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菊科植物二萜类成分研究进展

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摘　要:二萜类是广泛存在于菊科植物中的一类特征成分,结构多样,一直备受植物化学家的关注。本文就菊科植物中该类成分的结构和主要活性进行综述,以期为它们的进一步开发利用提供依据和参考。

关键词:菊科;二萜;药理活性;研究进展

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Research Progress of Diterpenoids from Compositae

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Abstract:Diterpenoids is one of characteristic constituents widely distributed in Compositae plants,which possessa large variety of structures. In this paper,the research progress of those compounds and their activities in Compositae were reviewed,in order to provide some reference for further development and research of diterpenoids from this family.

Key words:Compositae;diterpenoids;pharmacological activity;research progress

菊科(Compositae)是双子叶植物纲中的第一大科,也是种子植物中最大和最进化的科之一。我国境内约有 240 个属,2300 个种,全国各地均有分布[1]。现代研究表明:菊科植物中次生代谢产物类型丰富多样,主要包括萜类、黄酮类、生物碱类、香豆素类和多糖类等[2]。这些,以萜类成分较为特征,研究也最多。其中,二萜类化学成分结构类型多样,包括贝壳杉烷(kaurane)型、克罗烷(clerodane)型、海松烷(pimarane)型、古柯烷(erythroxylane)型以及二萜生物碱、链状二萜(acyclic diterpenes)等。本文综述了菊科植物中二萜类化合物的结构类型及其药理活性,旨为菊科该类成分的进一步开发利用提供依据和参考。

1　主要结构类型

1.1　无环和单环二萜(Acyclic and momo-cyclic diterpenes)

链状和单环二萜在自然界存在较少,如从 *Tithonia* Desf. ex Jussieu[3] 中分离得到的(2*E*,6*E*,10*E*)-3-(hydroxymethyl)-7, 11, 15-trimethyl-hexadeca-2,6,10-triene-1,14,15-triol(**1**),从 *Egletes viscosa*[4] 中分离得到单环二萜 centipedic acid(**2**)。

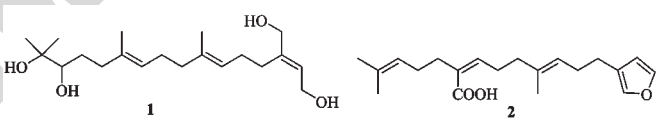

图 1　无环和单环二萜的化学结构

Fig. 1　Chemical structures of acyclicand momo-cyclic diterpenes

1.2　双环二萜(Bicyclic diterpenes)

该类成分主要分布于菊科 *Gymnosperma*、*Baccharis*、*Solidago* 和 *Microglossa* 属,结构类型主要为半日花烷型、克罗烷型和 halimane 型。

1.2.1　半日花烷型二萜(Labdane diterpenes)

半日花烷型双环二萜是菊科植物中最常见的二萜,结构如图 2 所示,基团变化最为丰富,主要分布在 *Lourteigia*[5]、*Gymnosperma*[6,7,22]、*Baccharis*[8,24,25]、*Grindelia*[9,17]、*Haplopappus*[10]、*Gutierreria*[10]、*Mikania*[11]、*Chrysothamnus*[12]、*Alomia*[13,14]、*Eupatorium*[15,16,19]、*Chrysothamnus*[18]、*Blumea*[20]、

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Pseudognaphalium[21]、*Aster*[23]和 *Solidago*[26-29]属等，来源如表 1 所示。

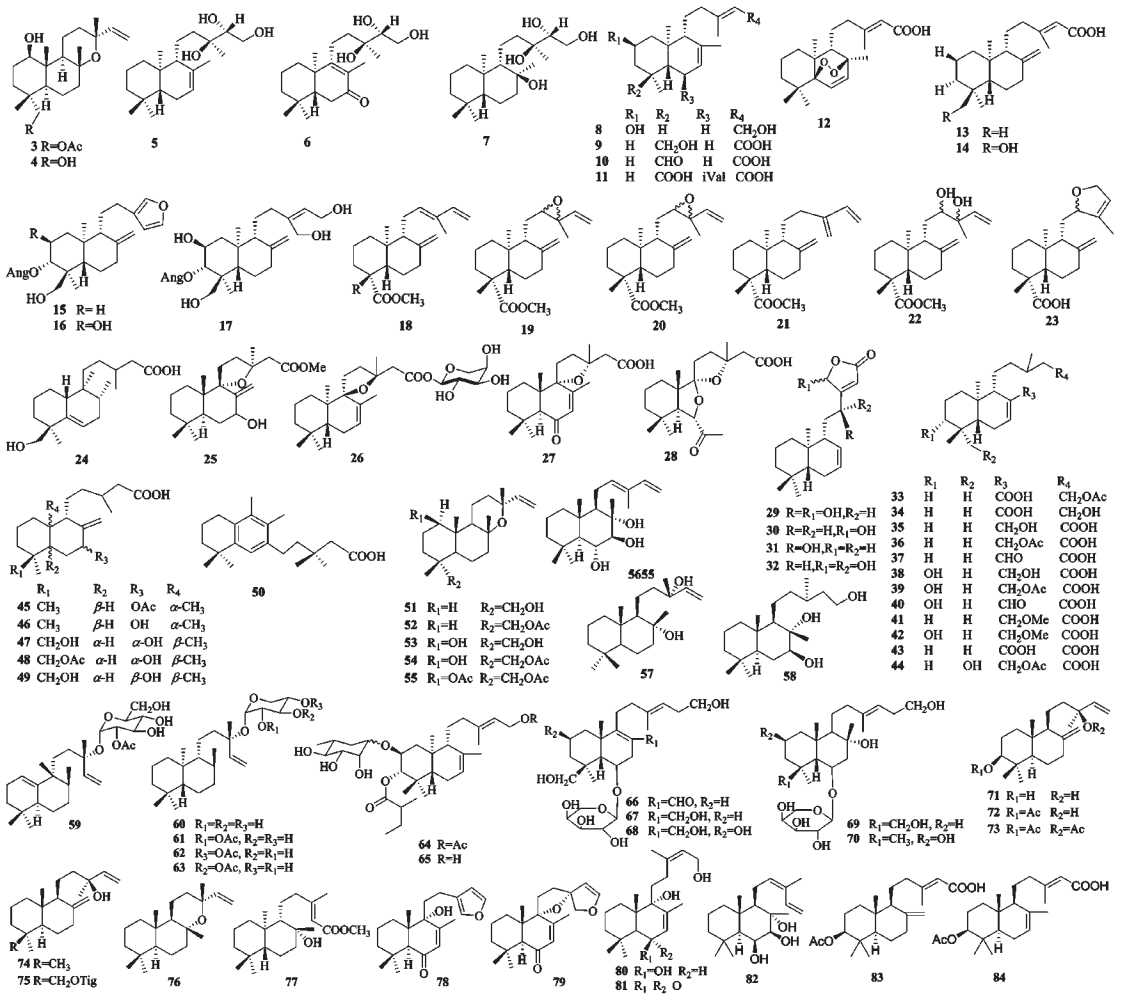

图 2 半日花烷型二萜的化学结构

Fig. 2 Chemical structures of labdane diterpenes

表 1 半日花烷型二萜及其来源植物

Table 1 Labdane diterpenes and their biological sources

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
3	jhanidiol acetate	*L. stoechadifolia*	44	-	*H. pectinatus*
4	jhanidiol	*L. stoechadifolia*	45	7-acetoxy-8(17)-labden-15oic acid	*E. salvia*
5	(+)-13*S*,14*R*,15-trihydroxy-*ent*-labd-7-ene	*G. glutinosum*	46	7-hydroxy-8(17)-labden-15-oic acid	*E. salvia*
6	(-)-13*S*, 14*R*, 15-trihydroxy-7-oxo-*ent*-labd-8(9)-ene	*G. glutinosum*	47	cordobic acid	*G. discoidea*
7	(+)-8*S*, 13*S*, 14*R*, 15-*ent*-labdanetetrol	*G. glutinosum*	48	cordobic acid 18-acetate	*G. discoidea*
8	Labda-7,13*E*-dien-2β,15-diol	*B. grisebachii*	49	7-epi-cordobic acid	*G. discoidea*

