黄精的化学组成及药理作用的研究进展

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摘 要:黄精是百合科黄精属(*Polygonatum* Mill.)植物,以根茎入药,具有健脾,润肺,补气等功效。黄精不仅是历代名贵的滋补药物,而且还是一味药食同源的药材。本文主要对 2020 版《中国药典》所收录的三种黄精的化学成分,药理作用及产品应用进行整理和归纳,为黄精的深入探索做铺垫。

关键词:黄精;化学成分;药理作用;黄精产品;多糖;百合科

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Advances in chemical constituents and pharmacological effects of Polygonati Rhizoma

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Abstract:Polygonati Rhizoma belongs to the *Polygonatum* Mill. in the Liliaceae family. It is used as a Chinese drug with rhizomes, with the functions of tonifying the spleen, moisturizing the lungs, and invigorating qi. Polygonati Rhizoma is not only a precious nourishing medicine in the past dynasties, but also a medicinal material with the same origin of medicine and food. This paper provides a summary of the research advances on chemical compositions, pharmacological effects and product application of *P. sibiricum*, *P. kingianum*, and *P. cyrtonema* recorded in Chinese Pharmacopoeia in 2020, and lays the foundation for further exploration of Polygonati Rhizoma.

Key words:*Polygonatum*;chemical compositions;pharmacological effects;product of *Polygonatum*;polysaccharide;Lillaceae

2020 年版《中国药典》中收载黄精 3 种,分别为黄精(*Polygonatum sibiricum* Red)、多花黄精(*Polygonatum cyrtonema* Hua)和滇黄精(*Polygonatum kingianum* Coll. et Hemsl.)。根据根部形状俗称为“鸡头黄精”“姜形黄精”“大黄精”[1]。黄精属植物分布广泛,我国就有 79 种[2]。在海拔 800 ~ 2 800 m 的山上都可以生长,黄精主要产自我国的东北三省,以及西北、河北、安徽东部、浙江等地;多花黄精主要产自四川、安徽、贵州、江苏、浙江、福建、湖南、湖北、广东、广西等地;滇黄精主要产自云南、四川、贵州等地。

黄精,始载于《名医别录》,“其味甘,平,无毒。主补中益气,除分湿,安五脏。久服轻身、延年、不饥”。因此,人们认为黄精是“长生不老和延年益寿药”[3],为补益之品,广泛应用于保健食品的开发中。Chen 等[4]以现代药理作用的角度归纳了黄精具有抗脂肪肝、抗糖尿病、保护肾脏、抗阿尔兹海默症、保护心脏及抗癌等作用。然而这些药理作用的不同与黄精中的化学成分密切相关,比如黄精多糖、生物碱、皂苷、黄酮、蒽醌类化合物、挥发性物质、植物甾醇、木脂素以及多种对人体有用的氨基酸等化合物[5],其中,多糖和皂苷是黄精中研究最广泛的化学成分。与已有综述[4]相比,本文将黄精的药理作用重新归类并补充了抗动脉粥样硬化,抗 HIV,抗氧化等作用,除此之外,还将药典规定的三种黄精已鉴别出的化学成分,黄精多糖和皂苷的合成通路以及黄精相关产品进行整理归纳,旨在为黄精治疗与预防现代疾病及保健品开发研究提供思路。

1 化学成分

1.1 多糖

黄精多糖是黄精化学组成的重要成分,也是衡量黄精质量的重要指标。2020 年药典规定黄精多

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糖的含量不能低于7.0%。在不同生长环境下,不同炮制方法及不同龄节的黄精多糖含量也有较大差异[6,7]。

