysis of common volatile constituents in herbal pair (HP) *Chuanxiong Rhizome* (CXR) - *Notoperygium root* (NR) and its single herb was performed by the method of alternative moving window factor analysis (AMWFA). In total, 65, 71, and 79 volatile chemical components in volatile oil of CXR, NR, and HP CXR-NR were separately determined qualitatively and quantitatively, accounting for 83.69%, 96.04% and 95.39% total contents of volatile oil of CXR, NR, and HP CXR-NR respectively. Analysis by the method of AMWFA indicates that there are 45 common volatile constituents in HP CXR-NR and single herb CXR, and 63 common volatile constituents in HP CXR-NR and single herb NR and 31 common volatile constituents among these three systems. The experimental results also show that the number of volatile chemical components in HP CXR-NR is almost equal to the sum of the number in the two single herbs, and volatile chemical components in HP CXR-NR are mainly from single herb NR.

**Key words:** herbal pair *Chuanxiong Rhizome-Notoperygium Root*; GC-MS; alternative moving window factor analysis; volatile oil; common constituent

药对是中药配伍的基本单位,是复方配伍中最基本、最常用的形式<sup>[1]</sup>。两个单味药配伍,或增强药物功效,或减低药物毒副作用。单味药配伍后,其化学成分有何变化及其与单味药的关系<sup>[2]</sup>,即药对化学,是复方化学的核心,值得深入研究。

川芎 羌活为常用的辛温解表药对<sup>[1]</sup>。川芎辛温香窜,可活血行气,祛风止痛;羌活散寒解表,祛风胜湿,除痹止痛<sup>[3]</sup>。川芎与羌活伍用,临床应用广泛。挥发油是解表药对的药效物质之一<sup>[4]</sup>,但药对川芎 羌活的挥发油成分尚未见报道。本文利用气相色谱-质谱(GC-MS)法分离检测药对川芎 羌活、单味药川芎和羌活的挥发油成分,然后采用交互移动窗口因子分析法(alternative moving window factor analysis, AMWFA)<sup>[5,6]</sup>对药对川芎 羌活与其单味药

收稿日期: 2007-03-23.

基金项目: 国家自然科学基金资助项目(20235020).

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川芎和羌活挥发油成分的共有组分进行了比较分析,再采用总体积分法对各个共有组分定量。

## 材料与方法

**仪器与药材** 日本岛津 QP2010型气相色谱仪-质谱仪。川芎、羌活均购自河南南阳药材公司,经湖南中医药研究院中药研究所袁晓清鉴定。

**药对挥发油的提取** 称取干燥的川芎 (*Chuanxiong Rhizome*, CXR)、羌活 (*Notopterygium Root*, NR) 各 100 g,混合,按中华人民共和国药典(2005版)挥发油提取法提取<sup>[7]</sup>。

**单味药挥发油的提取** 分别称取干燥的川芎和羌活各 100 g,按照上法提取。

**色谱条件** 色谱柱 OV-1 (30 m × 0.25 mm)。程序升温:起始温度 50 °C,以 2 °C · min<sup>-1</sup>升至 130 °C,再以 10 °C · min<sup>-1</sup>升至 230 °C,维持 20 min。载气: He; 流速 1.0 mL · min<sup>-1</sup>; 进口温度 250 °C,界面温度 280 °C。质谱条件: EI源电子能量 70 eV,离子源温度: 230 °C。倍增电压: 1.28 kV,扫描范围 20 ~ 600 amu;扫描速率: 3.8 scans · s<sup>-1</sup>,溶剂延迟 2 min。