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
9	6, 18-dihydroxy-ent-labda-7, 13*E*-dien-15-oic acid	*H. glutinosus*	50	chrysolic acid	*C. paniculatus*
10	–	*G. spathulata*	51	jhanol	*E. jhanii*
11	–	*G. spathulata*	52	jhanol acetate	*E. jhanii*
12	–	*G. spathulata*	53	jhanidiol	*E. jhanii*
13	–	*G. spathulata*	54	jhanidiol-18-monoacetate	*E. jhanii*
14	–	*G. spathulata*	55	diacetate	*E. jhanii*
15	–	*G. gilliesii*	56	austroinulin	*B. glomerata*
16	–	*G. gilliesii*	57	13-epi-sclareol	*P. Cheiranthifolium*
17	–	*G. gilliesii*	58	gymnospermn	*G. glutinosa*
18	labda-8(17), 12, 14-trien-19-oic methyl ester	*M.* sp. nov	59	astern-13(*R*)-1(10), 14-diene-13-*O*-α-L-2`-acetylrhamnopy ranoside	*A. homochlamydeus*
19	labda-12α-epoxy-8(17), 12, 14-trien-19-oic methyl ester	*M.* sp. nov	60	*ent*-manool-13-*O*-β-D-xylopyransy	*A. homochlamydeus*
20	labda-12β-epoxy-8(17), 14-dien-19-oic methyl ester	*M.* sp. nov	61	*ent*-manool-13-*O*-β-D-2′-acetylxylopy ranoside	*A. homochlamydeus*
21	labda-8(17), 13(16), 14-trien-19-oic methyl ester	*M.* sp. nov	62	*ent*-manool-13-*O*-β-D-4′-acetylxylpyranoside	*A. homochlamydeus*
22	labda-12, 13-dihydroxy-8(17), 14-dien-19-oic methyl ester	*M.* sp. nov	63	*ent*-manool-13-*O*-β-D-3′-acetylxylpyranoside	*A. homochlamydeus*
23	labda-12, 15-epoxy-8(17), 13-dien-19-oic acid	*M.* sp. nov	64	2β-(L-Rhamnopyranosyl)-3α-angeEoyloxy-15-acetyloxy-7, l3(14)*E*-dien-ent-labdane	*B. meduliosa*
24	–	*H. paucidentatus*	65	2β-(L-Rhamnopyranosyl)-3α-angeloyloxy-15-hydroxy-7, 13(14)*E*-dien-*ent*-labdane	*B. meduliosa*
25	methyl 7β-hydroxy-8(17)-dehydrogrindelate	*G. chiloensis*	66	15, 19-dihydroxy1abda-8(9)-13(14)*E*-dien-17-al-6α-*O*-α-L-arabinopyranoside	*B. gaudichaudmna*
26	Grindel icacid 15-*O*-arabinoside	*G. boliviana*	67	15, 17, 19-trihydroxylabda-8(9)-13(14)*E*-dien-6α-*O*-α-L-arabinopyranoside	*B. gaudichaudmna*
27	6-oxogrindelic acid	*C. paniculatus*	68	2α, 5, 17, 19-tetrahydroxy1abda-8(9)-13(14)*E*-dien-6α-*O*-α-L-arabinopyranoside	*B. gaudichaudmna*
28	Chrysothame	*C. paniculatus*	69	8α, 15, 19-tetrahydroxy1abda-13(14)*E*-en-6α-*O*-α-L-arabinopyranoside	*B. gaudichaudmna*
29	*ent*-12*R*, 16-dihydroxylabda-7, 13-dien-15, 16-olide	*A. myriadenia*	70	2α, 8α, 15-tetrahydroxy1abda-13(14)*E*-en-6α-*O*-α-L-arabinopyranoside	*B. gaudichaudmna*
30	*ent*-16-hydroxylabda-7, 13-dien-15, 16-olide	*A. myriadenia*	71	(+)-3β-Hydroxymanool	*S. rugosa*
31	*ent*-12R-hydroxylabda-7, 13-dien-15, 16-olide	*A. myriadenia*	72	3β-Acetoxymanool	*S. rugosa*
32	myriadenolide	*A. myriadenia*	73	(+)-3β, 13-Diacetoxymanool	*S. rugosa*
33	15-acetoxy-7-labden-17-oic acid	*E. glutinosum*	74	(+)-manool	*S. rugosa*
34	15-hydroxy-7-labden-17-oic acid	*E. glutinosum*	75	(+)-18-Tigloyloxymanool	*S. rugosa*
35	–	*H. pectinatus*	76	manoyloxide	*S. rugosa*
36	–	*H. pectinatus*	77	–	*S. altissima*
37	–	*H. pectinatus*	78	–	*S. canadensis*

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编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
38	–	*H. pectinatus*	79	–	*S. canadensis*
39	–	*H. pectinatus*	80	–	*S. canadensis*
40	–	*H. pectinatus*	81	–	*S. canadensis*
41	–	*H. pectinatus*	82	solidagol	*S. canadensis*
42	–	*H. pectinatus*	83	3β-acetoxycopalic acid	*S. canadensis*
43	–	*H. pectinatus*	84	sempervirenic acid	*S. canadensis*

1.2.2 克罗烷型二萜(Clerodane diterpenes)

该类二萜主要分布于 *Baccharis*[8,30-32,35,36]、*Crassocephalum*[33]、*Aster*[75] 属、*Microglossa*[34]、*Egletes*[4]、*Pulicaria*[37]、*Haplopappus*[10]、*Solidago*[27,28,38-44] 和 *Nannoglottis*[45] 属等,结构及来源分别见图 3 和表 2。

