

# 香椿的化学成分研究进展

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**摘要:**香椿是我国特有的珍贵速生药材树种,通过 SciFinder 等工具或数据库检索、查阅近期在国内外期刊上发表的相关论文,系统地综述了香椿化学成分的研究情况,为其进一步的研究与开发提供参考。到目前为止,共计报道了从香椿中分离得到的 100 个化合物,包括黄酮类 19 个、萜类 44 个、苯丙素类 7 个、酚类 14 个和 16 个其它类别化合物。香椿的化学成分研究以黄酮类和三萜类化合物为主导。

**关键词:**香椿;楝科;化学成分;黄酮;三萜;苯丙素

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## Research Progress on The Chemical Constituents of *Toona Sinensis*

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**KEY WORDS:** *Toona sinensis*; meliaceae; chemical constituents; flavonoids; triterpenoids; phenylpropanoids

香椿 *Toona sinensis* (A. Juss.) Roemor(旧拉丁名为 *Cedrela sinensis* A. Juss)又名春芽树、椿、椿树,在《植物名实图考》中称为红椿,为楝科(Meliaceae)香椿属(*Toona*)落叶乔木,是我国特有的珍贵速生药材树种,素有“中国桃花心木”(Chinese mahogany)之称<sup>[1]</sup>,主要分布于我国的山东、安徽、河南、河北等省份,其中又以安徽太和、河南焦作和山东西牟出产的香椿产品最为著名。

香椿全株具有特殊气味,并因富含多种生物活性物质而具有很高的药用价值,其叶、树皮和果实均可入药,应用历史十分悠久,始载于《唐本草》。香椿叶(Chinese toon 或 *Toona sinensis* folium)味苦、性温,具有清热收敛、消炎解毒、去燥湿等功效,主治肠炎、痢疾等疾病<sup>[2]</sup>;此外,香椿叶富含维生素 C、氨基酸、优质蛋白质和磷、铁等微量元素,是我国著名的传统时令蔬菜,已有两千多年的食用历史,曾与荔枝一同作为贡品进献宫廷御用,是蔬菜中不可多得的珍品,深受广大消费者的青睐,在国外被称为“绿色保健菜”,现多出口

至日本及东南亚国家<sup>[3]</sup>。香椿皮(*Toona sinensis* cortex)味苦涩、性凉,具有除热、燥湿、润肠止血、杀虫的功效,临床常用于治疗痢疾、肠炎、泌尿道感染、便血、白带、风湿腰腿痛等。香椿子(*Toona sinensis* fructus)味辛苦、性温,具祛风、散寒、止痛之功效,临床用于治疗风寒外感、心胃气痛、风湿关节痛、疝气及冷骨风等。

近年来,国内外对香椿的化学成分研究日趋增多,本文对相关的研究报道进行了总结与分析,并将“组分结构理论”与本实验室的研究结果进行关联,从而解释香椿叶中有效成分的“量比”结构与药材道地性的关系,以期为更好地促进香椿叶的进一步研究和开发提供有意义的参考。

### 1 黄酮类

从香椿中分离与鉴定了黄酮类化合物共计 19 个,包括黄酮苷元类 11 个,其中黄酮 2 个、黄酮醇 3 个、双黄酮 2 个、二氢黄酮 2 个和黄烷醇 2 个;另有黄酮苷类 8 个,全部为黄酮醇苷。见图 1、表 1。

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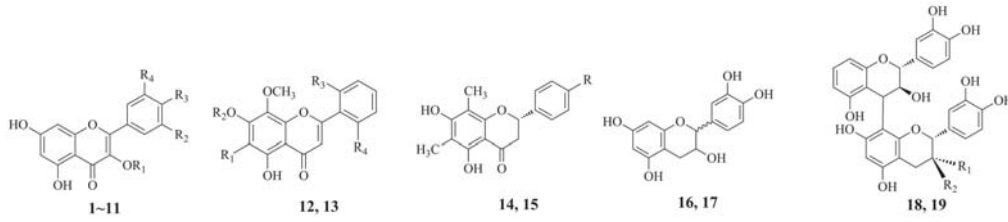


