洋甘菊的化学成分和药理作用研究进展及其质量标志物预测分析

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摘要：洋甘菊（*Matricaria chamomilla* L.）为菊科母菊属草本植物，是维吾尔医学常用药材，主产于中国新疆和欧洲等地。洋甘菊的化学成分主要包括黄酮、酚酸、挥发油、香豆素和其他类成分，具有抗炎、镇痛、抗菌、抗氧化、抗肿瘤、降血糖、降血脂、降血压和对胃肠道系统和神经系统的药理作用。本文在对洋甘菊化学成分、药理作用概述的基础上，对其质量标志物进行预测分析，推测黄酮、酚酸、倍半萜类成分可作为洋甘菊的质量标志物，为建立洋甘菊质量标准提供科学参考。

关键词：洋甘菊；黄酮；药理作用；质量标志物

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Research Progress on Chemical Constituents and Pharmacological Effects of *Matricaria chamomilia* L. and Predictive Analysis of Quality Markers

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ABSTRACT: *Matricaria chamomilla* L. is a herbaceous plant belonging to Asteraceae family. It is frequently used as medicinal herb in the Uygur medicines and is mainly produced in Xinjiang Uygur autonomous region, Europe and other places. Its chemical constituents mainly include flavonoids, phenolic acids, essential oil, coumarins and other compounds. This herb has anti-inflammatory, analgesic, antibacterial, antioxidant, anti-tumor, hypoglycemic, hypolipidemic, hypotensive and pharmacological effects on gastrointestinal and nervous system. Based on the overview of the chemical constituents and pharmacological effects of chamomile, this paper conducts a predictive analysis of its quality markers. It is speculated that flavonoids, phenolic acids and sesquiterpenoids can be used as quality markers of chamomile, providing scientific reference for establishing its quality standards.

KEY WORDS: *Matricaria chamomilla* L.; flavonoid; pharmacological activity; quality marker

洋甘菊（*Matricaria chamomilla* L.）为菊科母菊属一年生草本植物，主产于我国新疆北部和西部，欧洲、亚洲北部和西部也有分布[1]。洋甘菊在我国维吾尔民族医学中是常用药材，据《维吾尔药志》记载：维药洋甘菊也称“巴布那儿”，具有解痉、消炎、解热、促进溃疡愈合和杀菌等作用，功能主治为清热解表、镇静安神、驱风健胃、补脑强肾。用于感冒发烧，易惊失眠，精神不振，风寒胃痛，手足挛紧，腰膝酸软[2]。《中华人民共和国卫生部药品标准》（维吾尔药分册）已收载该药材及其3种复方制剂：复方木尼孜其颗粒、祖卡木颗粒和强力玛得士力阿亚特蜜膏[3]。洋甘菊在欧洲也有悠久的应用历史，可以追溯到古希腊和古罗马时期[4]，目前在26个国家的药典中均有收录[5]。传统上洋甘菊内服用于治疗胃肠道痉挛和炎症性疾病[6]，现代药理学研究表明，洋甘菊还具有抗菌、抗炎止痛、抗氧化、降糖降脂、降血压、抗肿瘤、抗寄生虫作用和对胃肠道系统、神经系统方面的诸多药理作用。本文拟从化学成分和药理作用方面进行综述，并对洋甘菊质量标志物（quality marker，Q-marker）进行预测分析，以期为药材质量控制与合理利用提供参考。

1　化学成分

随着色谱技术的提高与提取分离条件的优化，从洋甘菊中分离得到了黄酮、酚酸、香豆素、挥发油和其他多种类型的成分，这些化学成分与洋甘菊的药理药效密切相关。

1.1　黄酮类

黄酮类化合物是洋甘菊的主要活性成分，洋甘菊中黄酮类化合物绝大多数是黄酮、黄酮醇及其苷类，其次含有少量二氢黄酮和黄烷醇类。芹菜素是洋甘菊花中含量最丰富的黄酮类物质，少量以游离形式存在，其他以单糖苷、二糖苷和其乙酰化衍生物的形式存在[7]。主要的黄酮类成分见图1，表1。

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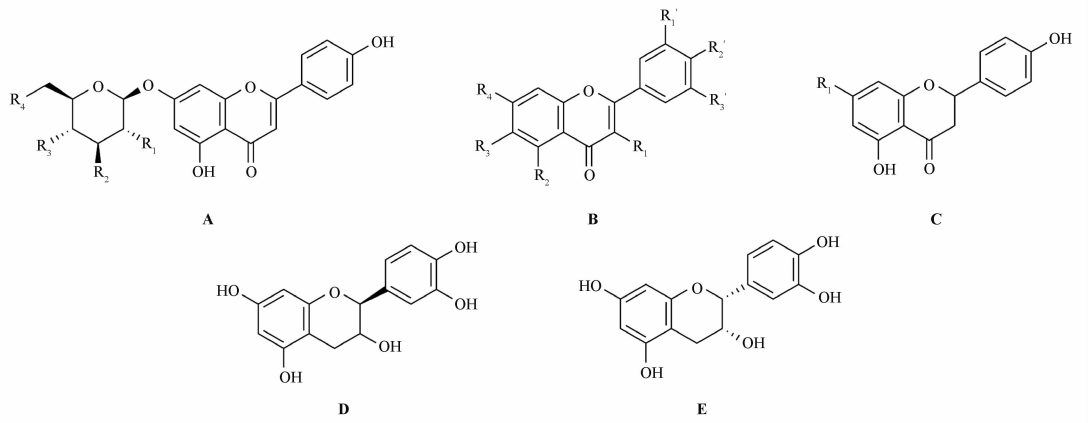