**数据分析** 数据分析在 Pentium III 850 计算机上进行,程序用 Matlab 6.1 编写,所分辨的质谱在 NIST107 标准质谱库中检索。

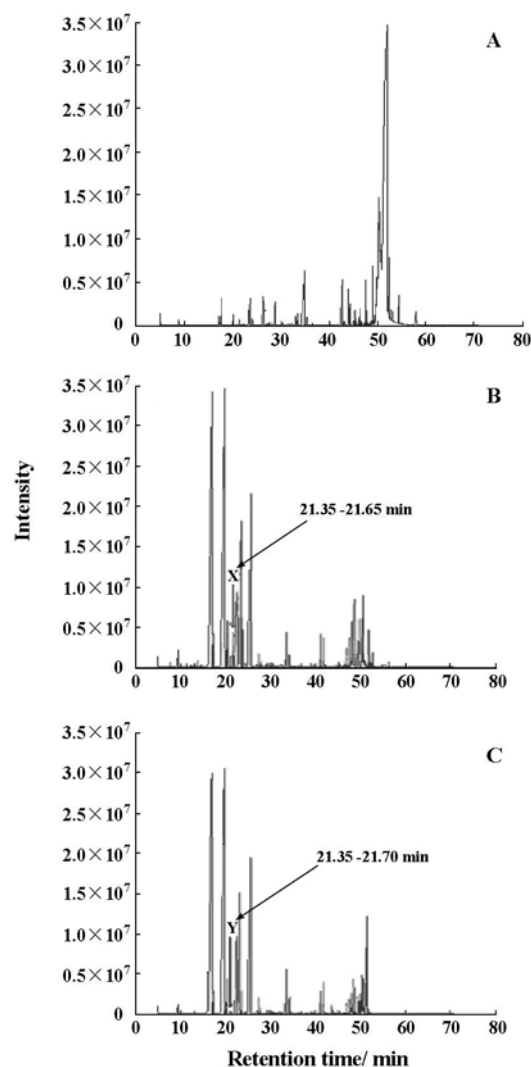
## 结果与讨论

### 1 AMWFA法对药对川芎 羌活与单味药羌活挥发油共有组分的比较分析

针对二维色谱-光谱矩阵数据进行解析的计量学方法,如渐进因子分析法 (evolving factor analysis, EFA)<sup>[8]</sup>,直观推导式演进特征投影法 (heuristic evolving latent projections, HELP)<sup>[9]</sup>,子窗口因子分析法 (subwindow factor analysis, SFA)<sup>[10]</sup>等,均存在组分色谱选择性信息不够的问题。作者最近建立的 AMWFA 是一种可对两个复杂体系之间进行快速比较的分析方法,是多组分光谱相关色谱法 (MSCC) 和子窗口因子分析法 (SFA) 的结合和延伸。它通过挖掘两个体系中的选择性信息,不仅可以获得不同样本间的共有组分数,还能同时得到各物质对应的光谱或质谱信息,是一种复杂体系解析和快速比较分析的强有力工具,其原理和分析方法见参考文献 [5, 6]。

图 1 中 A、B 和 C 分别是川芎、羌活和药对川芎 羌活挥发油成分 GC-MS 总离子流图 (TIC)。选

取羌活 TIC 中保留时间为 21.35 ~ 21.65 min 的 X 峰簇和药对川芎 羌活 TIC 中 21.35 ~ 21.70 min 的 Y 峰簇进行解析。



**Figure 1** TIC curves of volatile oils of *Chuanxiong Rhizome* (CXR, A), *Notopterygium Root* (NR, B) and herbal pair *Chuanxiong Rhizome-Notopterygium Root* (HP CXR-NR, C)

采用 MSCC 和 IP-MSCC (反投影多组分光谱相关色谱), 见图 2, 说明 X 和 Y 有两个共有组分。为进一步确定两个体系中的共有组分数, 采用 AMWFA 法进行共有秩分析。图 3 为共有秩分析的结果。该图中前两个的拟合值几乎为零, 从第 3 个开始逐渐增大, 说明 X 和 Y 包含两个共有组分。