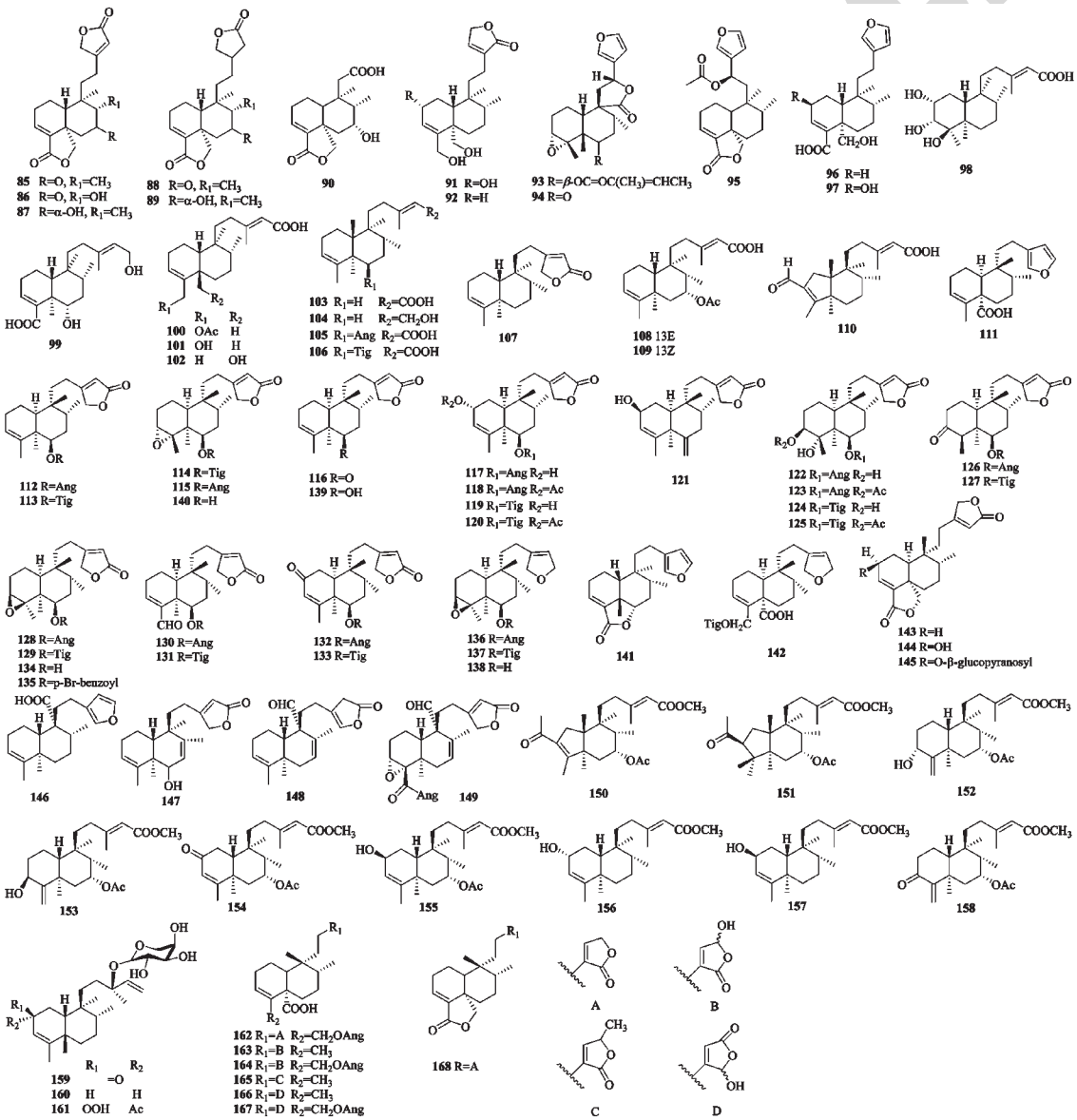

图 3 克罗烷型二萜的化学结构

Fig. 3 Chemical structures of clerodane diterpenes

表 2 克罗烷型二萜及其来源植物

Table 2 Clerodane diterpenes and their biological sources

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
85	audichanolides B	*B. gaudichaudiana*	127	–	*S. virgaurea*
86	baccharioI	*B. gaudichaudiana*	128	–	*S. virgaurea*
87	7α-hydroxy-3,13-clerodadiene-16,15:18,19-diolide	*B. trimera*	129	–	*S. virgaurea*
88	5*S*,8*R*,9*R*,10*R*-7-oxo-*ent*-clerodan-3,13-dien-18,19:15,16-diolide	*B. gaudichaudiana*	130	–	*S. virgaurea*
89	(+)-8*S*,13*S*,14*R*,15-*ent*-labdanetetrol	*B. genistelloides*	131	–	*S. virgaurea*
90	Labda-7,13*E*-dien-2β,15-diol	*B. genistelloides*	132	–	*S. virgaurea*
91	ent-2β, 18, 19-trihydroxycleroda-3, 13-dien-16,15-olide	*C. bauchiense*	133	–	*S. virgaurea*
92	18, 19-dihydroxy-5α, 10β-neo-cleroda-3,13(14)-dien-16,15-butenolide	*A. souliei*	134	–	*S. altissima*
93	6β-(2-methylbut-2(*Z*)-enoyl)-3α, 4α, 15, 16-bis-epoxy-8β, 10βH-*ent*-cleroda-13(16),14-dien-20,12-olide	*M. angolensis*	135	–	*S. altissima*
94	10β-hydroxy-6-oxo-3α, 4α, 15, 16-bis-epoxy-8βH-cleroda-13(16),14-dien-20,12-olide	*M. angolensis*	136	–	*S. altissima*
95	12-acetoxy-awtriwaic acid lactone	*E. viscosa*	137	–	*S. altissima*
96	hautriwaic acid	*B. sarothroides*	138	–	*S. altissima*
97	2-β-hydroxy hautriwaic acid	*B. sarothroides*	139	–	*S. altissima*
98	tucumanoic acid	*B. tucumanensis*	140	–	*S. altissima*
99	salvicin	*P. salviifolia*	141	–	*S. altissima*
100	–	*H. paucidentatus*	142	–	*S. altissima*
101	–	*H. paucidentatus*	143	2β-Hydroxy-6-deoxy-solidagolactone IV-18,19-olide	*S. gigantea*
102	–	*H. paucidentatus*	144	6-Deoxysolidagolactone IV-18,19-olide	*S. gigantea*
103	Kolavenic acid	*S. canadensis*	145	2β-*O*-β-D-glucopyranosyl-6-deoxy-solidagolactone IV-18,19-olide	*S. gigantea*
104	Kolavenol	*S. canadensis*	146	–	*S. canadensis*
105	6β-angeloyloxykolavenic acid	*S. canadensis*	147	–	*S. nemoralis*
106	6β-tigloyloxykolavenic acid	*S. canadensis*	148	–	*S. nemoralis*
107	Solidago lactone	*S. canadensis*	149	–	*S. nemoralis*
108	13*E*-7α-acetoxylkolavenic acid	*S. canadensis*	150	–	*S. altissima*
109	13*Z*-7α-acetoxylkolavenic acid	*S. canadensis*	151	–	*S. altissima*
110	*ent*-12*R*, 16-dihydroxylabda-7, 13-dien-15,16-olide	*S. altissima*	152	–	*S. altissima*
111	solidagoic acid A	*S. missouriensis*	153	–	*S. altissima*
112	–	*S. virgaurea*	154	–	*S. altissima*
113	–	*S. virgaurea*	155	–	*S. altissima*

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编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
114	–	*S. virgaurea*	156	–	*S. altissima*
115	–	*S. virgaurea*	157	–	*S. altissima*
116	–	*S. virgaurea*	158	–	*S. altissima*
117	–	*S. virgaurea*	159	(2*S*,5*S*,8*R*,9S,10*R*,13*S*)-2-oxo-13-*O*-α-L-arabinopyranosyl-3,14-clerodadiene	*N. carpesioides*
118	–	*S. virgaurea*	160	(2*S*,5*S*,8*R*,9*S*,10*R*,13*S*)-13-*O*-α-L-arabinopyranosyl-3,14-clerodadiene	*N. carpesioides*
119	–	*S. virgaurea*	161	(2*S*,5*S*,8*R*,9*S*,10*R*,13*S*)-2-hydroperoxy-13-*O*-α-L-arabinopyranosyl-3, 14-clerodadiene	*N. carpesioides*
120	–	*S. virgaurea*	162	Solidagoicacid D	*S. virgaurea*
121	–	*S. virgaurea*	163	Solidagoicacid E	*S. virgaurea*
122	–	*S. virgaurea*	164	Solidagoicacid F	*S. virgaurea*
123	–	*S. virgaurea*	165	Solidagoicacid G	*S. virgaurea*
124	–	*S. virgaurea*	166	Solidagoicacid H	*S. virgaurea*
125	–	*S. virgaurea*	167	Solidagoicacid I	*S. virgaurea*
126	–	*S. virgaurea*	168	cleroda-3,13(14)-dien-16,15;18,19-diolide	*S. virgaurea*

1.2.3 Halimane 二萜

该类化合物在菊科植物中分布很少,仅从 *Alomia myriadenia*[13] 中分离得到一种 halimane 型二萜,名为 *ent*-8*S*, 12*S*-epoxy-7*R*, 16-dihydroxyhalima-5(10),13-dien-15,16-olide(**169**)。

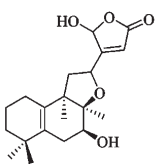

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图 4 halimane 二萜的化学结构

Fig. 4 Chemical structure of halimane diterpene

1.3 三环二萜(Tricyclic diterpenes)

1.3.1 松香烷型二萜(Abietane diterpenes)