A – 芹菜素-7-*O*-葡萄糖苷结构；B – 黄酮、黄酮醇结构；C – 二氢黄酮结构；D、E – 黄烷醇结构

图 1 洋甘菊黄酮类化合物的基本结构

表 1 洋甘菊中黄酮类化合物

编号	中文名称	英文名称	母核	R_1	R_2	R_3	R_4	R_1'	R_2'	R_3'	文献
1	芹菜素-7-*O*-(3″-乙酰基)-葡萄糖苷	Apigenin-7-*O*-(3″-acetyl)-glucoside	A	OH	Acetyl	OH	OH	–	–	–	[7-8]
2	芹菜素-7-*O*-(4″-乙酰基)-葡萄糖苷	Apigenin-7-*O*-(4″-acetyl)-glucoside	A	OH	OH	Acetyl	OH	–	–	–	[7-8]
3	芹菜素-7-*O*-(6″-乙酰基)-葡萄糖苷	Apigenin-7-*O*-(6″-acetyl)-glucoside	A	OH	OH	OH	Acetyl	–	–	–	[7-8]
4	芹菜素-7-*O*-(6″-咖啡酰基)-葡萄糖苷	Apigenin-7-*O*-(6″-caffeoyl)-glucoside	A	OH	OH	OH	Caffeoyl	–	–	–	[7-8]
5	芹菜素-7-*O*-(6″-丙二酰基)-葡萄糖苷	Apigenin-7-*O*-(6″-malonyl)-glucoside	A	OH	OH	OH	Malonyl	–	–	–	[7]
6	芹菜素-7-*O*-(4″-乙酰基,6″-丙二酰基)-葡萄糖苷	Apigenin-7-*O*-(4″-acetyl, 6″-malonyl)-glucoside	A	OH	OH	Acetyl	Malonyl	–	–	–	[7]
7	芹菜素-7-*O*-(4″,6″-二乙酰基)-葡萄糖苷	Apigenin-7-*O*-(4″, 6″-di-acetyl)-glucoside	A	OH	OH	Acetyl	Acetyl	–	–	–	[7]
8	芹菜素-7-*O*-(2″-乙酰基)-葡萄糖苷	Apigenin-7-*O*-(2″-acetyl)-glucoside	A	Acetyl	OH	OH	OH	–	–	–	[7]
9	芹菜素-7-*O*-(2″,3″-二乙酰基)-葡萄糖苷	Apigenin-7-*O*-(2″, 3″-di-acetyl)-glucoside	A	Acetyl	Acetyl	OH	OH	–	–	–	[7]
10	芹菜素-7-*O*-(3″,4″-二乙酰基)-葡萄糖苷	Apigenin-7-*O*-(3″, 4″-di-acetyl)-glucoside	A	OH	Acetyl	Acetyl	OH	–	–	–	[7]
11	芹菜素	Apigenin	B	H	OH	H	OH	H	OH	H	[7-8]
12	芹菜素-7-*O*-*β*-D-葡萄糖苷	Apigenin 7-*O*-*β*-D-glucopyranoside	B	H	OH	H	OGlc	H	OH	H	[7-8]
13	芹菜素-7-*O*-*β*-D-芸香糖苷	Apigenin-7-*O*-*β*-D-rutinoside	B	H	OH	H	$OGlc^{6}$-^{1}Rha	H	OH	H	[9]
14	木犀草素	Luteolin	B	H	OH	H	OH	OH	OH	H	[8,10]
15	木犀草素-7-*O*-*β*-D-葡萄糖苷	Luteolin-7-*O*-*β*-D-glucoside	B	H	OH	H	OGlc	OH	OH	H	[11]
16	木犀草素-4′-*O*-*β*-D-葡萄糖苷	Luteolin-4′-*O*-*β*-D-glucoside	B	H	OH	H	OH	OH	OGc	H	[12]
17	木犀草素-7-*O*-*β*-芸香糖苷	Luteolin-7-*O*-*β*-rutinoside	B	H	OH	H	$OGlc^{6}$-^{1}Rha	OH	OH	H	[12]
18	木犀草素-6-羟基-7-葡萄糖苷	Luteolin-6-hydroxy-7-glucoside	B	H	OH	OH	OGlc	OH	OH	H	[12]
19	高车前素	Hispidulin	B	H	OH	OCH_3	OH	H	OH	H	[10]
20	泽兰叶黄素	Eupafolin	B	H	OH	OCH_3	OH	OH	OH	H	[10]
21	5,7-二羟基-3,4′-二甲氧基黄酮	Ermanin	B	OCH_3	OH	H	OH	H	OCH_3	H	[10]
22	5,7,4′-三羟基-3,6-二甲氧基黄酮	5,7,4′-Trihydroxy-3,6-dimethoxyflavonone	B	OCH_3	OH	OCH_3	OH	H	OH	H	[10]
23	异山柰素-7-*O*-葡萄糖醛酸苷	Bracteoside	B	OCH_3	OH	H	OGlcA	H	OH	H	[10]
24	–	7-*O*-(*β*-D-Glucopyranosyl)-galactin	B	OH	OH	OH	OGlc	H	OH	H	[10]
25	槲皮素	Quercetin	B	OH	OH	H	OH	OH	OH	H	[8,10]
26	槲皮素-3-*O*-葡萄糖苷	Quercetin-3-*O*-glucoside	B	OGlc	OH	H	OH	OH	OH	H	[8]
27	3-甲氧基槲皮素	3-Methylquercetin	B	OCH_3	OH	H	OH	OH	OH	H	[10]
28	槲皮素-3-*O*-*β*-芸香糖苷(芦丁)	Quercetin-3-*O*-*β*-rutinoside	B	$OGlc^{6}$-^{1}Rha	OH	H	OH	OH	OH	H	[12]
29	槲皮素-3-*O*-*β*-半乳糖苷	Quercetin-3-*O*-*β*-galactoside	B	OGal	OH	H	OH	OH	OH	H	[12]
30	槲皮素-7-*O*-*β*-葡萄糖苷	Quercetin-7-*O*-*β*-glucoside	B	OH	OH	H	OGlc	OH	OH	H	[12]
31	山柰酚-3-*O*-*β*-葡萄糖苷	Kaempferol-3-*O*-*β*-glucoside	B	OGlc	OH	H	OH	H	OH	H	[12]
32	山柰酚	Kaempherol	B	OH	OH	H	OH	H	OH	H	[10]
33	6-甲氧基山柰酚	6-Methoxy kaempferol	B	OH	OH	OCH_3	OH	H	OH	H	[10]
34	高良姜素	Galangin	B	OH	OH	H	OH	H	H	H	[10]
35	泽兰素	Eupatolitin	B	OH	OH	OCH_3	OCH_3	OH	OH	H	[8]
36	猫眼草黄素	Chrysosplenetin	B	OCH_3	OH	OCH_3	OCH_3	OCH_3	OH	H	[8]
37	猫眼草酚 D	Chrysosplenol D	B	OCH_3	OH	OCH_3	OCH_3	OH	OH	H	[8]