获得了两个体系中的共有组分数后, 接着解析物质的纯质谱。按照 AMWFA 法, 在共有组分数为 1 的区域, 可以从其特征向量中获取对应的纯质谱。

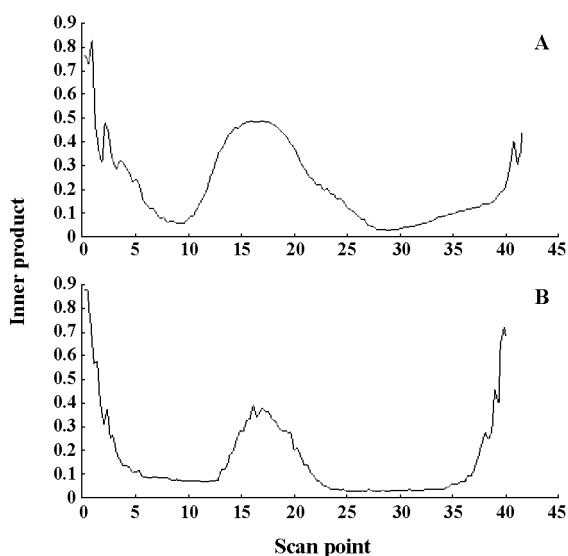


Figure 2 Results obtained by MSCC (A) and IP-MSCC (B) analysis

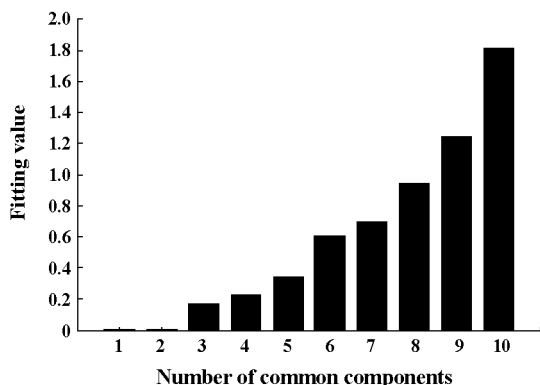


Figure 3 Results of common rank analysis

以 X 中的 5~40 区域为基矩阵,用移动窗口技术对 Y 矩阵中 5~40 区域进行扫描(移动窗口数为 2),

得到保留时间与共有组分数关系的共有组分秩图(图 4A)。在移动窗口扫描过程中,通过公式计算,得到各个时间点的质谱和相邻两点质谱的相似度。以相似度和保留时间作图,得到质谱自相关曲线(图 4B)。在共有组分秩图中,可获得两个共有组分数为 1 的区域(3~13, 24~38)。其对应的质谱自相关曲线也出现了两个平台,且相似度几乎为 1。可分别从这两个平台中的任意一点提取出共有组分的纯质谱,即组分 1 和组分 2 的质谱。解析出的质谱与 NIST107 库中的标准质谱比较,解析结果准确。通过解析,最后得到峰簇 X 和 Y 的色谱图, X 为一个三组分重叠形成的峰簇,而 Y 为一个两组分重叠在一起的峰簇。

### 2 挥发油组分的定量分析

对解析后的所有色谱采用总体积分法积分,可得到各个组分的定量分析结果,川芎、羌活和药对川芎、羌活鉴定的化合物数目分别为 65、71 和 79 个,定性组分含量分别占川芎、羌活和药对川芎、羌活挥发油总含量的 83.69%、96.04% 和 95.39%。三者挥发油的主要化学成分见表 1。

### 3 药对川芎、羌活与单味药羌活、羌活挥发油组分的比较

由表 1 可见,川芎挥发油主要组分为藁本内酯(57.71%)、丁烯基苯酞(5.42%)、松油烯-4-醇(4.31%)、2-甲氧基-4-乙烯基苯酚(2.41%)、丁基苯酞(2.34%)、 $\gamma$ -萜品烯(1.00%);羌活挥发油主要组分为  $\beta$ -蒎烯(27.65%)、 $\alpha$ -蒎烯(24.28%)、 $\gamma$ -萜品烯(12.15%)、D-柠檬烯(10.68%)、 $\beta$ -伞花烃(4.80%)、茅苍术醇(1.63%);药对川芎、羌活挥发油主要组分为  $\beta$ -蒎烯(24.71%)、 $\alpha$ -蒎烯(22.88%)、 $\gamma$ -萜品烯(13.74%)、D-柠檬烯(8.73%)、 $\beta$ -伞花烃