黄精多糖主要由单糖组成,包括甘露糖、葡萄糖、半乳糖、果糖、半乳糖醛酸、阿拉伯糖和葡萄糖醛酸等。Fang 等[8]通过水提醇沉法获得黄精多糖(PSP),并分离纯化得到 PSPI,其主要含有葡萄糖,化学结构分析表明 PSPI 结构的主链为 β-(1→2)键相连的酮糖,酮糖主链上连接着 α 构型的葡萄糖。Li 等[9]通过实验制备了 4 种多花黄精多糖(PCP),分别为 DASS、CASS、HBSS、CHSS,都是 β-糖苷键连接的吡喃型酸性多糖;此外,4 种多糖均含鼠李糖、甘露糖、阿拉伯糖、木糖、葡萄糖、半乳糖和半乳糖醛酸。Wang[10]通分离纯化得到 3 种 PCPs。PCPs-l 和 PCPs-2 主要由半乳糖和葡萄糖组成,PCPs-3 主要由半乳糖组成。Wu 等[11]从滇黄精中首次提取分离出滇黄精多糖(PKP),即一个大约含有 50 个葡萄糖单元的中性多糖 PKPI。

研究表明,PSP 生物合成可分为三个主要阶段。首先,蔗糖在 β-呋喃果糖苷酶(SacA)的作用下转化为葡萄糖-6-磷酸(Glc-6P)和果糖(Fru)[12],Glc-6P 通过磷酸葡糖苷酶(PGM)异构化为葡萄糖-1-磷酸(Glc-1P)[13],果糖通过已糖激酶(HK)和果糖激酶(Scrk)合成果糖-6-磷酸(Fru-6P)[14,15]。其次,尿苷二磷酸葡萄糖(UDP-Glc)立即衍生自 Glc-1P[16],而 Fru-6P 间接转化为鸟苷二磷酸甘露糖(GDP-Man)[17];UDP-Glc 和 GDP-Man 通过核苷二磷酸(NDP)糖相互转化酶(NSEs)的作用进一步转化成一些 NDP 糖[18]。最后,各种 NDP 糖在糖基转移酶(GTs)的作用下形成不断增长的多糖链[19]。在植物中,UDP-Glc 是 NDP 糖的关键前体[20](见图 1)。

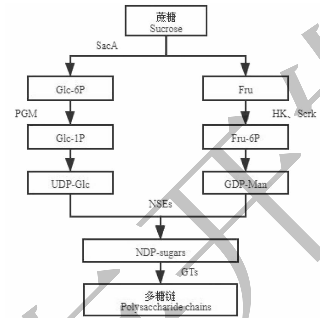

图 1 黄精多糖的生物合成

Fig. 1 The biosynthesis of PSP

1.2 皂苷

皂苷是黄精中另一主要化学成分,主要分为甾体皂苷和三萜皂苷。目前发现黄精、多花黄精以及滇黄精中共有 77 种甾体皂苷类化合物(化合物 **1 ~ 77**)[21-33],其中,黄精中有 43 种,滇黄精有 31 种,多花黄精 4 种。而黄精和滇黄精中共有 12 种三萜皂苷(化合物 **78 ~ 89**)(见图 2、图 3、表 1)。