续表 1

编号	中文名称	英文名称	母核	R_1	R_2	R_3	R_4	R_1'	R_2'	R_3'	文献
38	万寿菊素	Patuletin	B	OH	OH	OCH_3	OH	OH	OH	H	[8,12]
39	万寿菊素-7-*O*-葡萄糖苷	Patuletin-7-*O*-glucoside	B	OH	OH	OCH_3	OGlc	OH	OH	H	[12]
40	金圣草黄素	Chrysoeriol	B	H	OH	H	OH	OCH_3	OH	H	[13]
41	金圣草黄素-7-*O*-*β*-葡萄糖苷	Chrysoeriol-7-*O*-*β*-glucoside	B	H	OH	H	OGlc	OCH_3	OH	H	[12]
42	棕鳞矢车菊黄酮素	Jaceidin	B	OCH_3	OH	OCH_3	OH	OCH_3	OH	H	[12-13]
43	菠叶素	Spinacetin	B	OH	OH	OCH_3	OH	OCH_3	OH	H	[12-13]
44	甲氧基万寿菊素	Axillarin	B	OCH_3	OH	OCH_3	OH	OH	OH	H	[12-13]
45	3,5,4′-三羟基-6,7-二甲氧基黄酮	Eupalitin	B	OH	OH	OCH_3	OCH_3	H	OH	H	[12-13]
46	异鼠李素	Isorhamnetin	B	OH	OH	H	OH	OCH_3	OH	H	[12-13]
47	异鼠李素-7-*O*-*β*-葡萄糖苷	Isorhamnetin-7-*O*-*β*-glucoside	B	OH	OH	H	OGlc	OCH_3	OH	H	[12]
48	杨梅苷	Myricitrin	B	ORha	OH	H	OH	OH	OH	OH	[14]
49	柚皮素	Naringenin	C	OH	–	–	–	–	–	–	[15]
50	柚皮苷	Naringin	C	$OGlc^2-{}^1Rha$	–	–	–	–	–	–	[15]
51	儿茶素	Catechin	D	–	–	–	–	–	–	–	[15]
52	表儿茶素	Epicatechin	E	–	–	–	–	–	–	–	[16]

1.2 酚酸化合物

酚酸类化合物是洋甘菊中主要生物活性物质之一，洋甘菊中的酚酸化合物包含多种咖啡酰奎宁酸（**53**～**58**，**62**～**63**）、奎宁酸（**59**）、2-*β*-D-葡萄糖基-4-甲氧基肉桂酸异构体（**60**～**61**）、苯甲酸衍生物（**64**～**70**）和羟基肉桂酸衍生物（**71**～**75**），酚酸化合物成分见表 2，图 2。

表 2 洋甘菊中酚酸类化合物

编号	中文名称	英文名称	分子式	文献
53	绿原酸	Chlorogenic acid(3-*O*-Caffeoylquinic acid)	$C_{16}H_{18}O_9$	[12,17]
54	隐绿原酸	Cryptochlorogenic acid(4-*O*-Caffeoylquinic acid)	$C_{16}H_{18}O_9$	[12,17]
55	新绿原酸	Neochlorogenic acid(5-*O*-Caffeoylquinic acid)	$C_{16}H_{18}O_9$	[12,17]
56	异绿原酸 A	Isochlorogenic acid A(3,5-*O*-Dicaffeoylquinic acids)	$C_{25}H_{24}O_{12}$	[17]
57	异绿原酸 B	Isochlorogenic acid B(3,4-*O*-Dicaffeoylquinic acids)	$C_{25}H_{24}O_{12}$	[10,17]
58	异绿原酸 C	Isochlorogenic acid C(4,5-*O*-Dicaffeoylquinic acids)	$C_{25}H_{24}O_{12}$	[10,17]
59	奎宁酸	Quinic acid	$C_7H_{12}O_6$	[12]
60	(*Z*)-2-*β*-D-葡萄糖基-4-甲氧基肉桂酸	(*Z*)-2-*β*-D-glucopyranosyloxy-4-methoxycinnamic acid	$C_{16}H_{20}O_9$	[9,18-19]
61	(*E*)-2-*β*-D-葡萄糖基-4-甲氧基肉桂酸	(*E*)-2-*β*-D-glucopyranosyloxy-4-methoxycinnamic acid	$C_{16}H_{20}O_9$	[9,18-19]
62	1,3-二咖啡酰奎宁酸	1,3-Dicaffeoylquinic acid	$C_{25}H_{24}O_{12}$	[12]
63	1,5-二咖啡酰奎宁酸	1,5-Dicaffeoylquinic acids	$C_{25}H_{24}O_{12}$	[17]
64	原儿茶酸	Protocatechuic acid	$C_7H_6O_4$	[17]
65	没食子酸	Gallic acid	$C_7H_6O_5$	[14]
66	对羟基苯甲酸	4-Hydroxybenzoic acid	$C_7H_6O_3$	[10]
67	水杨酸	Salicylic acid	$C_7H_6O_3$	[20]
68	丁香酸	Syringic acid	$C_9H_{10}O_5$	[21]
69	大茴香酸	Anisic acid	$C_8H_8O_3$	[21]
70	香草酸	Vanillic acid	$C_8H_8O_4$	[21]
71	咖啡酸	Caffeic acid	$C_9H_8O_4$	[14]
72	阿魏酸	Ferulic acid	$C_{10}H_{10}O_4$	[22]
73	肉桂酸	Cinnamic acid	$C_9H_8O_2$	[15]
74	对香豆酸	*p*-Coumaric acid	$C_9H_8O_3$	[15]
75	芥子酸	Sinapic acid	$C_{11}H_{12}O_5$	[15]
76	鞣花酸	Ellagic acid	$C_{14}H_6O_8$	[15]

1.3 香豆素类

洋甘菊中已报道的香豆素类化合物共 11 种，包含羟基、甲氧基取代香豆素（**77**～**82**，**84**，**87**）和香豆素糖苷（**83**，**85**～**86**），均为简单香豆素类，见表 3，图 3。

1.4 挥发油

挥发油为混合物，其组分复杂，主要包括芳香族、萜类和脂肪族成分。洋甘菊精油的主要组成为倍半萜类、单萜类，还含有少量脂肪族化合物。*α*-红没药醇及其氧化物和母菊薁是洋甘菊精油的主要成分[25]。研究采用溶剂辅助蒸馏结合液相-液相色谱法[26]分离洋甘菊精油，并鉴定出 9 种倍半萜成分。洋甘菊花和茎叶中的精油组成与含量不同[27]，*α*-红没药醇氧化物 A 和 B，*α*-红没药烯氧化物 A 和母菊薁在花中含量较高，而桉油烯醇、(*E*)-*β*-金合欢烯和 *cis*-en-yn-Dicycloether 在茎叶中含量较高。见表 4。