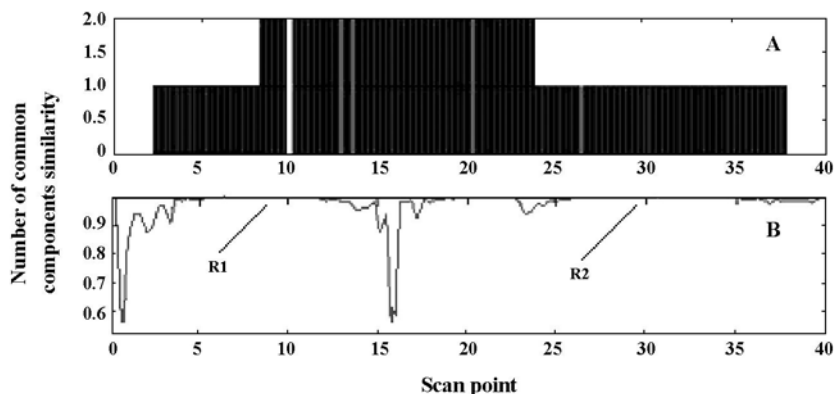


Figure 4 Resolution results of common components. A: Common rank map from AMWFA; B: Spectral auto-correlative curves from AMWFA

**Table 1** Main chemical components of volatile oils from CXR, NR and HP CXR-NR

No.	Component/molecular formula	CXR rc / rt	NR rc / rt	HP CXR-NR rc / rt
1	<i>n</i> -Hexanal/C <sub>6</sub> H <sub>12</sub> O	0.07/8.823	0.07/7.813	0.03/7.819
2	Heptanal/C <sub>7</sub> H <sub>14</sub> O	0.01/14.387	0.11/13.163	0.08/13.170
3	3-Ethyl-2,4-dimethylpentane/C <sub>9</sub> H <sub>20</sub>		0.06/13.862	
4	1-Ethyl-4-methylbenzene/C <sub>9</sub> H <sub>12</sub>		0.41/13.918	0.03/13.825
5	4-Methylnonane/C <sub>10</sub> H <sub>22</sub>		0.10/13.954	
6	$\alpha$ -Pinene/C <sub>10</sub> H <sub>16</sub>	0.19/17.265	24.28/16.847	22.88/16.667
7	Camphene/C <sub>10</sub> H <sub>16</sub>		0.52/17.435	0.47/17.439
8	3-Methylene-6-(1-methylthyl)-cyclohexene/C <sub>10</sub> H <sub>16</sub>	0.24/20.187		
9	$\beta$ -Pinene/C <sub>10</sub> H <sub>16</sub>	0.02/20.426	27.65/19.533	24.71/19.568
10	2-Pentylfuran/C <sub>9</sub> H <sub>14</sub> O	0.01/21.182	0.05/20.127	
11	<i>n</i> -Caprylaldehyde/C <sub>8</sub> H <sub>16</sub> O	0.01/21.357	0.35/20.277	0.31/20.287
12	7-Methyl-3-methylene-1,6-octadiene/C <sub>10</sub> H <sub>16</sub>	0.11/22.113	0.78/21.427	
13	2-Methyl-5-(1-methylthyl)-1,3-cyclohexadiene/C <sub>10</sub> H <sub>16</sub>	0.06/22.327	0.28/21.481	0.24/21.492
14	3-Carene/C <sub>10</sub> H <sub>16</sub>	0.45/22.490	0.83/21.574	0.06/21.577
15	$\beta$ -Cymene/C <sub>10</sub> H <sub>14</sub>	0.81/23.581	4.80/22.503	5.67/22.508
16	<i>D</i> -Limonene/C <sub>10</sub> H <sub>16</sub>	0.14/24.095	10.68/23.323	8.73/23.331
17	3,7-Dimethyl-1,3,6-octatriene/C <sub>10</sub> H <sub>16</sub>	0.09/24.210	0.82/23.743	0.62/23.754
18	$\gamma$ -Terpinene/C <sub>10</sub> H <sub>16</sub>	1.00/26.395	12.15/25.513	13.74/25.580
19	6,10-Dimethyl-5,9-undecadien-1-yne/C <sub>13</sub> H <sub>20</sub>	0.21/27.094		0.04/26.492
20	3,4-Epoxy-2,2,7,7-tetramethyl-octane/C <sub>12</sub> H <sub>24</sub> O	0.15/27.133		0.03/26.541
21	(+)-4-Carene/C <sub>10</sub> H <sub>16</sub>	0.75/28.517	0.32/27.370	0.44/27.376
22	2,6-Dimethyl-3,5,7-octatriene-2-ol/C <sub>10</sub> H <sub>16</sub> O		0.98/27.707	0.09/27.733
23	3,7-Dimethyl-1,5,7-octatrien-3-ol/C <sub>10</sub> H <sub>16</sub> O		0.13/27.953	0.18/27.957
24	2,2,3-Trimethyl-3-cyclopentene-1-acetaldehyde/C <sub>10</sub> H <sub>16</sub> O	0.01/29.985	0.75/29.087	0.06/29.093