该类化合物在菊科植物中分布不多,主要分布于 *Solidago* 属植物中,从 *S. petradoria*[10] 的地上部分分离出 succinate(**170**),从 *S. canadensis*[46] 中发现了一个 A 环开环的松香烷二萜(**171**),从 *S. rugosa*[26] 的提取物中鉴定了 6 个化合物,分别为 Entabieticacid(**172**)、18-Hydroxyabieta-7,13(14)-diene(**173**)、18-Tigloyloxyabieta-7,13(14)-diene(**174**)、7-Hydroxy-13, 15-dihydroxyabieta-8 (14)-ene-18-oic acid(**175**)、7-Hydroxy-13,15-dihyd roxyabieta-8(14)-ene-18-benzoic acid methyl ester(**176**)、15-Hydroxy-dehydroabietic acid(**177**),从 *Solidago nemoralis*[28] 中分离到(**178**~**181**)。

1.3.2 海松烷型二萜(Pimarane diterpenes)

目前,主要从 *Viguiera*[47-49]、*Siegesbeckia*[50,51]、*Mikania*[52]、*Aldama*[53] 和 *Smallanthus*[54] 属植物中发现该类二萜,结构变化主要集中在 8 位和 9 位的双键的位置,以及 2 位、3 位、16 位、17 位和 19 位的取

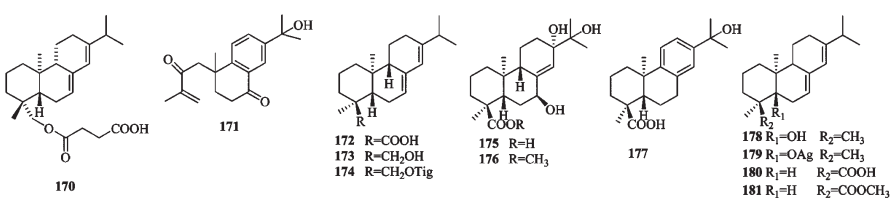

图 5 松香烷型二萜的化学结构

Fig. 5 Chemical structures of abietane diterpenes

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代基。另外,少量化合物为二萜苷类成分,糖的类型为葡萄糖,成苷位置主要为 16 位和 17 位,结构及来源分别如图 6 和表 3 所示。

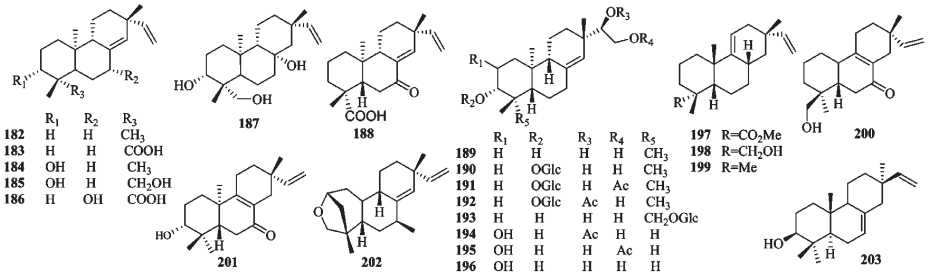

图 6 海松烷型二萜的化学结构

Fig. 6 Chemical structures of pimarane diterpenes

表 3 海松烷型二萜及其来源植物

Table 3 Pimarane diterpenes and their biological sources

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
182	*ent*-8(14),15-pimaradiene	*V. arenaria*	193	*ent*-(15*R*), 16, 19-trihydroxypimar-8(14)-ene-19-*O*-β-D-glucopyranoside	*S. orientalis*
183	*ent*-pimara-8(14),15-dien-19-oic acid	*V. arenaria*	194	*ent*-15-acetoxy-2α,16,19-trihydroxypimar-8(14)-ene	*S. orientalis*
184	*ent*-8(14),15-pimaradien-3β-ol	*V. arenaria*	195	*ent*-16-acetoxy-2α,15,19-trihydroxypimar-8(14)-ene	*S. orientalis*
185	*ent*-8(14),15-pimaradiene-3β,19-diol	*V. arenaria*	196	kirenol	*S. orientalis*
186	7β-hydroxy-*ent*-pimara-8(14), 15-dien-19-oic acid	*V. arenaria*	197	methyl-*ent*-pimara-9(11), 15-dien-19-oate	*M. triangularis*
187	*ent*-15-pimaradiene-8β,19-diol	*V. arenaria*	198	*ent*-pimara-9(11),15-dien-19-ol	*M. triangularis*
188	7-keto-*ent*-pimara-8(14),15-dien-19-oic acid	*V. arenaria*	199	*ent*-pimura-9(11),15-dien	*M. triangularis*
189	darutigenol	*S. orientalis*	200	*ent*-7-oxo-pimara-8,15-diene-18-ol	*A. discolor*
190	darutoside	*S. orientalis*	201	*ent*-2S,4S-2-19-epoxy-pimara-8(3),15-diene-7β-ol	*A. discolor*
191	hythiemoside A	*S. orientalis*	202	*ent*-7-oxo-pimara-8,15-diene-3β-ol	*A. discolor*
192	hythiemoside B	*S. orientalis*	203	Pimara-7,15-dien-3β-ol	*S. sonchifolius*

1.3.3 古柯烷型二萜(Erythroxylane diterpenes)

迄今为止,只从菊科植物 *Mikania* sp. nov[11] 中分离得到 1 个古柯烷型二萜 erythroxyla-3,15-dien-19-oic acid(**204**)。

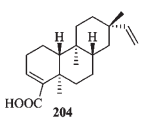

图 7 古柯烷型二萜的化学结构

Fig. 7 Chemical structure of erythroxylane diterpene

1.4 四环二萜(Tetracyclic diterpenes)

1.4.1 对映贝壳杉烷型二萜(ent-Kaurane diterpenes)

目前,主要从 *Wedelia*[55-57]、*Espeletia*[58]、*Artemisia*[59]、*Stevia*[58]、*Leontopodium*[60]、*Senecio*[61]、*Eupatorium*[62]、*Antennaria*[63]、*Psiadia*[64]、*Atractylis*[65]、*Aldama*[53]、*Gochnatia*[66,71]、*Mikania*[67-70]、*Solidago*[26,28,40]、*Ageratina*[72] 和 *Pulicaria*[73] 属植物中发现该类型化合物及其糖苷,但基本骨架变化较少,结构