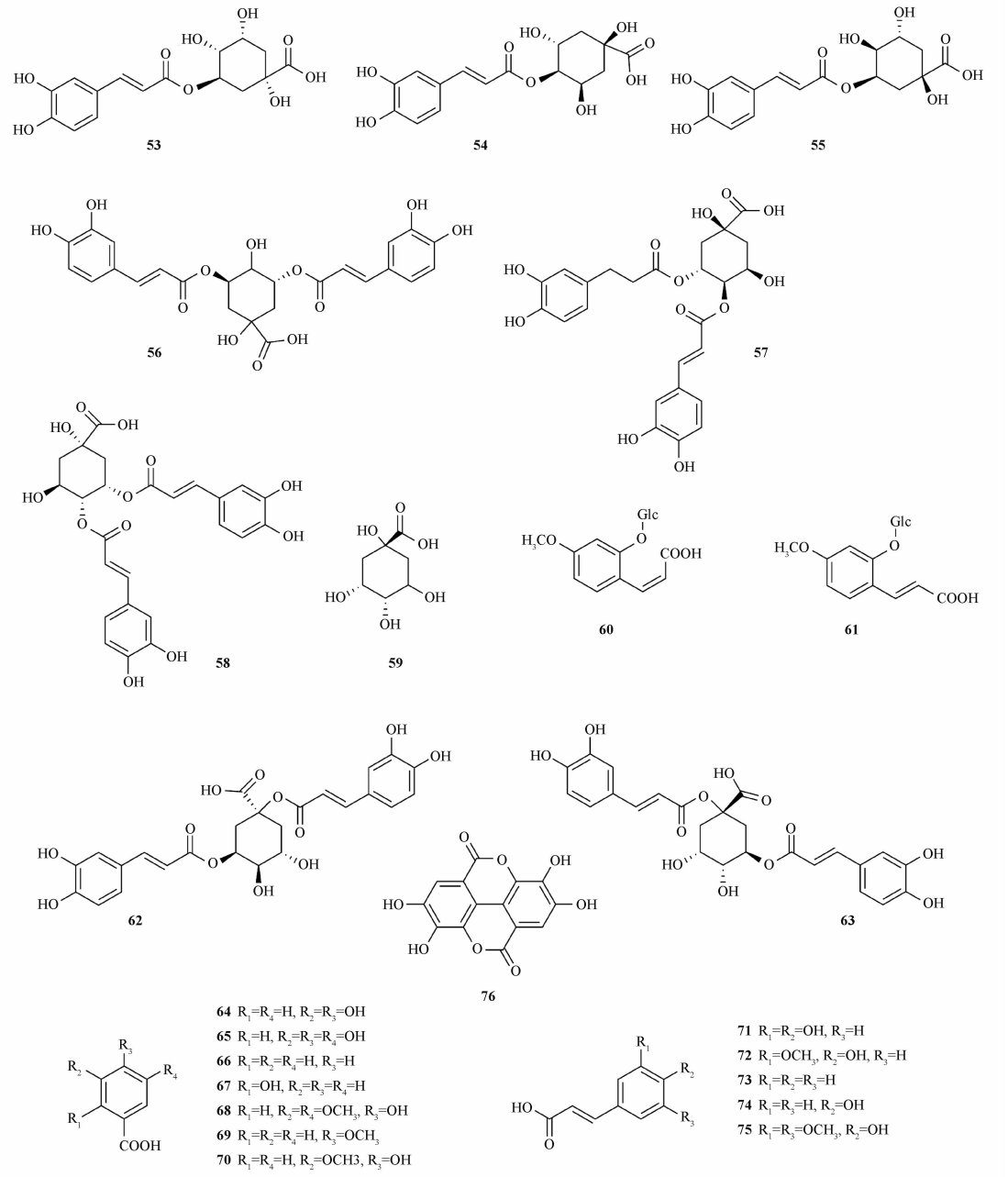
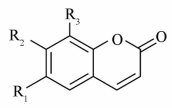


图 2 洋甘菊中酚酸类化合物结构

表 3 洋甘菊中香豆素类化合物

编号	中文名称	英文名称	分子式	文献
77	伞形酮	Umbelliferone	$C_9H_6O_3$	[18,23]
78	7-甲氧基香豆素	7-Methoxycoumarin	$C_{10}H_8O_3$	[18,23]
79	香豆素	Coumarin	$C_9H_6O_2$	[23]
80	秦皮乙素	Esculetin	$C_9H_6O_4$	[23]
81	东莨菪内酯	Scopoletine	$C_{10}H_8O_4$	[23]
82	异东莨菪内酯	Isoscopoletine	$C_{10}H_8O_4$	[23]
83	伞形酮-7-*O*-*β*-D-葡萄糖苷	Umbelliferone-7-*O*-*β*-D-glucoside	$C_{15}H_{16}O_8$	[18]
84	瑞香素	Daphnetin	$C_9H_6O_4$	[18]
85	瑞香素-7-*O*-*β*-D-葡萄糖苷	Daphnetin-7-*O*-*β*-D-glucoside	$C_{15}H_{16}O_9$	[18]
86	秦皮甲素	Aesculin	$C_{15}H_{16}O_9$	[15]
87	嗪皮啶	Fraxidin	$C_{11}H_{10}O_5$	[24]



77 R_1=R_3=H, R_2=OH
78 R_1=R_3=H, R_2=OCH_3
79 R_1=H, R_2=H, R_3=H
80 R_1=R_2=OH, R_3=H
81 R_1=OCH_3, R_2=OH, R_3=H
82 R_1=OH, R_2=OCH_3, R_3=H
83 R_1=R_3=H, R_2=OGlc
84 R_1=H, R_2=R_3=OH
85 R_1=H, R_2=OGlc, R_3=H
86 R_1=OGlC, R_2=OH, R_3=H
87 R_1=R_2=OCH_3, R_3=OH

图 3 洋甘菊中香豆素类化合物结构

1.5 其他类成分

研究表明洋甘菊中含有齐墩果酸、豆甾醇、β-谷甾醇、β-谷甾醇-葡萄糖苷[29]、根皮素、白藜芦醇和松柏醛[15]。除此之外，有研究从洋甘菊中[24]分离出对羟基苯乙酮、palmatoside A 和 matriisobenzofuran 3 种成分，Zhao 等[10]分离出 5-十五烷基间苯二酚，该化合物为首次从洋甘菊及母菊属植物中分离得到。

2 药理作用

随着现代药理学研究的深入，发现洋甘菊在传统应用于炎症性疾病的基础上，还具有抗菌止痛、抗氧化、降糖降脂、降血压、抗肿瘤、抗寄生虫作用及心血管系统和神经系统保护等广泛药理作用。洋甘菊药理作用的研究对象主要集中在洋甘菊水、醇提取物、挥发油及从洋甘菊中分离得到的单体化合物上，研究方向也由药效观察检测向药理作用机制探究上转变。