图1 香椿中黄酮类化合物的化学结构

表1 香椿中的黄酮类化学成分

编号	R 取代	化合物名称	Ref
1	R <sub>1</sub> =R <sub>4</sub> =H, R <sub>2</sub> =R <sub>3</sub> =OH	Quercetin	4
2	R <sub>1</sub> =glc(6-1)rha, R <sub>2</sub> =R <sub>3</sub> =OH, R <sub>4</sub> =H	Rutin	5
3	R <sub>1</sub> =glc, R <sub>2</sub> =R <sub>3</sub> =OH, R <sub>4</sub> =H	Quercetin-3-O-β-D-glucoside	6
4	R <sub>1</sub> =2''-O-galloyl-β-D-glc, R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =OH	Quercetin-3-O-(2''-O-galloyl)-β-D-glucoside	6
5	R <sub>1</sub> =rha, R <sub>2</sub> =R <sub>3</sub> =OH, R <sub>4</sub> =H	Quercetin-3-O-α-L-rhamnoside	5
6	R <sub>1</sub> =R <sub>3</sub> =H, R <sub>2</sub> =R <sub>4</sub> =OH	Kaempferol	4
7	R <sub>1</sub> =glc, R <sub>3</sub> =H, R <sub>2</sub> =R <sub>4</sub> =OH	Kaempferol-3-O-β-D-glucoside	5
8	R <sub>1</sub> =ara, R <sub>2</sub> =R <sub>4</sub> =OH, R <sub>3</sub> =H	Kaempferol-3-O-α-L-arabinoside	5
9	R <sub>1</sub> =rha, R <sub>2</sub> =R <sub>4</sub> =OH, R <sub>3</sub> =H	Kaempferol-3-O-α-L-rhamnoside	7
10	R <sub>1</sub> =H, R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =OH	Myricetin	8
11	R <sub>1</sub> =rha, R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =OH	Myricitrin	8
12	R <sub>1</sub> =R <sub>2</sub> =CH <sub>3</sub> , R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	6,7,8,2'-tetramethoxy-5,6'-dihydroxy flavone	9
13	R <sub>1</sub> =R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =H	5,7-dihydroxy-8-methoxy flavone	9
14	R=H	Demethoxymatteucinol	10
15	R=OCH <sub>3</sub>	Matteucinol	10
16	2R	(+)-Catechin	11
17	2S	(-)-Epicatechin	11
18	R <sub>1</sub> =H, R <sub>2</sub> =OH	Procyanidin B3	10
19	R <sub>1</sub> =OH, R <sub>2</sub> =H	Procyanidin B4	10