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及来源分别如图 8 和表 4 所示。

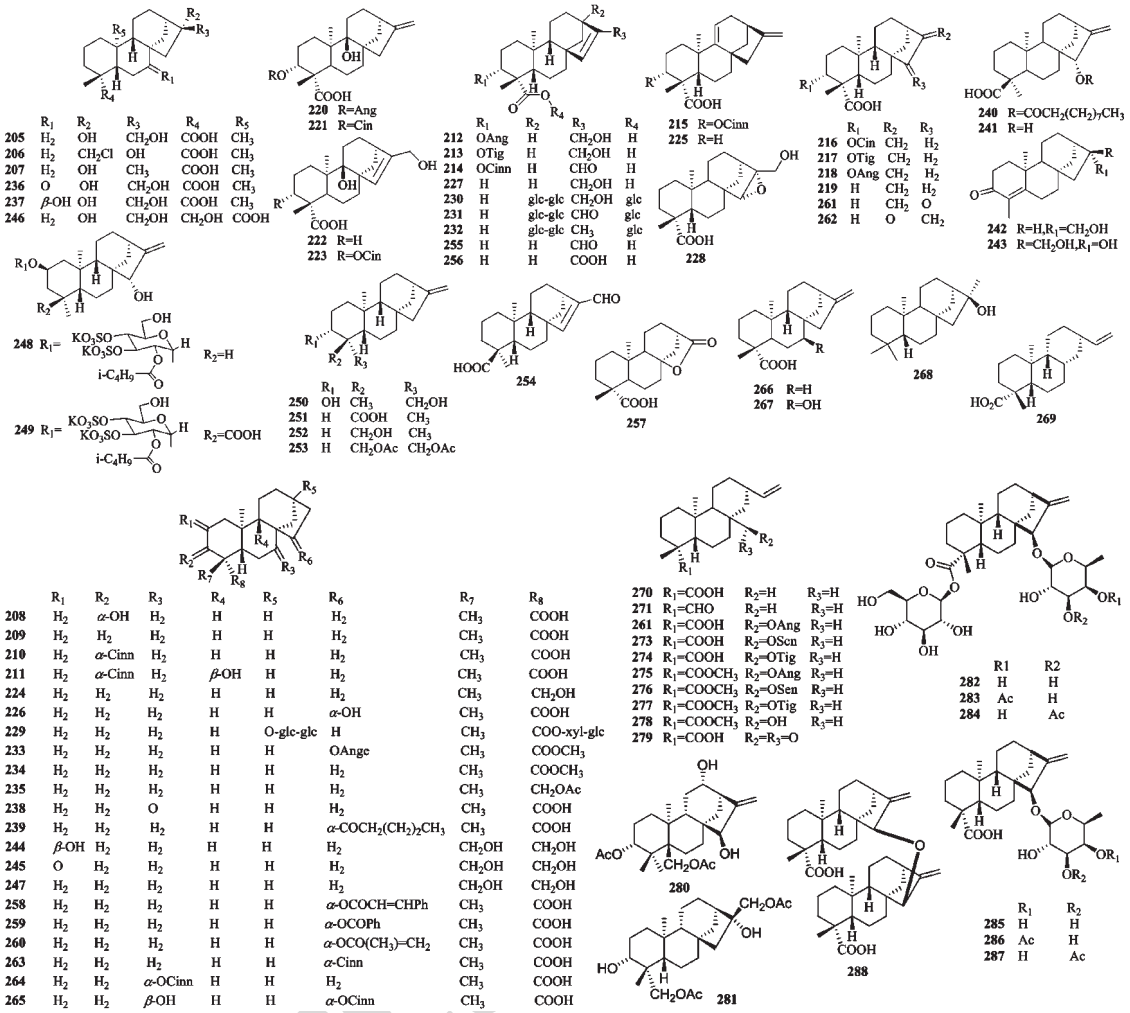

图 8 对映贝壳杉烷型二萜的化学结构

Fig. 8 Chemical structure of *ent*-kaurane diterpenes

表 4 对映贝壳杉烷型二萜及其来源植物

Table 4 *ent*-kaurane diterpenes and their biological sources

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
205	16α, 17, 19-trihydroxy-18-nor-*ent*-kauran-4β-ol	*W. trilobata*	247	18, 19-dihydroxy-kaur-16-en	*P. punctulata*
206	17-chloro-16β-hydroxy-*ent*-kauran-19-oic acid	*W. trilobata*	248	atractyloside	*A. gummifera*
207	(-)-16α-hydroxy-kauran-19-oic acid	*W. trilobata*	249	4-carboxy atractyloside	*A. gummifera*
208	3β-hydroxy-*ent*-kaur-16-en-19-oic acid	*W. trilobata*	250	*ent*-3-α-hydroxy-kaur-16-en-18-ol	*A. discolor* *G. polymorpha* ssp. *polymorpha*
209	*ent*-kaur-16-en-19-oic acid	*W. trilobata*	251	*ent*-kaur-16-en-18-oic acid	*M. banisteriae*
210	3α-cinnamoyloxy-*ent*-kaur-16-en-19-oic acid	*W. trilobata*	252	*ent*-kaur-16-en-18-ol	*M. banisteriae*

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
211	3α-cinnamoyloxy-9β-hydroxy-*ent*-kaur-16-en-19-oic acid	*W. trilobata*	253	18,19-diacetoxy-*ent*-kaur-16-ene	*M. banisteriae*
212	3α-angeloyloxy-17-hydroxy-*ent*-kaur-15-en-19-oic acid	*W. prostrata*	254	17-oxo-*ent*-kaur-15(16)-en-18-oic acid	*M. banisteriae*
213	3α-tigloyloxy-17-hydroxy-*ent*-kaur-15-en-19-oic acid	*W. prostrata*	255	17-oxo-kaur-15-en-18-oic acid	*M. hirsutissima*
214	wedelidin B	*W. prostrata*	256	kaur-15-ene-17,18-dioic acid	*M. hirsutissima*
215	3α-cinnamoyloxykaur-9(11),16-dien-19-oic acid	*W. prostrata*	257	2H-3,5α-methanonaphth[2,1β]oxepin-8-carboxylic acid	*M. hirsutissima*
216	3α-cinnamoyloxykaur-16-en-19-oic acid	*W. prostrata*	258	15-[(1-oxo-3-phenyl-2-propenyl)oxy]-kaur-16-en-18-oic acid	*M. hirsutissima*
217	*ent*-3β-tigloyloxykaur-16-en-19-oic acid	*W. prostrata*	259	15-(benzoyloxy)-kaur-16-en-18-oic acid	*M. hirsutissima*
218	*ent*-3β-angeloyloxykaur-16-en-19-oic acid	*W. prostrata*	260	15-[(2-methyl-1-oxo-2-propenyl)oxy]-kaur-16-en-18-? oic acid?	*M. hirsutissima*
219	*ent*-kaur-16-en-19-oic acid	*W. prostrata*	261	*ent*-kaur-15-oxo-16-en-19-oic acd	*M. hirsutissima*
220	3α-angeloyloxy-9β-hydroxy-*ent*-kaur-16-en-19-oic acid	*W. chinensis*	262	*ent*-kaur-16-oxo-18-oic acid	*M. hirsutissima*
221	3α-cinnamoyloxy-9β-hydroxy-*ent*-kaur-16-en-19-oic acid	*W. chinensis*	263	*ent*-15β-cinnamoyloxy-kaur-16-en-19-oic acid	*M. vitifolia*
222	17-hydroxy-*ent*-kaur-15-en-19-oic acid	*W. chinensis*	264	*ent*-7α-cinnamoyloxy-15β-hydroxy-kaur-16-en-19-oic acid	*M. vitifolia*
223	3α-cinnamoyloxy-17-hydroxy-*ent*-kaur-15-en-19-oic acid	*W. chinensis*	265	*ent*-15β-cinnamoyloxy-7α-hydroxy-kaur-16-en-19-oic acid	*M. vitifolia*
224	*ent*-kaur-16-en-19-ol	*E. schultzii*	266	(-)-kaur-16-en-19-oic aicd	*S. rigida*
225	grandiflorenic acid	*E. schultzii*	267	7β-hydroxy-(-)-kaur-16-en-19-oic acid	*S. rigida*
226	grandifloric acid	*A. korshinskyi*	268	(-)-kauran-16β-ol	*S. rigida*
227	17-hydroxy-*ent*-kaur-15-en-19-oic acid	*A. korshinskyi*	269	(-)-Kaur-16-en-19-oic acid	*S. rugosa*
228	15β, 16β-epoxy-17-hydroxy-*ent*-kauran-19-oic acid	*A. korshinskyi*	270	–	*S. nemoralis*
229	13-[(2-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)oxy]-kaur-16-en-18-oic acid-(6-*O*-β-D-Xylopyranosyl-β-D-glucopyranosyl) ester	*S. rebaudiana*	271	–	*S. nemoralis*
230	13-[(2-*O*-β-D-glucopyranosyl-β-$_D$-glucopyranosyl) oxy]-17-hydroxy-kaur-15-en-18-oic acid β-D-glucopyranosyl ester	*S. rebaudiana*	272	–	*S. nemoralis*
231	13-[(2-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)oxy]-17-oxo-kaur-15-en-18-oic acid β-D-glucopyranosyl ester	*S. rebaudiana*	273	–	*S. nemoralis*
232	13-[(2-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)oxy]-kaur-15-en-18-oic acid β-D-glucopyranosyl ester	*S. rebaudiana*	274	–	*S. nemoralis*
233	methyl-15β-angeloyloxy-*ent*-kaur-16-en-19-oate	*L. Franchetii*	275	–	*S. nemoralis*
234	methyl-*ent*-kaur-16-en-19-oate	*L. Franchetii*	276	–	*S. nemoralis*
235	19-acetoxy-*ent*-kaur-16-ene	*L. Franchetii*	277	–	*S. nemoralis*