表 4 洋甘菊中挥发性成分

编号	中文名称	英文名称	分子式	文献
88	母菊奠	Chamazulene	$C_{14}H_{16}$	[27-28]
89	α-红没药醇	α-Bisabolol	$C_{15}H_{26}O$	[27-28]
90	α-红没药烯氧化物 A	α-Bisabolone oxide A	$C_{15}H_{24}O_2$	[26-28]
91	α-红没药醇氧化物 A	α-Bisabolol oxide A	$C_{15}H_{26}O_2$	[26-28]
92	α-红没药醇氧化物 B	α-Bisabolol oxide B	$C_{15}H_{26}O_2$	[26-28]
93	(*E*)-β-金合欢烯	(*E*)-β-Farnesene	$C_{15}H_{24}$	[26-28]
94	桉油烯醇	Spathulenol	$C_{15}H_{24}O$	[26-28]
95	2-甲基丁酸乙酯	Ethyl 2-methylbutanoate	$C_7H_{14}O_2$	[27]
96	2-甲基丁酸丙酯	Propyl 2-methylbutanoate	$C_8H_{16}O_2$	[27]
97	α-侧柏烯	α-Thujene	$C_{10}H_{16}$	[28]
98	α-蒎烯	α-Pinene	$C_{10}H_{16}$	[28]
99	β-蒎烯	β-Pinene	$C_{10}H_{16}$	[28]
100	莰烯	Camphene	$C_{10}H_{16}$	[28]
101	香桧烯	Sabinene	$C_{10}H_{16}$	[28]
102	月桂烯	Myrcene	$C_{10}H_{16}$	[28]
103	α-水芹烯	α-Phellandrene	$C_{10}H_{16}$	[28]
104	α-萜品烯	α-Terpinene	$C_{10}H_{16}$	[28]
105	γ-萜品烯	γ-Terpinene	$C_{10}H_{16}$	[28]
106	邻伞花烃	*o*-Cymene	$C_{10}H_{14}$	[28]
107	柠檬烯	Limonene	$C_{10}H_{16}$	[28]
108	1,8-桉叶素	1,8-Cineole	$C_{10}H_{18}O$	[28]
109	(*Z*)-β-罗勒烯	(*Z*)-β-Ocimene	$C_{10}H_{16}$	[28]
110	(*E*)-β-罗勒烯	(*E*)-β-Ocimene	$C_{10}H_{16}$	[28]
111	别罗勒烯	*allo*-Ocimene	$C_{10}H_{16}$	[28]
112	蒿酮	Artemisia ketone	$C_{10}H_{16}O$	[26-28]
113	蒿醇	Artemisia alcohol	$C_{10}H_{18}O$	[27-28]
114	萜品油烯	Terpinolene	$C_{10}H_{16}$	[28]
115	芳樟醇	Linalool	$C_{10}H_{18}O$	[28]
116	薄荷酮	Menthone	$C_{10}H_{18}O$	[28]
117	异薄荷酮	*iso*-Menthone	$C_{10}H_{18}O$	[28]
118	薄荷醇	Menthol	$C_{10}H_{20}O$	[28]
119	甲基胡椒酚	Methyl chavicol	$C_{10}H_{12}O$	[28]
120	–	(2*E*)-Octenol acetate	$C_{10}H_{20}O_3$	[28]
121	2-壬烯酸甲酯	Methyl-(2*E*)-nonenoate	$C_{10}H_{18}O_2$	[28]
122	(3*Z*)-己烯醇 2-甲基丁酸酯	(3*Z*)-Hexenyl 2-methyl butanoate	$C_{11}H_{20}O_2$	[28]
123	乙酸薄荷酯	Menthyl acetate	$C_{12}H_{22}O_2$	[28]
124	–	*cis*-en-yn-Dicycloether	$C_{13}H_{12}O_2$	[26-27]
125	–	*trans*-en-yn-Dicycloether	$C_{13}H_{12}O_2$	[26-27]

续表 4

编号	中文名称	英文名称	分子式	文献
126	大马士酮	β-Damascenone	$C_{13}H_{18}O$	[27]
127	十三烷	Tridecane	$C_{13}H_{28}$	[28]
128	δ-榄香烯	δ-Elemene	$C_{15}H_{24}$	[28]
129	β-榄香烯	β-Elemene	$C_{15}H_{24}$	[28]
130	γ-榄香烯	γ-Elemene	$C_{15}H_{24}$	[28]
131	α-衣兰烯	α-Ylangene	$C_{15}H_{24}$	[28]
132	–	α-Isocomene	$C_{15}H_{24}$	[28]
133	–	(*E*)-Caryophyllene	$C_{15}H_{24}$	[28]
134	β-古巴烯	β-Copaene	$C_{15}H_{24}$	[28]
135	β-芹子烯	β-Selinene	$C_{15}H_{24}$	[28]
136	(*E*,*E*)-α-金合欢烯	(*E*,*E*)-α-Farnesene	$C_{15}H_{24}$	[28]
137	δ-杜松烯	δ-Cadinene	$C_{15}H_{24}$	[28]
138	γ-杜松烯	γ-Cadinene	$C_{15}H_{24}$	[28]
139	大根香叶烯 D	Germacrene D	$C_{15}H_{24}$	[27-28]
140	双环环大根香叶烯	Bicyclogermacrene	$C_{15}H_{24}$	[27-28]
141	(*E*)-橙花叔醇	(*E*)-Nerolidol	$C_{15}H_{26}O$	[28]
142	–	(*Z*)-Spiroether	$C_{15}H_{26}O$	[28]
143	–	(*E*)-Spiroether	$C_{15}H_{26}O$	[28]
144	喇叭茶醇	Ledol	$C_{15}H_{26}O$	[27]
145	荜澄茄油烯醇	Cubenol	$C_{15}H_{26}O$	[27]
146	τ-杜松醇	τ-Cadinol	$C_{15}H_{26}O$	[27]
147	棕榈酸	Palmitic acid	$C_{16}H_{32}O_2$	[27]
148	正十八醇	1-Octadecanol	$C_{18}H_{38}O$	[27]

2.1 胃肠道系统作用

洋甘菊可用于胃胀气、胃溃疡和胃肠道刺激等多种胃肠道疾病[25]。200 mg·kg^{-1}·d^{-1}洋甘菊水醇提取物组对乙醇致大鼠急性胃黏膜损伤的保护作用最强，大鼠胃溃疡指数最低[30]。25、50 和 100 mg·kg^{-1}·d^{-1}洋甘菊汤剂对乙醇诱导胃黏膜损伤和氧化应激具有保护作用，可以显著降低胃溃疡指数(46.77%、63.30% 和 90.95%)，是由于其抗氧化特性及加强胃黏膜防御因子的作用[31]。研究发现[6]洋甘菊能够抑制 AGS 人胃腺癌细胞的中性粒细胞弹性蛋白酶和基质金属蛋白酶-9(matrix metalloproteinase-9，MMP-9)的活性和分泌，MMP-9 表达的降低与抑制 NF-κB 驱动的转录有关。洋甘菊粉末水提物具有止泻作用，可以防止蓖麻油所致 Wistar 大鼠急性腹泻[32]，通过 K^+ 通道激活和弱 Ca^{2+} 拮抗发挥抗肠道积液分泌和抗痉挛活性[33]。