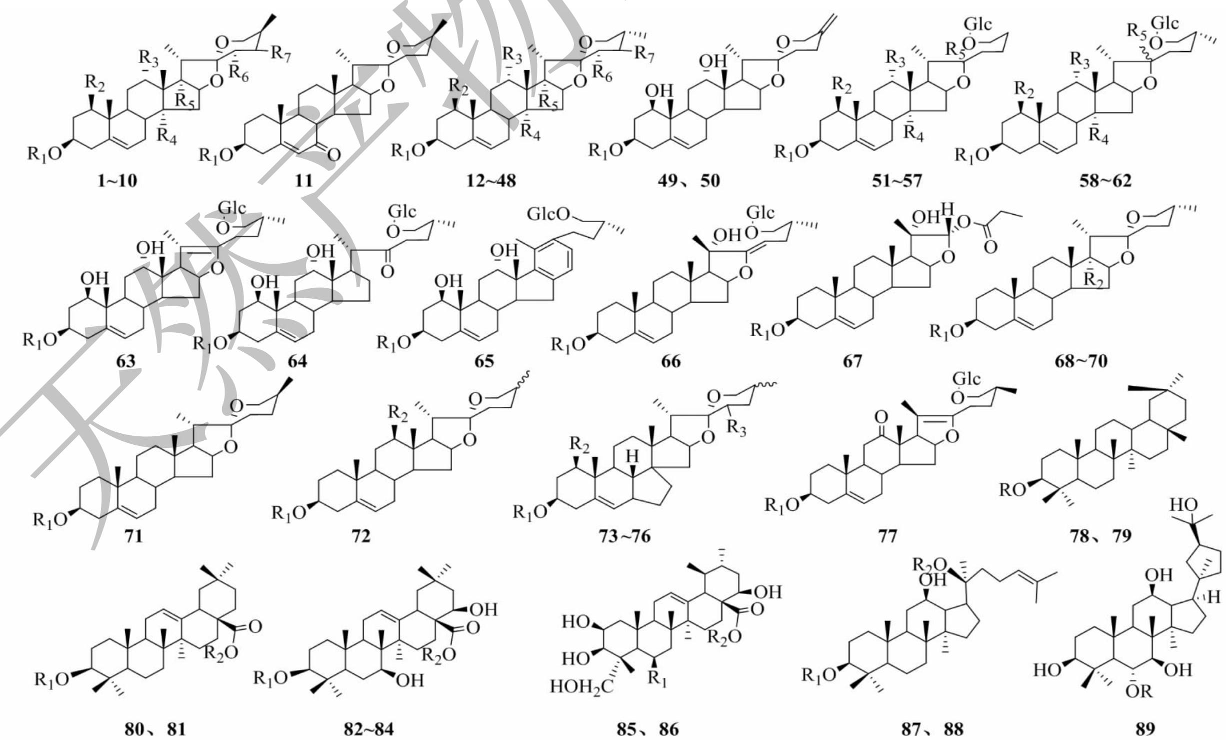

图 2 3 种黄精中皂苷化合物的结构

Fig. 2 Structures of saponins in three kinds of *Polygonatum*

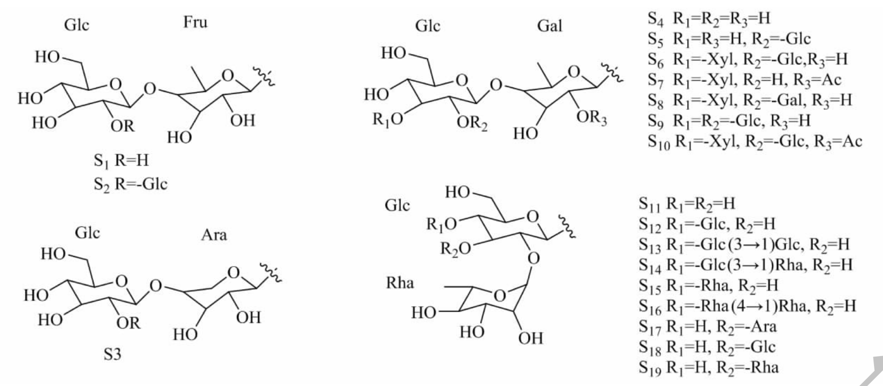

图 3 黄精中甾体皂苷的糖基结构

Fig. 3 Sugar moiety skeletons of steroidal saponin in three kinds of *Polygonatum*