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编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
236	*ent*-7-oxo-16α, 17-dihydroxykauran-19-oic acid	*S. erechtitoides*	278	–	*S. nemoralis*
237	*ent*-7β-hydroxykaur-16-en-19-oic acid	*S. erechtitoides*	279	–	*S. nemoralis*
238	*ent*-7-oxokaur-16-en-19-oic acid	*S. erechtitoides*	280	*ent*-3β,19-Diacetoxy-12α,15-β-dihydroxy-kaur-16-ene	*G. polymorpha*
239	15α-decanoyloxy-kaur-16-en-19-oic acid	*E. betonicaeforme*	281	*ent*-17, 19-Diacetoxy-3β, 16β-dihydroxykaurane	*G. polymorpha*
240	15α-decanoyloxy-kaur-16-en-19-oic acid	*E. betonicaeforme*	282	*ent*-15β-(β-L-Fucosyloxy) kaur-16-en-19-oic acid β-D-glucopyranosyl ester	*A. cylindrica*
241	15α-hydroxy-kaur-16-en-19-oic acid	*E. betonicaeforme*	283	*ent*-15β-(4-Acetoxy-β-L-fucosyloxy) kaur-16-en-19-oic acid β-D-glucopyranosyl ester	*A. cylindrica*
242	16β-H-17-hydroxy-3-oxo-19-nor-*ent*-kaur-4-ene	*A. geyeri*	284	*ent*-15β-(3-Acetoxy-β-L-fucosyloxy) kaur-16-en-19-oic acid β-D-glucopyranosyl ester	*A. cylindrica*
243	16α, 17-dihydroxy-3-oxo-19-nor-*ent*-kaur-4-ene	*A. geyeri*	285	*ent*-15β-(β-L-Fucosyloxy) kaur-16-en-19-oic acid	*A. cylindrica*
244	2β,18,19-triol-16-ene-kauran	*P. punctulata*	286	*ent*-15β-(4-Acetoxy-β-L-fucosyloxy) kaur-16-en-19-oic acid	*A. cylindrica*
245	18,19-dihydroxy-kaur-16-en-2-one	*P. punctulata*	287	*ent*-15β-(3-Acetoxy-β-L-fucosyloxy) kaur-16-en-19-oic acid	*A. cylindrica*
246	16,17,19-trihydroxy-kauran-20-oic acid	*P. punctulata*	288	15β, 15′β-oxybis (*ent*-kaur-16-en-19-oic acid)	*P. inuloides*

1.5 其他类型二萜(Other type diterpenes)

除了上述四种类型的二萜类成分,还从 *Artemisia korshinskyi*[59], *Jasonia montana*[74] 和 *Chrysothamnus paniculatw*[12] 三种植物中分离得到 6 种其他类型的二萜成分(**289 ~ 294**)。

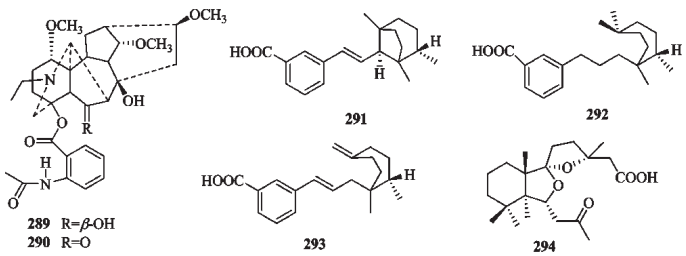

图 9 其他类型二萜的化学结构

Fig. 9 Chemical structure of other type diterpenes

表 5 其他类型二萜及其来源植物

Table 5 Other type diterpenes and their biological sources

编号 No.	化合物名称 Name	植物来源 Source	编号 No.	化合物名称 Name	植物来源 Source
289	artekorine	*A. korshinskyi*	292	jasonin-b	*J. montana*
290	6-ketoartekorine	*A. korshinskyi*	293	jasonin-c	*J. montana*
291	jasonin-a	*J. montana*	294	chrysothame	*C. paniculatw*

2 生物活性研究概况

2.1 抗菌活性

Serrano R 等人[7]采用了六种病原真菌,对从 *G. glutinosum* 中分离得到的化合物进行抗菌实验。结果表明 jhanidiol acetate(**3**)对实验中的五种真菌都具有活性,特别对镰孢和须发癣菌和纹枯病菌最敏感,IC_{100}分别为 0.230 and 0.240 mg/mL,IC_{50}分别

为 0.100 和 0.130 mg/mL。Porto TS 等人[48,49]研究了对映海松烷型二萜的抗菌效果,结果显示 *ent*-pimara-8(14),15-dien-19-oic acid(**176**)、*ent*-8(14),15-pimaradien-3β-ol(**177**)和 *ent*-15-pimaradiene-8β,19-diol(**180**)对革兰氏阳性菌的抑制作用较好,并且具有明显的抗龋齿作用。此外,张永红等人[75]从 *A. souliei* 中分离得到 18,19-dihydroxy-5α,10β-neocleroda-3,13(14)-dien-16,15-buteno-lide(**88**),对枯草芽孢杆菌、大肠杆菌和金黄色葡萄球菌具有一定的抑制作用。

2.2 抗炎活性

Calou IBF 等人[4]对 centipedic acid(**2**)和 12-acetoxyhawtriwaic acid lactone(**91**)进行急性和慢性老鼠耳朵发炎模型实验,结果表明抗皮炎机制是通过减少中性粒细胞汇集和炎症性细胞因子 TNF-α 和 IFN-γ 的产生。Wang 等人[76]对奇任醇(**189**)治疗胶原诱导性关节炎(CIA)的机制研究结果表明,奇任醇可通过减少 CIA 中滑液的炎症因子 IL-1β 的含量来阻止炎症反应的发生。另外,其与氢化泼尼松联合用药还能抑制炎症因子 NF-κB 的活性。

2.3 细胞毒活性

刘晓月等[77]以活性为导向,从加拿大一枝黄花花序的乙酸乙酯萃取物中分离得到两个抗癌活性成分,6β-当归酰克拉文酸(**101**)和 6β-巴豆酰克拉文酸(**102**)。二者对肝癌 SMMC77221、乳腺癌 Bcap37、白血病 K562 和肺癌 SPC-A 四种人体癌细胞的半数抑制浓度为 7-12 μg/mL 之间。高雪[78]研究发现,从暗花金挖耳(*Carpesium triste*)中分离得到的链状二萜(2*E*,6*Z*,11*S*,12*R*)-3,7,11,15-teramethylhexadeca-2,6,14-triene-7-[(acetyloxy)methyl]-12,19-diol-1-acetate 对人肝癌细胞 SMMC-7721 和白血病细胞 HL-60 的生长具有明显的抑制作用,推测其活性可能与这类化合物中 C-1 位上乙酰氧基的存在与否和乙酰氧基的个数有关。

2.4 α-葡萄糖苷酶抑制活性

2011 年,项峥等人[79]研究发现,*S. sonchifolius* 的粗提取物有明显的降血糖作用。他们从该植物中分离得到 26 个化合物,其中含有 α,β-不饱和脂肪酸结构的亚贡二萜酸类成分 A ~ D 均对 α-葡萄糖苷酶显示出抑制活性,且最大抑制率均高于 70%,与阳性药相当。

2.5 抗血管生成活性

Huang W 等人[57]对从 *Wedelia chinensis* 中分离的对映贝壳杉烷型二萜 **220 ~ 223** 进行斑马鱼血管生成实验,斑马鱼胚胎的剂量依赖性抑制血管生成浓度在 2.5 ~ 10 μM,而 CHKA(**221**)具有最好的抑制作用,VEGF-VEGF receptor 2(Kdr)和 angpiopoietin(Ang)-Ang receptor(Tie)是血管生成的两个主要信号通路,CHKA 可以显著减少 VEGF 的基因表达,不同浓度的 CHKA 对 HUVECs 细胞均没有显著的细胞毒性,在非细胞毒剂量下对 VEGF 诱导的细胞增殖有明显的抑制作用。

3 结语

近年来,天然产物中不断有新的二萜骨架被发现。根据 The Combined Chemical Dictionary 的记载,迄今二萜类共有 119 种骨架,10000 多种化合物。这类化合物不仅结构多样,而且生物活性良好,从中涌现出不少明星分子,如紫杉醇、穿心莲内酯、雷公藤内酯、甜菊苷等。除此之外,根据文献调研,菊科中其他二萜类成分活性研究普遍较少,深度较浅。在我国,有药用记载的该科植物约有 120 属,500 多种[80,81],大多数味甘性寒,入肝、肺两经,主要具有清热解毒、疏风、平肝明目等功效,可治疗感冒发热、头痛、眼目昏花、心胸烦热等疾病。笔者认为,从基源植物的传统功效出发研究菊科二萜类化合物的生物活性,有效结合现代药理学研究方法,是快速发现该类活性先导化合物的有效途径之一。

参考文献

1 Li YP(李玉平),*et al*. A brief review on the Compositae resource and its utilization. *J Northwest A&F Univ*,*Nat Sci*(西北农林科技大学学报,自科版),2003,31:150-156.