25	1-Methyl-4-(1-methylthyl)-2-cyclohexen-1-ol/C <sub>10</sub> H <sub>18</sub> O	0.11/30.450	0.07/29.347	0.10/29.351
26	2,6-Dimethyl-1,3,5,7-octatetraene/C <sub>10</sub> H <sub>14</sub>	0.02/31.479	0.22/30.217	0.06/30.243
27	1,5,5-Trimethyl-6-methylene-cyclohexene/C <sub>10</sub> H <sub>16</sub>		0.01/30.405	0.18/30.413
28	1-Methyl-4-(1-methylthyl)-2-cyclohexen-1-ol/C <sub>10</sub> H <sub>18</sub> O	0.09/31.762	0.01/30.553	0.01/30.584
29	2-Methylene-5-(1-methylthyl)-cyclohexanol/C <sub>10</sub> H <sub>16</sub> O		0.09/30.903	0.10/30.933
30	Pentylbenzene/C <sub>11</sub> H <sub>16</sub>	0.25/33.180		0.07/32.097
31	<i>p</i> -Mentha-1,5-dien-8-ol/C <sub>10</sub> H <sub>16</sub> O		0.11/32.327	0.19/32.335
32	1,3,5-Undecatriene/C <sub>11</sub> H <sub>18</sub>	0.32/33.617		0.01/32.553
33	4-(1-Methylthyl)-2-cyclohexen-1-one/C <sub>9</sub> H <sub>14</sub> O		0.08/32.813	0.05/32.847
34	Terpinen-4-ol/C <sub>10</sub> H <sub>18</sub> O	4.31/34.703	1.25/33.513	2.53/33.547
35	4-Trimethyl-3-cyclohexene-1-methanol/C <sub>10</sub> H <sub>18</sub> O	0.20/35.400	0.30/34.243	0.58/34.297
36	3-Methyl-6-(1-methylthyl)-2-cyclohexen-1-ol/C <sub>10</sub> H <sub>18</sub> O	0.04/36.577	0.01/35.560	0.01/35.597
37	2-Methyl-5-(1-methylthyl)-2-cyclohexen-1-ol/C <sub>10</sub> H <sub>18</sub> O	0.01/37.087	0.03/36.120	0.02/36.132
38	9-Methyl-4-undecene/C <sub>12</sub> H <sub>24</sub>			0.09/38.197
39	Benzylidenemalonaldehyde/C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>			0.01/38.433
40	4-(1-Methylthyl)-1-cyclohexene-1-carboxaldehyde/C <sub>10</sub> H <sub>16</sub> O	0.02/40.497	0.07/39.700	0.07/39.647
41	1,7,7-Trimethyl, endo-bicyclo[2.2.1]heptan-2-ol, acetate/C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>		0.68/41.170	0.57/41.154
42	2-Methoxy-4-vinylphenol/C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	2.41/42.507	0.82/41.977	1.09/41.957
43	1-Phenyl-1-pentanone/C <sub>11</sub> H <sub>14</sub> O	0.81/44.013		0.14/43.617
44	2,2-Dimethyl-1-phenyl-3-buten-1-one/C <sub>12</sub> H <sub>14</sub> O	0.42/44.243		0.08/43.892
45	Pentylbenzenemethanol/C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>	0.46/45.227		
46	Copaene/C <sub>15</sub> H <sub>24</sub>		0.12/45.193	0.13/45.043
47	2-Methylene-5-(1-methylvinyl)-8-methylbicyclo[5.3.0]decane/C <sub>15</sub> H <sub>24</sub>	0.04/45.620	0.04/45.527	0.04/45.507
48	4-Acetoxy-3-methoxyacetophenone/C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>		0.03/45.833	
49	Cedrene/C <sub>15</sub> H <sub>24</sub>	0.01/46.214	0.04/46.170	0.05/46.162