表 1 3 种黄精分离得到的皂苷

Table 1 Saponins from three kinds of *Polygonatum*

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
甾体皂苷 Steroidal saponins				
1	(25*S*)-Spirost-5-en-12-one-3-*O*-*β*-*D*-glucopyranosyl-(1→2)-*β*-*D*-glucopyranosyl-(1→3)-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_9, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PC	21
2	Neoprazerigenin A 3-*O*-*β*-ycotetraoside	$R_1 = S_6, R_2 = R_3 = R_4 = R_6 = R_7 = H, R_4 = OH$	PS	22
3	新西伯利亚蓼苷 A Neosibiricoside A	$R_1 = S_2, R_2 = R_3 = R_4 = R_5, R_6 = R_7 = H$	PS	23
4	新西伯利亚蓼苷 B Neosibiricoside B	$R_1 = S_6, R_2 = OAc, R_3 = R_4 = R_5 = R_6 = R_7 = H$	PS	23
5	新西伯利亚蓼苷 C Neosibiricoside C	$R_1 = S_7, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PS	23
6	新西伯利亚蓼苷 D Neosibiricoside D	$R_1 = S_5, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$ (25*R*,*S*)	PS	23
7	(25*S*)-Pratioside D_1	$R_1 = S_5, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PK	24
8	(25*S*)-滇黄精苷 A (25*S*)-Kingianoside A	$R_1 = S_4, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PK	24
9	滇黄精苷 H Kingianoside H	$R_1 = S_4, R_2 = R_4 = R_5 = R_6 = H, R_3 = O, R_7 = OH$	PK	25
10	滇黄精苷 I Kingianoside I	$R_1 = S_5, R_2 = R_4 = R_5 = R_6 = H, R_3 = O, R_7 = OH$	PK	25
11	滇黄精苷 K Kingianoside K	$R_1 = S_{17}$	PK	26
12	Sibiricogenin 3-*O*-*β*-lycotetraoside	$R_1 = S_6, R_2 = R_3 = R_5 = R_7 = H, R_4 = R_6 = OH$	PS	22
13	Huangjingenin	$R_1 = R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
14	Huangjinoside C	$R_1 = -Ara, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
15	Huangjinoside D	$R_1 = -Fuc, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
16	Huangjinoside E	$R_1 = S_1, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
17	Huangjinoside F	$R_1 = S_4, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
18	Huangjinoside G	$R_1 = S_2, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
19	Huangjinoside H	$R_1 = S_2, R_4 = R_5 = R_6 = R_7 = H, R_2 = R_3 = OH$	PS	27
20	Huangjinoside I	$R_1 = S_3, R_2 = R_3 = R_6 = OH, R_4 = R_5 = R_7 = H$	PS	27
21	Huangjinoside J	$R_1 = S_1, R_2 = R_3 = R_6 = OH, R_4 = R_5 = R_7 = H$	PS	27
22	Huangjinoside K	$R_1 = S_4, R_2 = R_3 = R_6 = OH, R_4 = R_5 = R_7 = H$	PS	27

续表 1(Continued Tab. 1)