2.2 抗氧化与保肝作用

洋甘菊抗氧化活性成分包括总酚[34]、总黄酮[35]、倍半萜类[36]，作用表现为清除活性氧代谢物，抑制脂质过氧化能力，改善氧化应激水平。连续 8 周给糖尿病大鼠 200 mg·kg^{-1}·d^{-1}洋甘菊提取物，大鼠肝脏丙二醛(malondialdehyde，MDA)水平降低，超氧化物歧化酶(superoxide dismutase，SOD)活性增强到健康对照组正常水平[37]。500 mg·kg^{-1}·d^{-1}的洋甘菊花提取物 4 周显著提高了链脲佐菌素诱导糖尿病大鼠肝脏 SOD、过氧化氢酶(catalase，CAT)和谷胱甘肽过氧化物酶(glutathione peroxidase，GSH-Px)活性，抑制了脂质过氧化水平[38]。洋甘菊水提取物抑制人中性粒细胞活性氧的产生[39]，对红细胞氧化应激具有保护作用，同时，25、50、100 mg·kg^{-1}·d^{-1}洋甘菊水提物剂量依赖性地逆转了由乙醇诱导的大鼠抗氧化酶 SOD，CAT 与 GSH-Px 水平的降低，高浓度洋甘菊水提物的抗氧化作用效果与抗氧剂抗坏血酸相当。在百草枯致雄性 Wistar 大鼠肝脏氧化损伤模型中[40]，灌胃给予 50 mg·kg^{-1}·d^{-1}洋甘菊提取物 7 d 增加了大鼠肝组织总巯基分子水平，降低丙氨酸氨基转移酶(alanine aminotransferase，ALT)和门冬氨酸氨基转移酶(aspartate aminotransferase，AST)水平，通过清除自由基和稳定氧化状态来防止肝损伤。

2.3 抗炎、镇痛作用

洋甘菊在减少口腔炎症、加速创面修复和镇痛等方面具有有效作用[41]。对口腔黏膜炎[42]、扁平苔藓[43]和灼口综合征[44]具有临床疗效。洋甘菊抑制尼龙线结扎所致大鼠牙槽骨炎症模型中肿瘤坏死因子 α(Tumor Necrosis Factor-α，TNF-α)和白细胞介素-1β(Interleukin-1β，IL-1β)表达，减少牙周组织白细胞浸润，降低髓过氧化物酶活性至正常组水平，免疫组化结果显示洋甘菊通过降低 RANKL/OPG 比值来防止大鼠牙槽骨炎症[45]。洋甘菊软膏治疗减少大鼠上皮细胞凋亡和 TNF-α 表达，促进糖尿病大鼠创伤性口腔溃疡的愈合[46]。含有洋甘菊的复方制剂能降低注射弗氏完全佐剂所致类风湿性关节炎大鼠模型中 IL-1β 的表达，减少关节炎症反应[47]。洋甘菊中主要化学成分(–)-α-红没药醇[48]、芹菜素与槲皮素[49]抑制 IL-1β、白细胞介素-6(interleukin-6，IL-6)、TNF-α、一氧化氮合酶(inducible nitric oxide synthase，iNOS)、环氧合酶(cyclooxygenase-2，COX-2)的表达来减轻炎症，母菊萼显著下调 IL-1β 诱导的软骨细胞中 MMP-3、

MMP-9和 NF-κB 的表达，通过调节 MMPs 和 NF-κB 通路来逆转骨关节炎炎症进展[50]。精油成分下调 LPS 诱导的人角质形成细胞中 IL-6 mRNA 表达，调控 p38 MAPK 和 mTOR 两条信号通路来降低炎性损伤[51]。

洋甘菊精油提取物可剂量依赖性抑制大鼠炎症性模型的痛觉过敏[52]，减少膝关节骨性关节炎患者镇痛药使用量[53]，减轻乳腺炎患者的轻中度乳腺痛[54]及偏头痛患者的疼痛、恶心等症状[55]。洋甘菊镇痛作用机制与抗炎作用相关，(－)-α-红没药醇在内脏和躯体痛觉的炎症模型中发挥镇痛作用，减轻炎症中的痛觉过敏[56]。

2.4 抗菌作用

洋甘菊精油具有抗菌作用，对单核增生李斯特菌、大肠杆菌[28]、蜡状芽孢杆菌、黄曲霉菌[22]、黑曲霉菌[4]具有抑菌活性。主要成分 α-红没药醇可抑制金黄色葡萄球菌、大肠杆菌和铜绿假单胞菌，其中对金黄色葡萄球菌的抑制效果最好，最低抑菌浓度为 161.27 $\mu g \cdot mL^{-1}$[57]，对与口臭相关的莫雷梭菌也有抑菌活性[58]。α-红没药醇对真菌如白色念珠菌、克鲁塞念珠菌、热带念珠菌具有抑制作用[59]，还能抑制皮肤癣菌病病原体毛癣菌属红色毛癣菌和趾间毛癣菌[60]，在皮肤癣菌病治疗中具有应用潜力。