50	1,2,3,4,4a,7-Hexahydro-1,6-dimethyl-4-(1-methylthyl)-naphthalene/C <sub>15</sub> H <sub>24</sub>	0.20/46.370	0.01/46.300	0.01/46.361
51	Germacrene/C <sub>15</sub> H <sub>24</sub>	0.03/46.518	0.07/46.549	0.06/46.547
52	Caryophyllene/C <sub>15</sub> H <sub>24</sub>		0.22/46.946	0.15/47.067
53	Isoldene/C <sub>15</sub> H <sub>24</sub>	0.06/47.417	0.53/47.447	0.38/47.462
54	Decahydro-1,6-bis(methylene)-4-(1-methylthyl)-naphthalene/C <sub>15</sub> H <sub>24</sub>	0.48/47.667	0.01/47.633	0.38/47.624
55	3,7,7-Trimethyl-1-methylene-spiro[5.5]undec-2-ene/C <sub>15</sub> H <sub>24</sub>	0.30/47.820	0.61/47.914	0.73/47.927
56	Elemol/C <sub>15</sub> H <sub>24</sub> O		1.02/48.751	0.42/48.757
57	(-)-Spathulenol/C <sub>15</sub> H <sub>24</sub> O	0.96/49.230	0.34/49.314	0.25/49.307
58	1,2,3,4,5,6,7,8-Octahydro- $\alpha$ , $\alpha$ ,3,8-tetramethyl-5-azulenemethanol/C <sub>15</sub> H <sub>24</sub> O	0.44/49.627	1.01/49.651	0.40/49.637
59	Butylidenephthalide/C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	5.42/49.913		1.57/50.057
60	1,2,3,4,4a,5,6,8a-Octahydro-4a,8-dimethyl-2-(1-methylthyl)-naphthalene/C <sub>15</sub> H <sub>24</sub>		1.05/50.207	0.01/50.197
61	Cadinol/C <sub>15</sub> H <sub>26</sub> O		0.01/50.377	0.01/50.317
62	Hinesol/C <sub>15</sub> H <sub>26</sub> O		1.63/50.560	1.50/50.557
63	1,2,3,3a,4,5,6,7-Octahydro,3,8-tetramethyl-5-azulenemethanol/C <sub>15</sub> H <sub>26</sub> O		0.04/50.720	0.01/50.710
64	Butylphthalide/C <sub>12</sub> H <sub>14</sub> O <sub>2</sub>	2.34/50.450		0.98/51.124
65	Ligustilide/C <sub>12</sub> H <sub>14</sub> O <sub>2</sub>	57.71/52.002		3.10/51.470
66	(Z)-(-)-1,9-Heptadecadiene-4,6-diene-3-falcarinol/C <sub>17</sub> H <sub>24</sub> O		0.08/56.253	
67	<i>n</i> -Hexadecanoic acid/C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	0.95/54.387		0.04/53.647
68	9,12-Octadecadienoic acid/C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	0.66/57.860		

rc: Relative content (%); rt: Retention time (min)

(5.67%)、藁本内酯(3.10%)。川芎、羌活挥发油中分别有17种和8种成分在药对中消失,如川芎中的3-methylene-6-(1-methylethyl)-cyclohexene和pentyl-benzenemethanol等,羌活中的4-methyl-nonane和4-acetoxy-3-methoxyacetophenone等,而药对挥发油中产生了2个新成分,即9-methyl-4-undecene和benzylidenemalonaldehyde,但含量都很低。特别是川芎挥发油的主要组分藁本内酯,在药对中的含量仅为3.10%。原因可能是,一方面,藁本内酯在室温下不稳定,极易异构化成其他丁烯基呋内酯类化合物<sup>[11]</sup>,在空气中可被氧化,另一方面,在配伍煎煮过程中氧化作用更强,使藁本内酯和其异构化产物丁烯基呋内酯类氧化,因而使其含量降低。从组分数量及含量来看,药对挥发油组分主要来自于单味药羌活,但化学成分种类基本为两个单味药的加和,且含量也有变化。

药对川芎羌活与单味药川芎共有的挥发油组分为45个,与单味药羌活共有的挥发油组分为63个,药对川芎羌活、川芎、羌活三者共有的挥发油组分为31个。

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