

# 香附化学成分研究进展

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**[摘要]** 香附是中医常用的一种妇科良药, 具有疏肝理气, 调经止痛之功效。现代药理研究也证明其具有抗抑郁、抗肿瘤、抑制乙酰胆碱酯酶活性、抗糖尿病等作用。迄今为止从香附中已分离得到 100 多个化合物, 其中倍半萜类化合物就近 70 个, 且骨架类型多样, 有桉烷型、广藿香烷型、胡椒烷型、Rotundane 型等, 此外, 还有黄酮类和三萜类化合物等。本文对其化学成分进行系统、全面的综述, 为其进一步的开发利用提供参考。

**[关键词]** 香附; 倍半萜; 黄酮, 生物碱

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## Advances in Studies on Chemical Constituents of Rhizomes of *Cyperus rotundus*

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**[Abstract]** The rhizomes of *Cyperus rotundus* is a traditional chinese medicine for the treatment of dispersing the depressed liver-energy, regulating vital energy, dysmenorrhea, and menstrual disorders and so on. Modern pharmacological studies have proven the broad range of biological activities, such as antidepressant, anti-cancer, acetylcholinesterase inhibitory activity, anti-diabetic. Previous phytochemical investigations have described the presence of more than 100 compounds in it, among of which about 70 ones are sesquiterpenes with diverse skeletons such as eudesmane, patchoulane, copane, rotundane and so on. This paper reviews the progress of the constituents of it which provides references for further development and utilization of it.

**[Key words]** *Cyperus rotundus*; sesquiterpenes; flavones; alkaloids

香附 (Rhizoma Cyperi) 为莎草科植物莎草 *Cyperus rotundus* L. 的干燥根茎。香附始载于《名医别录》, 是中医常用的妇科良药, 具疏肝理气, 调经止痛之功效。《中国药典》自 1985 年版开始收载。其性平, 味辛、微苦、甘, 具有理气解郁, 调经止痛功效, 用于肝郁气滞, 胸、胁、脘腹胀痛, 消化不良, 月经不调, 经闭痛经, 寒疝腹痛, 乳房胀痛等病症。香附主产于山东、浙江、湖南、河南等地。国外对香附挥发油的倍半萜类化合物研究较多, 其他类成分研究较少, 国内对香附化学成分研究较少。香附中挥发油的含量约 1%, 其中主要

含有多种单萜、倍半萜及其氧化物。此外, 还有黄酮类、糖类、生物碱、酚类和三萜类化合物等。香附的化学成分研究报道较早、较多, 本文对其进行综述。

### 1 萜类化合物

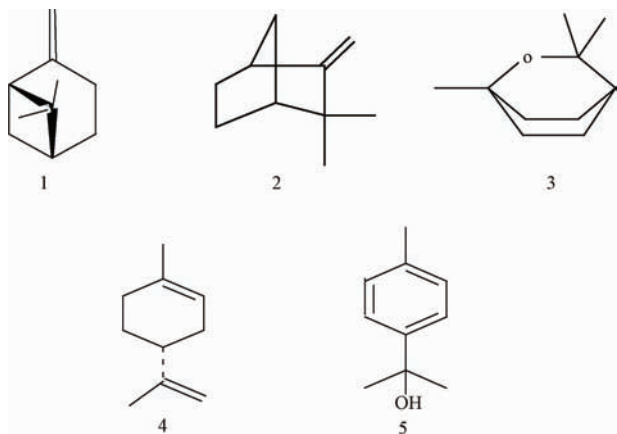
**1.1 单萜类** 从香附中分离得到的单萜类化合物有  $\beta$ -蒎烯 ( $\beta$ -pinene, 1)、樟烯 (camphene, 2)、桉叶素 (1, 8-cineole, 3)、柠檬烯 (limonene, 4)、 $\gamma$ -聚伞花素 ( $\gamma$ -cymene, 5)<sup>[1]</sup>。