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
23	Huangjinoside L	$R_1 = S_4, R_2 = R_3 = R_5 = R_6 = OH, R_4 = R_7 = H$	PS	27
24	Huangjinoside M	$R_1 = S_1, R_2 = R_3 = R_6 = R_7 = OH, R_4 = R_5 = H$	PS	27
25	Huangjinoside N	$R_1 = S_1, R_2 = R_3 = R_6 = OH, R_4 = R_5 = H, R_7 = OGlc$	PS	27
26	Huangjinoside O	$R_1 = S_1, R_2 = R_3 = OH, R_4 = R_5 = R_6 = H, R_7 = OGlc$	PS	27
27	Spirost-5-en-3*β*,14*α*-diol-3-*O*-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*-xylopyranosyl-(1→3)]-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_6, R_2 = R_3 = R_5 = R_6 = R_7 = H, R_4 = OH$ (25*R*,*S*)	PS	23
28	Spirost-5-en-3*β*-ol-3-*O*-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*-xylopyranosyl-(1→3)]-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside(PO-2)	$R_1 = S_6, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$ (25*R*,*S*)	PS	23
29	3-*O*-*β*-*D*-Glucopyranosyl (1→4)-[*α*-*L*-rhamnopyranosyl (1→2)]-*β*-*D*-glucopyranosyl-diosgenin (PO-3)	$R_1 = S_{12}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PS	28
30	3-*O*-*α*-*L*-Rhamnopyranosyl (1→4)-[*α*-*L*-rhamnopyranosyl (1→2)]-*β*-*D*-glucopyranosyl-diosgenin	$R_1 = S_{15}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PS	28
31	3-*O*-*β*-*D*-Glucopyranosyl(1→3)-*β*-*D*-glucopyranosyl(1→4)-[*α*-*L*-rhamnopyranosyl (1→2)]-*β*-*D*-glucopyranosyl-diosgenin	$R_1 = S_{13}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PS	28
32	(25*R*)-Spirost-5-en-12-one-3-*O*-*β*-*D*-glucopyranosyl-(1→2)-*β*-*D*-glucopyranosyl-(1→3)-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_9, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PC	21
33	Spirost-5-en-12-one-3-*O*-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*-xylopyranosyl-(1→3)]-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_8, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$ (25*R*,*S*)	PC	21
34	3-Hydroxyspirost-5-en-12-one	$R_1 = R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$ (25*R*,*S*)	PC	21
35	滇黄精苷 A Kingianoside A	$R_1 = S_4, R_2 = R_4 = R_5 = R_6 = R_7 = H$, R3 = O	PK	29
36	滇黄精苷 B Kingianoside B	$R_1 = S_1, R_2 = R_4 = R_5 = R_6 = R_7 = H$, R3 = O	PK	29
37	Funkioside C	$R_1 = S_4, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PK	29
38	(25*R*)-滇黄精苷 G (25*R*)-Kingianoside G	$R_1 = S_5, R_2 = R_4 = R_5 = R_7 = H, R_3 = O, R_6 = OH$	PK	24
39	Pratioside D_1	$R_1 = S_5, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PK	26
40	(25*R*)-Spirost-5-en-3*β*,17*α*-diol-3-*O*-*α*-*L*-rhamnopyranosyl-(1→4)-*α*-*L*-rhamnopyranosyl-(1→4)-[*α*-*L*-rhamnopyranosyl-(1→2)]-*β*-*D*-glucopyranoside	$R_1 = S_{16}, R_2 = R_4 = R_6 = R_7 = H, R_3 = O, R_5 = OH$	PK	25
41	(25*R*)-Spirost-5-en-3*β*,17*α*-diol-3-*O*-*β*-*D*-glucopyranosyl-(1→3)-[*α*-*L*-rhamnopyranosyl-(1→2)]-*β*-*D*-glucopyranoside	$R_1 = S_{12}, R_2 = R_4 = R_6 = R_7 = H, R_3 = O, R_5 = OH$	PK	25
42	Polygonatoside C_1	$R_1 = S_{17}, R_2 = R_4 = R_6 = R_7 = H, R_3 = O, R_5 = OH$	PK	25
43	Ophiopogonin C′	$R_1 = S_{12}, R_2 = R_4 = R_5 = R_6 = R_7 = H, R_3 = O$	PK	25
44	Gracillin	$R_1 = S_{18}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PK	26
45	Dioscin	$R_1 = S_{19}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PK	26
46	Saponin Tb	$R_1 = S_{11}, R_2 = R_3 = R_4 = R_6 = R_7 = H, R_5 = OH$	PK	26
47	Saponin Pa	$R_1 = S_{15}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PK	26
48	Parissaponin Pb	$R_1 = S_{16}, R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = H$	PK	26
49	Huangjinoside A	R_1 = -Ara	PS	27
50	Huangjinoside B	$R_1 = S_6$	PS	27
51	黄精皂苷 A Sibiricoside A	$R_1 = S_4, R_2 = R_3 = R_4 = H, R_5 = OMe$	PS	22
52	黄精皂苷 B Sibiricoside B	$R_1 = S_4, R_2 = R_3 = H, R_4 = OH, R_5 = OMe$	PS	22
53	(25*S*)-滇黄精苷 C (25*S*)-Kingianoside C	$R_1 = S_4, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	27