2 Kunming Institute of Botany,Chinese Academy of Sciences(中国科学院昆明植物研究所). Flora of Yunnan(云南植物志). Beijing:Science Press,2004. Vol 13,1.

3 Chagas-Paula DA,*et al*. Ethnobotany,chemistry and biological activities of the *Genus tithonia*(Asteraceae). *Chem Biodivers*,2012,9:210-235.

4 Calou IBF,*et al*. Topically applied diterpenoids from *Egletes viscosa*(Asteraceae) attenuate the dermal inflammation in mouse ear induced by tetradecanoylphorbol 13-acetate-and oxazolone. *Biol Pharm Bull*,2008,31:1511-1516.

5 Mondolis E,*et al*. Vasorelaxant effects in aortic rings of eight diterpenoids isolated from three Venezuelan plants. *Revista Brasileira de Farmacognosia*,2013,23:769-775.

6 Quintanilla-Licea R,*et al*. Bioassay-guided isolation and identification of cytotoxic compounds from*Gymnosperma glutinnosum* leaves. *Molecules*,2012,17:11229-11241.

7 Serrano R,*et al*. Ent-labdane type diterpene with antifungal activity from *Gymnosperma glutinnosum*(Spreng.) Less.

(Asteraceae). *BLACPMA*, 2009, 8: 412-418.

8 Abad MJ, *et al*. *Baccharis* (Compositae): a review update. *Arkivoc*, 2007, 7: 76-96.

9 De LAMM, *et al*. A new depigmenting-antifungal methylated grindelane from *Grindelia chiloensis*. *Chem Biodivers*, 2017.

10 Jakupovi J, *et al*. Further diterpenes from plants of the compositae, subtribe solidagininae. *Phytochemistry*, 1986, 25: 1873-1881.

11 Nunez CV, *et al*. Diterpene acids from *Mikania* sp. nov (Asteraceae). *Biochem Syst Ecol*, 2004, 32: 233-237.

12 Hoffmann JJ, *et al*. Constituents of *Chrysothamnus paniculatus* (Compositae): chrysothame, a new diterpene and 6-oxogrindelic acid. *J Org Chem*, 1982, 47: 1725-1727.

13 Scio E, *et al*. Diterpenes from *Alomia myriadenia* (Asteraceae) with cytotoxic and trypanocidal activity. *Phytochemistry*, 2003, 64: 1125-1131.

14 Souza-Fagundes EM, *et al*. *In vitro* activity of labdane diterpene from *Alomia myriadenia* (Asteraceae): immunosuppression via induction of apoptosis in monocytes. *IntImmunopharm*, 2003, 3: 383-392.

15 El-Seedi HR, *et al*. Antimicrobial diterpenoids from *Eupatorium glutinosum* (Asteraceae). *J Ethnopharmacol*, 2002, 81: 293-296.

16 Urzua A, *et al*. Antimicrobial study of the resinous exudate and of diterpenoids isolated from *Eupatorium salvia* (Asteraceae). *J Ethnopharmacol*, 1998, 62: 251-254.

17 Timmermann BN, *et al*. Labdane diterpenoids from *Grindelia discoidea* (Asteraceae). *Phytochemistry*, 1986, 25: 1389-1392.

18 Timmermann BN, *et al*. Constituents of *Chrysothamnus paniculatus* (Compositae). *J Org Chem*, 1982, 47: 4114-4116.

19 Gonzalez AG, *et al*. Five new labdane diterpene oxides from *Eupatorium jhanii*. *Phytochemistry*, 1977, 16: 107-110.

20 Ohtsuki T, *et al*. Isolation of austroinulin possessing cell cycle inhibition activity from *Blumea glomerata* and revision of its absolute configuration. *Planta Med*, 2004, 70: 1170-1173.

21 Mendoza L, *et al*. Antibacterial activity of 13-epi-sclareol, a labdane type diterpene isolated from *Pseudognaphalium heterotrichium* and *P. cheiranthifolium* (Asteraceae). *Boletín de la Sociedad Chilena de Química*, 2002, 47: 91-98.

22 Miyakado M, *et al*. A new labdantriol from *Gymnosperma glutinosa*. *Phytochemistry*, 1974, 13: 189-190.

23 Yang CX, *et al*. Diterpene glycosides from *Aster homochlamydeus*. *Die Pharmazie-An IntJ Pharm Sci*, 2005, 60: 461-463.

24 Cifuente DA, *et al*. Two new labdane diterpene from flowers of *Baccharismedullosa* DC. *Nat Prod Lett*, 2001, 15: 425-431.

25 Fullas F, *et al*. Gaudichaudiosides A-E, five novel diterpene glycoside constituents from the sweet-tasting plant, *Baccharis gaudichaudiana*. *Tetrahedron*, 1991, 47: 8515-8522.

26 Lu T, Vargas D, *et al*. Diterpenes from *Solidago rugosa*. *Phytochemistry*, 1995, 38: 451-456.

27 Tori M, *et al*. Nine new clerodane diterpenoids from rhizomes of *Solidago altissima*. *Phytochemistry*, 1999, 52: 487-493.

28 Bohlmann F, *et al*. Sesquiterpene and diterpene derivatives from *Solidago* species. *Phytochemistry*, 1980, 19: 2655-2661.

29 Li J, *et al*. In vitro evaluation of potential bitterness-masking terpenoids from the Canada goldenrod (*Solidago canadensis*). *J Nat Prod*, 2014, 77: 1739-1743.

30 Januário AH, *et al*. Neo-clerodane diterpenoid, a new metalloprotease snake venom inhibitor from *Baccharis trimera* (Asteraceae): anti-proteolytic and anti-hemorrhagic properties. *Chem Biol Interact*, 2004, 150: 243-251.

31 Akaike S, *et al*. A New ent-Clerodane Diterpene from the Aerial Parts of *Baccharis gaudichaudiana*. *Chem Pharm Bull*, 2003, 51: 197-199.

32 Kuroyanagi M, *et al*. Studies on the constituents of *Baccharis genistelloides*. *Chem Pharm Bull*, 1985, 33: 5075-5078.

33 Tchinda AT, *et al*. A new ent-clerodane diterpenoid from*Crassocephalum bauchiense* Huch. (Asteraceae). *Nat Prod Res*, 2015, 29: 1990-1994.

34 Tene M, *et al*. Clerodane diterpenoids from *Microglossa angolensis*. *Tetrahedron*, 2005, 61: 2665-2658.

35 Wollenweber E, *et al*. Flavonoids and Terpenoids from the Exudates of Some *Baccharis* Species. *Zeitschrift Für Naturforschung C*, 2014, 41: 87-93.

36 Rossomando PC, *et al*. A diterpene acid from *Baccharis tucumanensis*. *Phytochemistry*, 1985, 24: 787-790.

37 Nurmukhamedova MR, *et al*. Diterpenoids of *Pulicaria salviifolia*. II. Structure of salvicin. *Chem Nat Compd*, 1986, 22: 277-279.