2 酚类及其衍生物

物共计 14 个。见图 2、表 2。

近年来,从香椿中已分离与鉴定了酚类化合物及其衍生

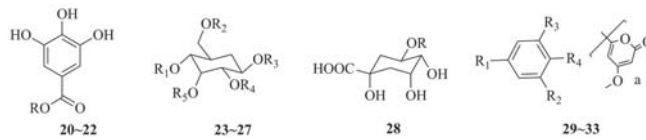


图2 香椿中酚类及其衍生物的化学结构

表2 香椿中的酚类化学成分及其衍生物

编号	R 取代	化合物名称	Ref
20	R=H	Gallic acid	6
21	R=CH <sub>3</sub>	Methyl gallate	6
22	R=CH <sub>2</sub> CH <sub>3</sub>	Ethyl gallate	8
23	R <sub>1</sub> =R <sub>3</sub> =R <sub>4</sub> =R <sub>5</sub> =H, R <sub>2</sub> =galloyl	6-O-galloyl-β-D-glucose	5
24	R <sub>1</sub> =R <sub>2</sub> =H, R <sub>3</sub> =R <sub>4</sub> =R <sub>5</sub> =galloyl	1,2,3-tri-O-galloyl-β-D-glucopyranose	5
25	R <sub>1</sub> =R <sub>5</sub> =H, R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =galloyl	1,2,6-tri-O-galloyl-β-D-glucopyranose	6
26	R <sub>1</sub> =H, R <sub>2</sub> =galloyl, R <sub>3</sub> =R <sub>4</sub> =R <sub>5</sub> =galloyl	1,2,3,6-tetra-O-galloyl-β-D-glucopyranose	5
27	R <sub>1</sub> =R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =R <sub>5</sub> =galloyl	1,2,3,4,6-penta-O-galloyl-β-D-glucopyranose	7
28	R=galloyl	5-O-galloylquinic acid	6
29	R <sub>1</sub> =COOH, R <sub>2</sub> =R <sub>4</sub> =OH, R <sub>3</sub> =galloyl×2	Trigallic acid	5
30	R <sub>1</sub> =COOH, R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	Syringic acid	12
31	R <sub>1</sub> =CHO, R <sub>2</sub> =H, R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	Vanillin	13
32	R <sub>1</sub> =CH <sub>2</sub> CH <sub>2</sub> OH, R <sub>2</sub> =H, R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	4-hydroxy-3-methoxy benzene-ethanol	12
33	R <sub>1</sub> =R <sub>3</sub> =OH, R <sub>2</sub> =CH <sub>3</sub> , R <sub>4</sub> =a	4-methoxy-6-(2',4'-dihydroxy-6'-methylphenyl)-pyran-2-one	12