### 1.2 倍半萜类

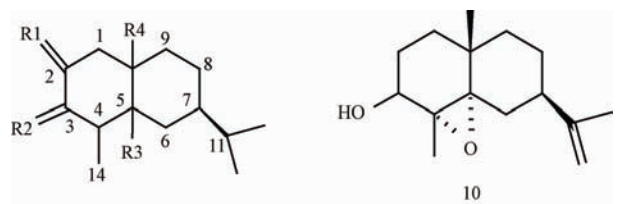
**1.2.1 桉烷型倍半萜 (eudesmane type)** 从香附中分离得到的桉烷型倍半萜类化合物有芹子三烯 (selinatriene, 6)、 $\beta$ -芹子烯 ( $\beta$ -selinene, 7)、 $\alpha$ -香附酮 ( $\alpha$ -cyperone, 8)、 $\beta$ -香附酮 ( $\beta$ -cyperone, 9)<sup>[1]</sup>。4 $\alpha$ , 5 $\alpha$ -环氧-11-3 $\alpha$ -烯 桉叶醇 (4 $\alpha$ , 5 $\alpha$ -oxidoeudesm-11-en-3 $\alpha$ -ol, 10)<sup>[2]</sup>。 $\alpha$ -莎草醇 ( $\alpha$ -rotunol, 11)、 $\beta$ -莎草醇 ( $\beta$ -rotunol, 12)<sup>[3]</sup>。香附醇 (cyperol, 13)、异香附醇

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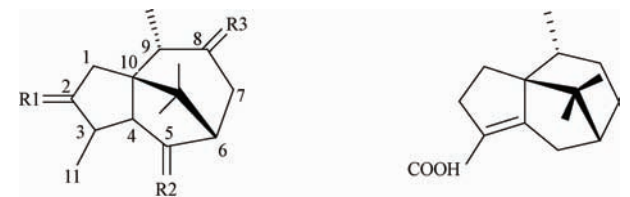
( isocyperol, 14 )<sup>[4]</sup>。1 ( 10 ), 11-eremo-philadien-2-one ( nootkatone, 15 )<sup>[5-6]</sup>, eudesma-4 ( 14 ), 11-dien-3 $\beta$ -ol (17)<sup>[8]</sup>。另外 GC-MS 检测还含有 nootkatene (16)<sup>[7]</sup>。 $\alpha$ -芹子烯 ( $\alpha$ -selinene, 18), epi- $\alpha$ - selinene (19), valencene (20)<sup>[7]</sup>。



- 6: R1 = R2 = H, H, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (14), 8 (9), 7 (11)  
10  
7: R1 = R2 = H, H, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (14), 11  
8: R1 = H, H, R2 = O, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (5), 11  
9: R1 = H, H, R2 = O, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (5), 6  
11: R1 = O, R2 = H, R3 = OH, R4 = CH<sub>3</sub>,  $\Delta^3$ , 11 (5 $\alpha$ -form)  
12: R1 = O, R2 = H, R3 = OH, R4 = CH<sub>3</sub>,  $\Delta^3$ , 11 (5 $\beta$ -form)  
13: R1 = H, H, R2 = H, OH, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (5), 11  
14: R1 = H, H, R2 = H, OH, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (14), 11 (3 $\alpha$ -form)  
15: R1 = O, R2 = H, H, R3 = CH<sub>3</sub>, R4 = H,  $\Delta^4$  (5), 11  
16: R1 = H, R2 = H, H, R3 = CH<sub>3</sub>, R4 = H,  $\Delta^1$ , 9, 11  
17: R1 = H, H, R2 = H, OH, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^4$  (14), 11 (3 $\beta$ -form)  
18: R1 = H, H, R2 = H, R3 = H, R4 = CH<sub>3</sub>,  $\Delta^3$  (4), 11  
19: 18-epimer  
20: R1 = R2 = H, H, R3 = CH<sub>3</sub>, R4 = H,  $\Delta^1$  (10), 11

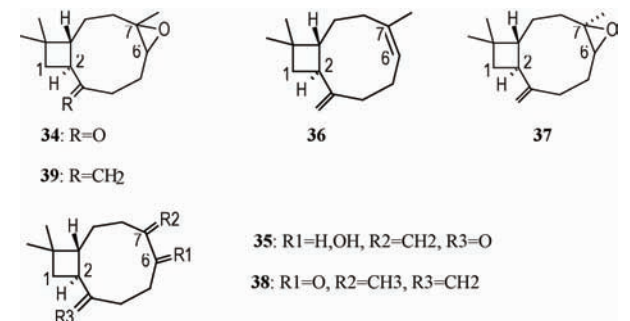
**1.2.2 广藿香烷型倍半萜 (patchoulane type)** 从香附中分离得到的广藿香烷型倍半萜有香附子烯 (cyperene, 21)<sup>[1]</sup>。