2.5 对心血管系统作用

2.5.1 降血糖作用 洋甘菊水、醇提取物连续给药 28 d 均能够降低四氧嘧啶致糖尿病模型小鼠的空腹血糖，改善糖耐量[61-63]。临床研究中[64]，2 型糖尿病患者服用洋甘菊茶后血清胰岛素水平、胰岛素、糖化血红蛋白、胰岛素抵抗指数分别降低 11.09%、32.59%、5.01% 和 39.76%。α-淀粉酶和 α-葡萄糖苷酶催化碳水化合物 α-(1,4)糖苷键水解，会导致血糖水平升高[65]，洋甘菊中分离得到芹菜素对两种酶均有抑制活性，且对 α-葡萄糖苷酶的抑制作用更强[66]。芹菜素及芹菜素-7-*O*-葡萄糖苷、(*Z*)和(*E*)-2-*β*-D-葡萄糖氧基-4-甲氧基肉桂酸[19]均能在体外通过抑制 α-淀粉酶和麦芽糖酶活性调节碳水化合物的消化与吸收。槲皮素、木犀草素与 6,7-二羟基香豆素抑制 α-葡萄糖苷酶、糖原磷酸化酶活性，抑制肝糖原分解[67]。洋甘菊花乙醇提取物能显著增加胰岛素水平和胰岛素敏感性，降低糖尿病大鼠糖蛋白磷脂酶 D 水平[68]。低浓度葡萄糖和果糖的摄取分别依赖钠-葡萄糖转运蛋白 1(sodium-glucose co-transporters1，SGLT1)和葡萄糖转运蛋白 5(glucose transporter 5，GLUT5)转运蛋白转运，高浓度主要依赖 GLUT2 转运[69]。洋甘菊在不同浓度下通过抑制 GLUT2 与 GLUT5 来抑制果糖和葡萄糖的吸收[70]。低浓度时抑制 SGLT1，减少体外肠道对葡萄糖的吸收[20]，高浓度时芹菜素与芹菜素 7-*O*-葡萄糖苷作为 GLUT2 选择性抑制剂，直接与 GLUT2 转运蛋白相互作用[19]。洋甘菊还可通过激活过氧化物酶体增殖物激活受体 γ(peroxisome proliferators-activated receptors-γ，PPARγ)来调节糖脂代谢[71]。

2.5.2 降血脂作用 临床试验中[72]，糖尿病患者服用 4 周洋甘菊茶后，总胆固醇(total cholesterol，TC)和低密度脂蛋白胆固醇(low density lipoprotein cholester，LDL-C)水平显著下降。300$mg \cdot kg^{-1} \cdot d^{-1}$洋甘菊提取物可以降低糖尿病大鼠 TC、三酰甘油(triglyceride，TG)、LDL-C 和极低密度脂蛋白胆固醇，升高高密度脂蛋白胆固醇水平[73]，显著降低 ALT、AST 和碱性磷酸酶水平[74]。洋甘菊总黄酮对胰腺脂肪酶具抑制作用[75]，可以有效降低肠道对 TG 的吸收[76]。在 $ApoE^{-/-}$模型小鼠中，总黄酮通过下调 ACC/FAS/DGAT2 信号通路蛋白表达，抑制 TG 合成，改善血脂水平[77]，升高 PPARα、CPT1A、ACOX1 蛋白的表达水平[78]，上调 PPARα 蛋白表达来促进脂肪酸的氧化，进而减少肝组织中的脂质沉积。

2.5.3 降血压作用 洋甘菊水和丁醇提取物在体外对人血浆中血管紧张素转化酶(angiotensin-I converting enzyme，ACE)活性具有抑制作用[79]，IC_{50} 值分别为 1.292 和 0.353 $mg \cdot mL^{-1}$，降压机制可能是非竞争性 ACE 抑制作用。洋甘菊提取物灌胃给药 8 周可降低左旋硝基精氨酸诱导高血压大鼠 AngⅡ、Ang1-7、Cys-C 含量，改善氧化应激，缓解高血压引起的心、肾损伤[80]。

2.6 抗肿瘤作用

洋甘菊对人恶性细胞具有选择性细胞毒性作用。洋甘菊对宫颈癌 HeLa、乳腺癌 MDA-MB-361 和结肠癌 LS174 细胞均有显著的抑制作用，对人慢性粒细胞白血病 K562 细胞的抑制活性最强[81]。研究比较了洋甘菊水浸液、水煎液和甲醇提取物的抗肿瘤活性[17]，结果显示洋甘菊水煎剂无抗肿瘤活性，甲醇提取物和水浸液中有机酸和黄酮类化合物含量均高，抑制结肠癌 HCT-15 和 HeLa 细胞活性。洋甘菊总黄酮与酚酸具有 A375 人黑色素瘤细胞系抗增殖和促凋亡作用[82]，洋甘菊还可以通过剂量依赖性下调血管内皮生长因子(vascular endothelial growth factor，VEGF)信号通路中 VEGF2 蛋白表达水平来抑制 HepG2 人肝癌细胞中肿瘤血管的生成[83]。在 1,2-二甲基肼诱导的小鼠结直肠癌模型中，洋甘菊水提物通过抑制 Wnt 通路，显著下调 Wnt5a、β-catenin、Tcf4、Lef1、c-Myc 和 Cyclin D1 的表达水平[84]。

2.7 对神经系统的作用

2.7.1 神经系统保护作用 洋甘菊乙醇提取物对甲醛诱导的大鼠海马神经元损伤具有保护作用[85]，是通过降低海马区 MDA 水平，提高总抗氧化能力实现的。洋甘菊治疗结合耐力训练共同减少了糖尿病大鼠海马 CA3 区神经细胞的坏死，明显改善大鼠认知功能[86]，通过抑制乙酰胆碱酯酶活性来防止胆碱能功能障碍，剂量依赖性增加大鼠海马脑源性神经营养因子 mRNA，降低 IL-1β mRNA 水平，改善记忆缺陷，抗神经炎症[87]。

2.7.2 抗焦虑与催眠作用 中重度广泛性焦虑症患者短期[88]与长期[89]使用洋甘菊后，焦虑症状均有所减轻。一项研究[90]将 179 名广泛性焦虑症患者依据是否共病抑郁症分为 2 组，接受洋甘菊提取物 1 500 $mg \cdot d^{-1}$治疗 8 周后，均观察到抗焦虑作用，在共病抑郁症组的受试者中，抑郁评定量表核心症状评分下降趋势更明显，提示其可能产生抗抑郁作用。Chang 等[91]采用 3 种量表评估洋甘菊对产后妇女睡眠质量、疲劳和抑郁的影响，洋甘菊茶干预 2 周能显著改善产

后妇女睡眠和抑郁症状。洋甘菊镇静催眠是由芹菜素与黄酮成分与苯二氮卓受体结合而发挥作用[92]。

2.8 抗寄生虫作用

洋甘菊精油主要成分 α-红没药醇具有抗寄生虫作用,对捻转血矛线虫[93]、棘阿米巴原虫[94]、棘阿米巴滋养体阶段[95]和利什曼原虫[96]具有杀虫活性。α-红没药醇诱导细胞凋亡[97],引起磷脂酰丝氨酸外化和细胞膜损伤,降低线粒体膜电位和总 ATP 水平。