3 萜类

到目前为止,已从香椿中分离与鉴定了 40 个三萜类化合物;此外,还有倍半萜、二萜类化合物共计 4 个。

3.1 三萜类

见图 3、表 3。

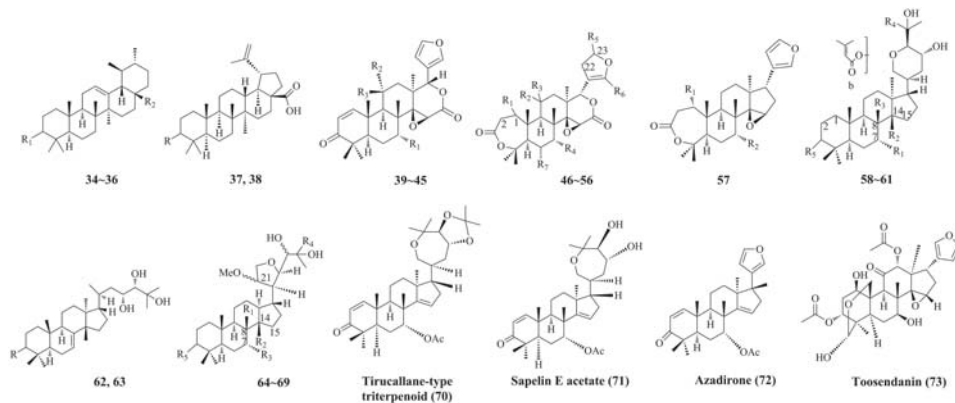


图 3 香椿中三萜类化合物的化学结构

表 3 香椿中的三萜类化学成分

编号	R 取代	化合物名称	Ref
34	R <sub>1</sub> = O, R <sub>2</sub> = COOH	3-oxo-12-en-28-oic acid	11
35	R <sub>1</sub> = OH, R <sub>2</sub> = CH <sub>3</sub>	$\alpha$ -betulin	12
36	R <sub>1</sub> = OH, R <sub>2</sub> = COOH	Ursolic acid	11
37	R = O	Betulonic acid	11
38	R = OH	Betulic acid	11
39	R <sub>1</sub> = OAc, R <sub>2</sub> = OH, R <sub>3</sub> = H	11 $\alpha$ -hydroxygedunin	14
40	R <sub>1</sub> = OAc, R <sub>2</sub> = H, R <sub>3</sub> = OH	11 $\beta$ -hydroxygedunin	14
41	R <sub>1</sub> = H, R <sub>2</sub> = OH, R <sub>3</sub> = H	7-deacetoxy-7 $\alpha$ , 11 $\alpha$ -dihydroxygedunin	14
42	R <sub>1</sub> = H, R <sub>2</sub> = H, R <sub>3</sub> = OH	7-deacetoxy-7 $\alpha$ , 11 $\beta$ -dihydroxygedunin	14
43	R <sub>1</sub> = OAc, R <sub>2</sub> = R <sub>3</sub> = H	Gedunin	14
44	R <sub>1</sub> = OAc, R <sub>2</sub> = R <sub>3</sub> = H	7-deacetoxy-7 $\alpha$ -hydroxygedunin	14
45	R <sub>1</sub> = OAc, R <sub>2</sub> = R <sub>3</sub> = O	11-oxogedunin	14
46	R <sub>1</sub> = R <sub>2</sub> = R <sub>4</sub> = OAc, R <sub>3</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, $\Delta^{22,23}$	Toonin A	12
47	R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>4</sub> = OAc, $\Delta^{1,2\&22,23}$	Proceranone	12
48	R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = R <sub>4</sub> = R <sub>5</sub> = R <sub>6</sub> = H, R <sub>7</sub> = OAc, $\Delta^{1,2\&22,23}$	6-acetoxyobacunyl acetate	15
49	R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>4</sub> = OAc, $\Delta^{1,2\&22,23}$	7 $\alpha$ -obacunyl acetate	15
50	R <sub>1</sub> = R <sub>4</sub> = OAc, R <sub>2</sub> = R <sub>3</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, $\Delta^{22,23}$	7 $\alpha$ -acetoxydihydronormilin	15
51	R <sub>1</sub> = R <sub>2</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>3</sub> = OH, R <sub>4</sub> = OAc, $\Delta^{1,2\&22,23}$	11 $\beta$ -hydroxy-7 $\alpha$ -obacunyl acetate	16
52	R <sub>1</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>2</sub> = R <sub>3</sub> = O, R <sub>4</sub> = OAc, $\Delta^{1,2\&22,23}$	11-oxo-7 $\alpha$ -obacunyl acetate	16
53	R <sub>1</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>2</sub> = R <sub>3</sub> = O, R <sub>4</sub> = OH, $\Delta^{1,2\&22,23}$	11-oxo-7 $\alpha$ -obacunyl	16
54	R <sub>2</sub> = R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>3</sub> = OH, R <sub>1</sub> = R <sub>4</sub> = OAc, $\Delta^{22,23}$	11 $\beta$ -hydroxycorin G	16
55	R <sub>5</sub> = R <sub>6</sub> = R <sub>7</sub> = H, R <sub>2</sub> = R <sub>3</sub> = O, R <sub>1</sub> = R <sub>4</sub> = OAc, $\Delta^{22,23}$	11 $\beta$ -oxocorin G	16
56	R <sub>1</sub> = R <sub>4</sub> = OAc, R <sub>2</sub> = R <sub>3</sub> = R <sub>7</sub> = H, R <sub>5</sub> = R <sub>6</sub> = OH	Cedrellin	15
57	R <sub>1</sub> = R <sub>2</sub> = OAc	Toonin B	12
58	R <sub>1</sub> = OAc, R <sub>2</sub> = Nil, R <sub>3</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>5</sub> = O, $\Delta^{1,2\&14,15}$	Grandifoliolenone	17
59	R <sub>1</sub> = H, R <sub>2</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>3</sub> = Nil, R <sub>5</sub> = O, $\Delta^{7,8}$	Bourjotinolone A	12
60	R <sub>1</sub> = H, R <sub>2</sub> = Nil, R <sub>3</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>5</sub> = b, $\Delta^{14,15}$	Tirucallane-type triterpenoid	17
61	R <sub>1</sub> = H, R <sub>2</sub> = Nil, R <sub>3</sub> = CH <sub>3</sub> , R <sub>4</sub> = CH <sub>2</sub> OH, R <sub>5</sub> = b, $\Delta^{14,15}$	Tirucallane-type triterpenoid	17
62	R = O	Piscidinol A	17
63	R = $\beta$ -OH	Hispidol B	17
64	R <sub>1</sub> = Nil, R <sub>2</sub> = CH <sub>3</sub> , R <sub>3</sub> = H, 21R, $\Delta^{7,8}$	21 $\alpha$ -methlmeliandioli	17
65	R <sub>1</sub> = Nil, R <sub>2</sub> = CH <sub>3</sub> , R <sub>3</sub> = H, 21S, $\Delta^{7,8}$	21 $\beta$ -methlmeliandioli	17
66	R <sub>1</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>2</sub> = Nil, R <sub>3</sub> = OH, R <sub>5</sub> = O, 21R, $\Delta^{14,15}$	3-O-acetyl-21R-O-methyltoosendanpentol	17
67	R <sub>1</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>2</sub> = Nil, R <sub>3</sub> = OH, R <sub>5</sub> = O, 21S, $\Delta^{14,15}$	3-O-acetyl-21S-O-methyltoosendanpentol	17
68	R <sub>1</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>2</sub> = Nil, R <sub>3</sub> = OH, R <sub>5</sub> = b, 21R, $\Delta^{14,15}$	Tirucallane-type triterpenoid	17
69	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = Nil, R <sub>3</sub> = OH, R <sub>4</sub> = CH <sub>2</sub> OH, R <sub>5</sub> = b, 21S, $\Delta^{14,15}$	Tirucallane-type triterpenoid	17