广藿香烯酮 (patchoulone, 22)<sup>[9]</sup>。异广藿香烯酮 (isopatchoulone, cyperotundone, cyperenone, 23)<sup>[10-13]</sup>。isopatchoula-3, 5-diene (24)<sup>[11]</sup>。香附子烯 2, 5, 8-三醇 (sugetriol, 25)<sup>[14]</sup>, sugetriol triacetate (26)<sup>[8, 15-16]</sup>, sugeonol (27)<sup>[17]</sup>。香附子烯-2-酮-8-醇乙酸酯 (sugeonyl acetate, 28), 广藿香烯醇乙酸酯 (patchoulenyl acetate, 29)<sup>[18]</sup>。( - )-cypera-2, 4 (15)-diene (30)<sup>[7]</sup>, 另外 GC-MS 检测还含有 cypera-2, 4-diene (31)<sup>[7]</sup>。近年来又从香附中分离得到 cyperenoic acid (32) 和一个新的广藿香烷型倍半萜 sugebiol (33)<sup>[39]</sup>。



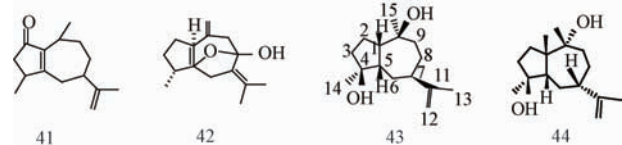
- 21: R1 = R2 = R3 = H, H,  $\Delta^3$   
22: R1 = R3 = H, H, R2 = O,  $\Delta^3$   
23: R1 = O, R2 = R3 = H, H,  $\Delta^3$   
25: R1 = H, OH, R2 = H, OH, R3 = H, OH,  $\Delta^3$   
26: R1 = H, OAc, R2 = H, OAc, R3 = H, OAc,  $\Delta^3$   
27: R1 = O, R2 = H, OH, R3 = H, H,  $\Delta^3$   
28: R1 = O, R2 = H, OAc, R3 = H, H,  $\Delta^3$   
29: R1 = H, H, R2 = H, OAc, R3 = H, H,  $\Delta^3$   
30: R1 = H, R2 = H, H, R3 = H, H,  $\Delta^1$ , 3 (11)  
31: R1 = H, R2 = H, H, H, R3 = H, H,  $\Delta^1$ , 3  
33: R1 = H, OH, R2 = H, OH, R3 = H, H,  $\Delta^3$

**1.2.3 丁香烷型倍半萜 (caryophyllane type)** 从香附中分离得到的丁香烷型倍半萜有考布松 (kobusone, 34)、异考布松 (isokobusone, 35)<sup>[19]</sup>。丁香烯 (caryophyllene, 36)<sup>[20-21]</sup>。caryophyllene-6, 7-oxide ( $\beta$ -caryophyllene 6, 7-oxide, 37), carophylla-6-one (38)<sup>[11-22]</sup>, caryophyllene- $\alpha$ -oxide (39)<sup>[23]</sup>。

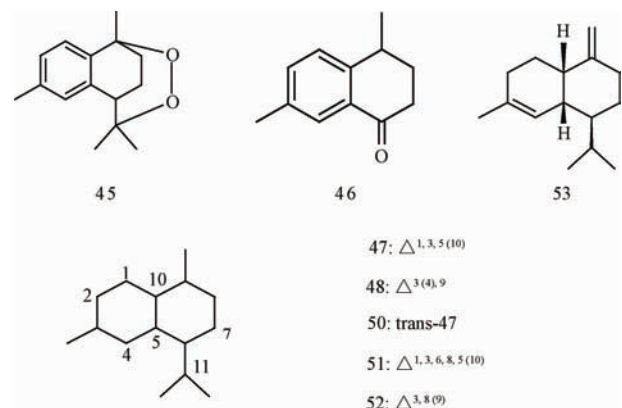


**1.2.4 愈创木烷型倍半萜 (Guaiane type)** 从香附中分离得到的愈创木烷型倍半萜有环氧莎草萜 (epoxy-quaine, 40)、莎草萜酮 (rotundone, 41)<sup>[24]</sup>, isocurcumenol (42)<sup>[6]</sup>, 其外, 近年来又从香附中分离得到愈创木烷型倍半萜的一对异构体 guaidiol (43) 和 epi-guaidiol (44), 其中 epi-guaidiol (44) 是一个新