38 LU T, *et al*. Polyacetylenes and diterpenes from *Solidago canadensis*. *Phytochemistry*, 1993, 32: 1483-1488.

39 Bohlmann F, *et al*. A diterpene with a new carbon skeleton from *Solidago altissima*. *Phytochemistry*, 1985, 24: 1114-1115.

40 Le Quesne PW, *et al*. Oxidized kaurene derivatives from leaves of *Solidago missouriensis* and *S. rigida*. *Phytochemistry*, 1985, 24: 1785-1787.

41 Goswami A, *et al*. Clerodanes from *Solidago virgaurea*. *Phytochemistry*, 1984, 23: 837-841.

42 Nishino C, *et al*. Piscicidal cis-clerodane diterpenes from *solidago altissima* 1: absolute configurations of 5α, 10α-cis-clerodanes. *Tetrahedron lett*, 1984, 25: 2809-2812.

43 Jurenitsch J, *et al*. Diterpenebutenolides in *Solidago gigantea*. *Phytochemistry*, 1988, 27: 626-627.

44 Starks CM, *et al*. Antibacterial clerodane diterpenes from Goldenrod (*Solidago virgaurea*). *Phytochemistry*, 2010, 71: 104-109.

45 Meng X H, *et al*. New clerodane diterpenoid glycosides from the aerial parts of *Nannoglottis carpesioides*. *Fitoterapia*,

www.lrcwlae.cn

2014,93:39-46.

46 Anthonsen T, *et al*. Constituents of Solidago species-I: The constitution and stereochemistry of diterpenoids from *Solidago canadensis* L. *Tetrahedron*,1969,25:2233-2239.

47 Ambrosio SR, *et al*. Trypanocidal activity of pimarane diterpenes from *Viguiera arenaria* (Asteraceae). *Phytother Res*, 2008,22:1413-1415.

48 Porto TS, *et al*. Antimicrobial ent-pimarane diterpenes from *Viguiera arenaria* against gram-positive bacteria. *Fitoterapia*, 2009,80:432-436.

49 Porto TS, *et al*. Pimarane-type diterpenes: antimicrobial activity against oral pathogens. *Molecules*,2009,14:191-199.

50 Giang PM, *et al*. *Ent*-Pimarane-Type Diterpenoids from *Siegesbeckia orientalis* L. *Chem Pharm Bull*,2005,53:232-234.

51 Xiong J, *et al*. The constituents of *Siegesbeckiaorientalis*. *Nat Pro Sci*,1997,3:14-18.

52 Knudsen FS, *et al*. Pimaradiene diterpenes from *Mikania triangularis*. *Phytochemistry*,1986,25:1240-1242.

53 Nogueira MS, *et al*. *ent*-Pimarane and *ent*-Kaurane diterpenes from *Aldama discolor* (Asteraceae) and their antiprotozoal activity. *Molecules*,2016,21:1237.

54 Gallo MBC, *et al*. Endophytic fungi found in association with *Smallanthus sonchifolius*(Asteraceae) as resourceful producers of cytotoxic bioactive natural products. *J Basic Microbiol*, 2009,49:142-151.

55 Ren H, *et al*. Two new ent-? kaurane diterpenoids from *Wedelia trilobata* (L.) Hitchc. *Phytochemistry Lett*, 2015, 11:260-263.

56 Wu Z, *et al*. Three new ent-kaurane diterpenes from the herbs of *Wedelia prostrata*. *J Nat Med*,2016:1-5.

57 Huang W, Liang Y, Wang J, et al. Anti-angiogenic activity and mechanism of kaurane diterpenoids from *Wedelia chinensis*. *Phytomedicine*,2016,23:283-292.

58 Chaturvedula VSP, *et al*. Minor diterpenoid glycosides from the leaves of *Stevia rebaudiana*. *Phytochemistry Lett*,2011,4: 209-212.

59 Sham′yanov ID, *et al*. Sesquiterpene lactones and new diterpenoid alkaloids from *Artemisia korshinskyi*. *Chem Nat Comp*, 2012,48:616-621.

60 Safer S, *et al*. Metabolic fingerprinting of *Leontopodium* species (Asteraceae) by means of ^{1}H NMR and HPLC-ESI-MS. *Phytochemistry*,2011,72:1379-1389.

61 Ndom JC, *et al*. New alkamide and ent-kaurane diterpenoid derivatives from *Senecio erechtitoides* (Asteraceae). *Phytochemistry Lett*,2010,3:201-206.

62 Albuquerque MRJR, *et al*. Terpenoids, flavonoids and other constituents of *Eupatorium betonicaeforme* (Asteraceae). *J Brazil Chem Soc*,2006,17:68-72.

63 Ahmed AA, *et al*. Nor-ent-kaurane diterpenes and hydroxylactones from *Antennaria geyeri* and *Anaphalis margaritacea*. *Phytochemistry*,2004,65:2539-2543.

64 Midiwo JO, *et al*. Bioactive compounds from some Kenyan ethnomedicinal plants: Myrsinaceae, Polygonaceae and *Psiadia punctulata*. *Phytochemistry Rev*,2002,1:311-323.

65 Camarda L, *et al*. The structure and the stereochemistry of atractyliretin. *Planta Medica*,1986,52:363-365.

66 Catalan CAN, *et al*. Coumarins and a kaurane from *Gochnatia polymorpha* ssp. polymorpha from Paraguay. *Biochem Syst Ecol*,2003,31:417-422.

67 Lobitz GO, *et al*. Diterpenes and sesquiterpenes from *Mikania banisteriae*. *Phytochemistry*,1997,46:161-164.

68 Ohkoshi E, *et al*. A novel bisnorditerpenelactone from *Mikania hirsutissima*. *Chem Pharm Bull*,2000,48:1774-1775.

69 Ohkoshi E, *et al*. Studies on the constituents of *Mikania hirsutissima* (Compositae). *Chem Pharm Bull*,1999. 47:1436-1438.

70 Lobitz GO, *et al*. Kaurene diterpenes from *Mikania vitifolia*. *Phytochemistry*,1998,49:805-809.

71 Sacilotto ACBC, *et al*. Ent-kaurene diterpenes from *Gochnatia polymorpha* var. polymorpha. *Phytochemistry*,1997,44:659-661.

72 Bustos-Brito C, *et al*. ent-Kaurene glycosides from *Ageratina cylindrica*. *J Nat Prod*,2015,78:2580-2587.

73 Galala A A, *et al*. New *ent*-kaurane diterpenoid dimer from *Pulicaria inuloides*. *Nat Prod Res*,2016,30:2468-2475.

74 Al-Howiriny TA, *et al*. Three new diterpenes and the biological activity of different extracts of *Jasonia montana*. *Nat Prod Res*,2005,19:253-265.

75 Zhang YH (张永红), *et al*. A bioactive diterpene from the Chinese herb *Aster souliei*. *J Chin Pharm Sci* (中国药学), 2004,13:285-287.

76 Wang ZM, *et al*. Kirenol upregulates nuclear annexin-1 which interacts with NF-κB to attenuate synovial inflammation of collagen-induced arthritis in rats. *J Ethnopharmacology*, 2011,137:774-782.

77 Liu XY, *et al*. Antitumor activity of diterpenoids from *Solidago canadensis* L. *J Zhejiang Univ*(*Sci Ed*) (浙江大学学报, 理学版),2007,34:661-664.

78 Gao X (高雪). Studies on the chemical constituents from three Compositae and one Labiatae species and their bioactivities. Lanzhou: Lanzhou University (兰州大学), PhD. 2007.

79 Xiang Z(项峥), *et al*. Research and development of*Smallanthus sonchifolius* (Poepp. et Endl.) H. Robinso leaves. The 11th National Symposium on Traditional Chinese Medicine and Natural Medicines (第十一届全国中药和天然药物学术研讨会),2011,10.

80 Yin CX (殷彩霞), *et al*. Systematical cluster analysis of medicinal plants in composite. *Computers Appl Chem* (计算机与应用化学),1999,16:157-160.

81 Ding JH (丁景和), *et al*. Medicinal Botany (药用植物学). Shanghai: Science &Technical Press,1985. 137,153.

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