续表 1(Continued Tab. 1)

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
54	(25*S*)-滇黄精苷 D (25*S*)-Kingianoside D	$R_1 = S_1, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	27
55	(25*S*)-滇黄精苷 E (25*S*)-Kingianoside E	$R_1 = S_5, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	27
56	22-Hydroxylwattinoside C	$R_1 = S_4, R_2 = R_5 = OH, R_3 = O, R_4 = H$	PK	27
57	(25*S*)-滇黄精苷 F (25*S*)-Kingianoside F	$R_1 = S_5, R_2 = R_5 = OH, R_3 = O, R_4 = H$	PK	27
58	滇黄精苷 C Kingianoside C	$R_1 = S_4, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	29
59	滇黄精苷 D Kingianoside D	$R_1 = S_1, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	29
60	滇黄精苷 E Kingianoside E	$R_1 = S_5, R_2 = R_4 = H, R_3 = O, R_5 = OH$	PK	27
61	(25*R*,22)-Hydroxylwattinoside C	$R_1 = S_4, R_2 = R_5 = OH, R_3 = O, R_4 = H$	PK	27
62	滇黄精苷 F Kingianoside F	$R_1 = S_5, R_2 = R_5 = OH, R_3 = O, R_4 = H$	PK	27
63	Huangjinoside P	$R_1 = S_1$	PS	27
64	Huangjinoside Q	$R_1 = S_6$	PS	27
65	Huangjinoside R	$R_1 = S_3$	PS	27
66	Polygonoide A	$R_1 = S_{14}$	PS	30
67	Polygonoide B	$R_1 = S_{12}$	PS	30
68	(25*R*)-Spirost-5-en-3*β*,17*α*-diol-3-*O*-*β*-*D*-glucopyranosyl (1→4)-*β*-*D*-fucopyranoside	$R_1 = S_1, R_2 = OH$(25*R*)	PS	31
69	(25*S*)-Spirost-5-en-3*β*,17*α*-diol-3-*O*-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-fucopyranoside	$R_1 = S_1, R_2 = OH$(25*S*)	PS	31
70	(25*R*)-Spirost-5-en-3*β*,17*α*-diol-3-*O*-*β*-*D*-glucopyranosyl(1→2)-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-fucopyranoside	$R_1 = S_2, R_2 = OH$(25*R*)	PS	31
71	(25*S*)-Spirost-5-en-3*β*-ol-3-*O*-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-fucopyranoside	$R_1 = S_1$	PS	31
72	(25*R/S*)-Spirost-5-en-3*β*,12*β*-diol-3-*O*-*β*-*D*-glucopyranosyl(1→4)-*β*-*D*-fucopyranoside	$R_1 = S_2, R_2 = OH$(25*R*,*S*)	PS	31
73	(23*S*,24*R*,25*R*)-1-*O*-Acetylspirost-5-ene-1*β*,3*β*,23,24-tetrol 3-*O*-*β*-*D*-glucopyranosyl-(1→2)-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-fucopyranoside	$R_1 = S_2, R_2 = OAc, R_3 = R_4 = OH$	PS	32
74	(25*S*)-1-*O*-Acetylspirost-5-ene-1*β*,3*β*-diol3-*O*-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*-xylopyranosyl-(1→3)]-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_6, R_2 = OAc, R_3 = H$(25*S*)	PS	32
75	(25*S*)-Spirost-5-en-3a-ol3-*O*-*β*-*D*-glucopyranosyl-(1→2)-[*β*-*D*-xylopyranosyl-(1→3)]-*β*-*D*-glucopyranosyl-(1→4)-2-*O*-acetyl-*β*-*D*-galactopyranoside	$R_1 = S_{10}, R_2 = R_3 = H$(25*S*)	PS	32
76	(25*R*,*S*)-Spirost-5-en-3*β*-ol3-*O*-*β*-*D*-glucopyranosyl-(1→2)-*β*-*D*-glucopyranosyl-(1→4)-*β*-*D*-galactopyranoside	$R_1 = S_5, R_2 = R_3 = H$(25*R*,*S*)	PS	32
三萜皂苷 Triterpene saponins				
77	Kingianoside Z	$R_1 = S_5$	PS	33
78	3*β*-羟基-(3→1)葡萄糖-(4→1)葡萄糖-齐墩果烷 3*β*-Hydroxy-(3→1)glucose-(4→1)glucose-oleanane	R = -Glc(4→1)Glc	PS	27
79	3*β*-羟基-(3→1)葡萄糖-(2→1)葡萄糖-齐墩果酸 3*β*-Hydroxy-(3→1)glucose-(2→1)glucose-oleanolic acid	R = -Glc(2→1)Glc	PS	27
80	3*β*-羟基-(3→1)葡萄糖-(4→1)葡萄糖-(28→1)阿拉伯糖-(2→1)阿拉伯糖-齐墩果酸 3*β*-Hydroxy-(3→1)glucose-(4→1)glucose-(28→1)arabinose-(2→1)arabinose-oleanolic acid	R_1 = -Glc(2→1)Glc, $R_2 = H$	PS	27
81	3*β*,30*β*-二羟基-(3→1)葡萄糖-(2→1)葡萄糖-齐墩果烷 3*β*,30*β*-Dihydroxy-(3→1)glucose-(2→1)glucose-oleanane	R_1 = -Glc(4→1)Glc, R_2 = -Ara(2→1)Ara	PS	27
82	Polygonoide C	R_1 = -Glc(4→1)Glc(2→1)Rha, $R_2 = H$	PS	27