3.2 其它萜类

见图4。

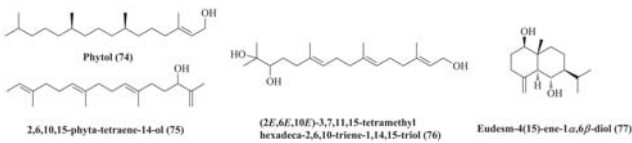


图4 香椿中其它萜类化合物的化学结构

4 苯丙素类

从香椿中分离、鉴定了香豆素类化合物3个以及木脂素类化合物4个。见图5、表4。

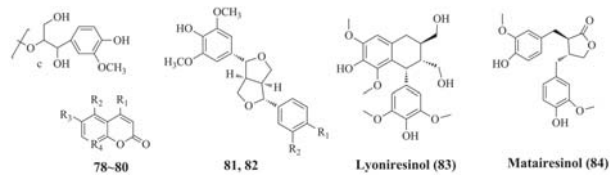


图5 香椿中苯丙素类化合物的化学结构

表4 香椿中的苯丙素类化学成分

编号	R 取代	化合物名称	Ref
78	R <sub>1</sub> =R <sub>2</sub> =H, R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	Scopoletin	10
79	R <sub>1</sub> =R <sub>2</sub> =H, R <sub>3</sub> =OCH <sub>3</sub> , R <sub>4</sub> =OH	Isoscapoletin	12
80	R <sub>1</sub> =R <sub>4</sub> =OCH <sub>3</sub> , R <sub>2</sub> =CH <sub>3</sub> , R <sub>3</sub> =H	4,7-dimethoxy-5-methyl coumarin	7
81	R <sub>1</sub> =c, R <sub>2</sub> =OCH <sub>3</sub>	Ficusesquilignans A	18
82	R <sub>1</sub> =OCH <sub>3</sub> , R <sub>2</sub> =c	Ficusesquilignans B	18

5 含硫化合物

见图6、表5。

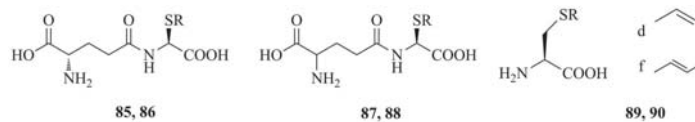


图6 香椿中含硫化合物的化学结构

表5 香椿中的含硫化合物

编号	R 取代	化合物名称	Ref
85	R=d	(S,S)-γ-glutamyl-(cis-S-1-propenyl)thioglycine	19
86	R=f	(S,S)-γ-glutamyl-(trans-S-1-propenyl)thioglycine	19
87	R=d	γ-glutamyl-(cis-S-1-propenyl)-cysteine	19
88	R=f	γ-glutamyl-trans-S-1-propenyl-L-cysteine	19
89	R=d	cis-S-1-propenyl-L-cysteine	19
90	R=f	trans-S-1-propenyl-L-cysteine	19