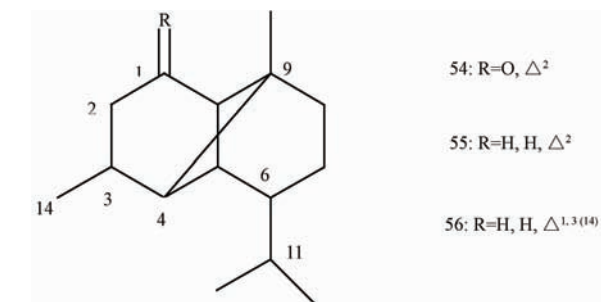
的愈创木烷型倍半萜<sup>[39]</sup>。



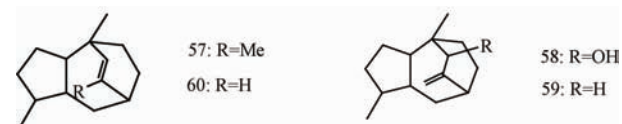
**1.2.5 杜松烷型倍半萜 (cadinane type)** 从香附中分离得到的杜松烷型倍半萜有 10, 12-peroxycalamenene (45), 4, 7-二甲基-1-四氢萘酮(4, 7-dimethyl- 1-tetralone, 46)<sup>[23]</sup>。另外 GC-MS 检测还含有 calamenene (47),  $\delta$ -cadinene (48)<sup>[18]</sup>,  $\gamma$ -calacorene (49), trans-calamenene (50), cadalene (51),  $\alpha$ -muurolene (52),  $\gamma$ - muurolene(53)<sup>[7]</sup>。



**1.2.6 胡椒烷型倍半萜 (copane type)** 从香附中分离得到的胡椒烷型倍半萜 mustakone (54)、古巴烯 (copaene, 55)<sup>[25]</sup>, 古巴二烯 (copadiene, 56)<sup>[24]</sup>。

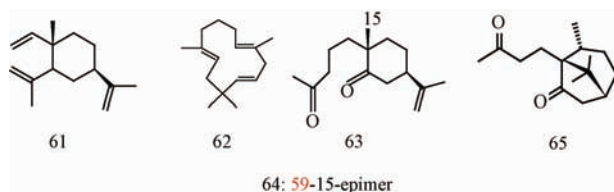


**1.2.7 rotundane type** 从香附中分离得到的 rotundane type 型倍半萜有 rotundene (57), rotundenol (58)<sup>[26]</sup>。(-)-isorotundene (59), (-)-norrotundene (60)<sup>[7]</sup>。

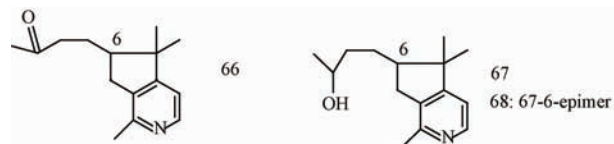


**1.2.8 单环倍半萜** 从香附中分离得到的单环倍半萜有  $\beta$ -榄香烯( $\beta$ -elemene, 61),  $\alpha$ -葎草烯( $\alpha$ -humulene, 62)<sup>[27]</sup>, 4, 5-secoeudesmane (63) 及其异构体(64)<sup>[5]</sup>, (+)-cyperadione (65)<sup>[7]</sup>。