2.9 其他作用

洋甘菊能减轻甲醛对雄性大鼠生殖系统的不良影响,500 mg·kg^{-1}·d^{-1}的洋甘菊提取物使甲醛处理大鼠睾酮水平和促黄体生成素水平升高,精子计数与活力均显著增强[98]。洋甘菊提取物能上调多囊卵巢综合征大鼠的血清雌激素水平,作用可能与 PI3K/AKT 通路相关[99]。服用洋甘菊提取物可以增加哺乳期妇女的产乳量[100]。油包水乳剂外用于皮肤,能减少皮肤水分流失,减轻光老化所致皮肤的粗糙度、鳞状和皱纹水平,提高皮肤水分含量[101]。洋甘菊金水对小儿热痱具有较好的治疗效果[102],每日局部外用洋甘菊精油可以降低单症状遗尿儿童的夜尿频率[103]。洋甘菊正丁醇提取物可改善哮喘小鼠肺功能,气道高反应性降低,呼吸间隔显著缩短[104],总黄酮可提高 KIF3A 的水平影响 Hedgehog 信号通路,KIF3A 可能是洋甘菊治疗哮喘的潜在靶蛋白[105]。

3 质量标志物(Q-Marker)预测

中药 Q-Marker 是存在于中药材和中药产品中固有的或加工制备过程中形成的、与中药功能属性密切相关的化学物质,作为反映中药安全性和有效性的标志性物质进行质量控制[106]。《中华人民共和国卫生部药品标准》(维吾尔药分册)收载了洋甘菊药材基源、性状、鉴别,尚未收载含量测定项[107]。《美国药典》《英国药典》《欧洲药典》均以芹菜素-7-*O*-葡萄糖苷含量作为质量评价标准,专属性较低[21]。为更好地评价洋甘菊药材质量,从植物亲缘学及化学成分特有性、临床药效和传统药性、成分可测性及成分有效性方面对洋甘菊的 Q-marker 进行预测分析,为建立药材科学合理的质量控制方法提供参考。

3.1 基于植物亲缘学及化学成分特有性证据的 Q-marker 预测分析

我国境内的菊科植物约有 240 个属,2 300 个种,化学成分 30 余类,主要有萜类、黄酮类、香豆素类等[108]。其中母菊属植物全球约 40 种,分布于欧洲、亚洲(西部、北部和东部)、非洲南部以及西北美,我国有洋甘菊和同花母菊两种[109]。在同花母菊中鉴定出 28 个挥发油成分,丙酸香叶酯和金合欢烯为主要成分[110]。金合欢烯也是洋甘菊挥发油的主要成分,此外还有 α-红没药醇、母菊奥等倍半萜。母菊奥是挥发油中最有价值的成分之一,由于其性状为蓝色黏稠液体,也被称作“蓝油”,常作为评定药材质量的标准[111]。通过分析母菊属植物和洋甘菊的特征性成分,可将黄酮、倍半萜类化学成分作为洋甘菊的 Q-marker。

3.2 基于化学成分有效性的 Q-marker 预测分析

现代药理研究表明,洋甘菊提取物具有多种药理活性。其中以倍半萜为主导的挥发油成分和黄酮类成分含量较高,也是主要的药效物质基础。洋甘菊总黄酮[77]通过下调 ACC/FAS/DGAT2 信号通路蛋白表达改善血脂水平;芹菜素及其糖苷[19]、槲皮素、木犀草素与 6,7-二羟基香豆素[67]通过抑制 α-淀粉酶和 α-葡萄糖苷酶的吸收发挥降血糖作用;α-红没药醇[48]、芹菜素、槲皮素[49]与母菊奥[50]体内体外实验中均能够抑制炎性因子表达,母菊奥可通过调节 NF-κB 信号通路发挥抗炎作用。因此,黄酮类及挥发油成分为洋甘菊的主要药效物质基础,可作为其 Q-marker 的选择参考。

3.3 基于成分与传统功效的相关性

在维吾尔药志中记载洋甘菊花解痉、消炎、解热、促进溃疡愈合和杀菌等作用。现代药理学研究表明,洋甘菊中倍半萜成分 α-红没药醇与母菊奥具有抗炎镇痛、抑菌、抗肿瘤,黄酮成分芹菜素、槲皮素具有抗氧化、解热镇痛抗炎等活性,作用与洋甘菊传统功效相对应,因此可选择 α-红没药醇、母菊奥、芹菜素、槲皮素作为洋甘菊的 Q-marker。

3.4 基于化学成分可测性的 Q-marker 预测分析

Leng 等[112]采用 HPLC 法同时测定 3 批洋甘菊中槲皮素、木犀草素和芹菜素含量。Su[113]测定了洋甘菊野生和栽培品种中绿原酸的含量。Zhao[21]研究发现洋甘菊中咖啡酰奎宁酸成分(绿原酸和异绿原酸 A、B、C)含量高,可作为指标成分。Orav 等[114]测定欧洲不同国家洋甘菊精油的成分与含量,8 个样品中红没药醇氧化物 A 含量最高,3 个样品中 α-红没药醇含量最高,母菊奥含量范围为 0.7%-15.3%。Viapiana 等[115]建立了 HPLC 指纹图谱,显示 12 个特征峰,从中指认了咖啡酸、丁香酸、阿魏酸和槲皮素,4 种成分分离度高,具有可测性,结合定量分析测定 4 种黄酮与 5 种酚酸成分的浓度,结果显示槲皮素 > 杨梅素 > 丁香酸 > 咖啡酸 > 山柰酚 > 阿魏酸 > 芦丁 > 没食子酸 > 对香豆酸。咖啡酸、丁香酸和杨梅素含量浓度范围较大,不考虑作为 Q-maker 的参考,因此可选择咖啡酰奎宁酸类成分(绿原酸、异绿原酸 A、B、C)总含量、红没药醇氧化物 A、α-红没药醇、槲皮素作为洋甘菊药材质量标志物的指标。

4 结 语

洋甘菊用药历史悠久,化学成分丰富,药理作用广泛,应用前景广阔。本文在综述洋甘菊化学成分与药理活性的基础上,在“中药质量标志物”理论的指导下,对洋甘菊 Q-marker进行了预测分析,筛选出黄酮类(如芹菜素、槲皮素)、酚酸类(如绿原酸和异绿原酸 A、B、C、阿魏酸)、倍半萜类(如 α-红没药醇、母菊奥、金合欢烯)作为其质量标志物,为洋甘菊质量评价体系进一步的研究提供参考。值得注意的是,在我国维吾尔民族医药中使用的洋甘菊也称为母菊,来源于菊科母菊属,另外有来源于菊科黄春菊属的植物罗马洋甘菊(*Anthemis nobile* L.),二者在外观上极为相似,应注意

鉴别。相较于国外,我国学者对洋甘菊的研究较少,今后的研究应拓宽思路,进一步挖掘洋甘菊有效成分的作用靶点,加强药理作用机制的研究,研发更多诸如祖卡木颗粒等,临床疗效优良的复方制剂,更加深入、有效地开发利用该药材资源。

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