6 其它化合物

除以上化合物外,还从香椿中分离、鉴定了二十碳酸乙酯(Eicosanoic acid ethyl ester, 91)<sup>[20]</sup>、正二十六烷醇(n-Hexacosanol, 92)<sup>[20]</sup>、月桂烷(n-Dodecane, 93)<sup>[13]</sup>、木质素酸(Lignoceric acid, 94)<sup>[13]</sup>、芦荟大黄素(Aloeemodin, 95)<sup>[12]</sup>、腺苷(Adenosine, 96)、b-谷甾醇(b-Sitosterol, 97)<sup>[12]</sup>、豆甾醇(Stigmasterol, 98)<sup>[13]</sup>、3-羟基-5,6-环氧-7-megastigmen-9-酮(3-hydroxy-5,6-epoxy-7-megastigmen-9-one, 99)<sup>[9]</sup>和棟素C(Toonin C, 100)<sup>[12]</sup>等。见图7。

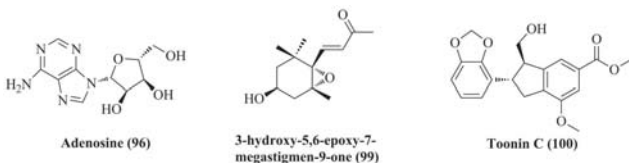


图7 香椿中其它化合物的化学结构

7 香椿叶有效成分的量比结构与药材道地性的关系

在中医药理论的指导下,基于中药研究的系统性和整体性,本课题组贾晓斌教授创新性地提出中药“组分结构理论”新观点<sup>[21]</sup>,构建了符合中药多组分结构特点的“从宏观到微观”和“从微观到宏观”的物质基础解析技术体系;该理论认为中药物质基础是一个有序稳定的整体,具有“三个层次多

维结构”,其内涵为:一是组成物质基础的最基本单元为单体成分,具有稳定化学结构;二是由同一类别化学成分构成的组分,组分中各单体成分之间存在配伍配比关系,这是另一维结构;三是由多组分构成的整体即中药的物质基础,其各组分间存在配伍配比关系,这也是一维结构。

本课题组基于“组分结构理论”探讨了香椿叶等道地药材的物质基础组分结构特征,通过对不同产地香椿叶进行分析后发现,两个有效成分即没食子酸及其甲酯的含量及比例差异很大。一般认为,道地药材中所含的有效成分应明显高于其它产地药材;然而,香椿叶道地药材中没食子酸甲酯的含量却显著低于其它产区,这一结果与传统认识不一致。此外,山东、河南两个道地产区香椿叶中没食子酸的含量明显高于没食子酸甲酯,两者比例分别为6.67和4.51,而山西、四川两地香椿叶中两者比例则均小于1,显示了特定的量比结构,并表明组分内单体成分所具有的特定量比结构与药材的道地性存在一定关系<sup>[22]</sup>。

8 挥发油类化学成分的分析

吴艳霞<sup>[23]</sup>等以GC-MS对香椿茎中挥发性成分进行了分析,共鉴定了30种化学成分。陈丛瑾<sup>[24]</sup>等采用HS-SPME/GC-MS联用技术从香椿芽萃取物中鉴定出26个成

分,从香椿叶萃取物中鉴定出 46 种成分。

## 9 总结与展望

香椿是一种用途较广、来源丰富的药用植物,其叶、树皮和果实的应用历史悠久,具有确切的药效。现代研究表明,香椿中的化学成分有抗肿瘤、抗氧化、降血脂等多种生物活性;国内外学者对香椿中的化学成分开展了一些较为深入的研究,发现其所含化合物的种类丰富,是值得进一步研究、开发前景良好的一种药食同源植物资源。此外,有必要分析香椿叶中黄酮类等组分中个单体成分的含量和量比结构,并明确组分之间的关系,以期更为全面地阐释香椿叶物质基础组分结构特征和香椿叶药材的道地性。

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