**1.2.9 倍半萜生物碱** 从香附中分离得到的倍半萜生物碱有 rotundines A (66), B (67), and C (B-6-epimer, 68)<sup>[28]</sup>。

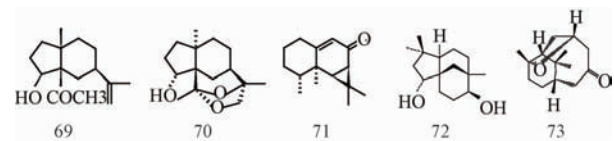


64: 59-15-epimer



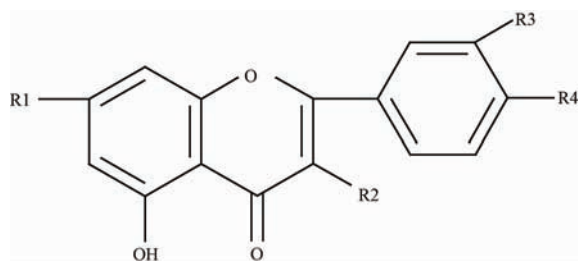
68: 67-6-epimer

**1.2.10 其他类型倍半萜** 从香附中分离得到的其他类型倍半萜有香附醇酮 (cyperolone, 69)<sup>[29-30]</sup>, cyclic acetal (70)<sup>[5]</sup>, aristolone (71)<sup>[6]</sup>。此外,从香附中又分离得到(-)-clovane-2, 9-diol (72) 和一个新的倍半萜 norcyperone (73)<sup>[40]</sup>。



## 2 黄酮类化合物

从香附中分离得到的黄酮类化合物有鼠李素-3-O-鼠李糖基(1 $\rightarrow$ 4)-吡喃鼠李糖苷 (rhamnetin 3-O- rhamnosyl-(1 $\rightarrow$ 4)-rhamnopyranoside, 74)<sup>[31]</sup>, leucocyanidin (75)<sup>[32]</sup>, chrysoeriol (76), kaempferol (77), luteolin (78), quercetin (79), quercetin-3- O- $\beta$ -D- rutinoside (80)<sup>[33]</sup>。



74: R1 = R3 = R4 = OH, R2 = -O-rhamnosyl-(1 $\rightarrow$ 4)-rhamnopyranoside,

75: R1 = R2 = R3 = R4 = OH,

76: R1 = OH, R2 = H, R3 = OMe, R4 = OH,

77: R1 = OH, R2 = OH, R3 = H, R4 = OH,

78: R1 = OH, R2 = H, R3 = OH, R4 = OH,

79: R1 = OH, R2 = OH, R3 = OH, R4 = OH,

80: R1 = OH, R2 = -O- $\beta$ -D-rutinoside, R3 = OH, R4 = OH,

## 3 三萜及甾醇类化合物

从香附中分离得到的三萜及甾醇类化合物有 oleanolic acid (81)<sup>[6]</sup>, 3-O-(2-rhamnosylglucosyl) oleanolic acid (82)<sup>[34]</sup>,  $\beta$ -sitosterol (83)<sup>[16]</sup>,  $\beta$ -sitosterol glucoside (84), stigmasterol (85), stigmasterol glucoside (86)<sup>[33]</sup>, 5 $\alpha$ , 8 $\alpha$ -表二氧-(20S, 22E, 24R)-麦角甾-6, 22-二烯-3 $\beta$ -醇(87)<sup>[40]</sup>。H

M Sayed 等从香附中分离得到 1 个新的甾体皂苷 sitosteryl (6-hentriacontanoyl)- $\beta$ -D-galactopyranoside (99)<sup>[38]</sup>。

#### 4 其他类化合物

从香附中分离得到的其他类化合物有 D-葡萄糖(88), D-果糖(89)<sup>[35]</sup>, 蔗糖(90)<sup>[36]</sup>, catechol(91), chlorogenic acid(92)<sup>[32]</sup>, p-coumaric(93), ferulic(94), vanillic(95), p-hydroxy-benzoic(96), protocatechuic acids(97)<sup>[37]</sup>, khellol glucoside(98)<sup>[33]</sup>, benzo- $\alpha$ -pyrone(coumarin)(100), khellin(101), visnagin(102), salicylic acid(103), caffeic acid(104), protocatechuic acid(105), ammiol(106), triclin(107), isorhamnetin(108)<sup>[38]</sup>。此外,从香附中还分离得到一个二萜类化合物玫瑰酮内酯(roseonolactone, 109)<sup>[40]</sup>。

#### 5 小结

香附是多年生的草本植物,资源丰富。香附是一种常用中药具有广泛的药理作用,如对中枢神经系统的作用,对心血管系统的作用,对消化系统的作用,雌激素样作用和抗菌消炎作用等等。对香附的化学成分和药理作用的研究虽然取得了一定的成果,但是目前药效学的研究多集中在提取物或复方制剂,对活性单体化合物的研究较少。为实现中药现代化,打破传统的中药观念,笔者对其化学成分进行了系统整理,有利于进一步对其化学成分和药理作用进行深入研究,对临床指导用药和新药的开发具有重要意义。

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