续表 1(Continued Tab. 1)

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
83	Polygonoide D	R_1 = -Glc(4→1)Glc(2→1)Rha, R_2 = CH_3	PS	27
84	Polygonoide E	R_1 = -Glc[(2→1)Rha](4→1)Glc(3→1)Glc, R_2 = -Glc(3→1)Glc(3→1)Glc	PS	27
85	积雪草苷 Asiaticoside	R_1 = H, R_2 = -Glc(6→1)Glc(4→1)Rha	PS	27
86	羟基积雪草苷 Madecassoside	R_1 = OH, R_2 = -Glc(6→1)Glc(4→1)Rha	PS	27
87	人参皂苷 Rc Ginsenoside Rc	R_1 = -Glc(2→1)Glc, R_2 = -Glc(2→1)Ara	PK	27
88	人参皂苷 Rb_1 Ginsenoside Rb_1	R_1 = -Glc(2→1)Glc, R_2 = -Glc(6→1)Glc	PK	27
89	伪人参皂苷 F_{11} Pseudoginsenoside F_{11}	R = -Glc(2→1)Rha	PK	27

注:PS:黄精;PC:多花黄精;PK:滇黄精。
Note:PS:*Polygonatum sibiricum*;PC:*P. cyrtonema*;PK: *P. kingianum*.

黄精皂苷主要以甾体皂苷为主,其生物合成分为3条代谢途径[34,35],第一条途径是萜类化合物骨架生物合成,即由MEP(2-C-甲基-D-赤藓醇-4-磷酸途径)和MVA(甲羟戊酸途径)通过IPPI(异戊烯基二磷酸异构酶)介导最终生成DMAPP(二甲丙烯焦磷酸)和IPP(异戊烯基焦磷酸);第二条途径是倍半萜和三萜的生物合成,DMAPP和IPP通过缩合反应合成FPP(法尼基焦磷酸),再通过SS(角鲨烯合酶)、SM(角鲨烯环氧化酶)的催化形成OS(2,3-氧化角鲨烯);第三条途径是甾体生物合成,OS在CAS(环阿屯醇合酶)的催化下形成CA(环阿屯醇),随后在一系列酶的作用下合成甾体皂苷元,最后在甾体皂苷糖基转移酶合成甾体皂苷(见图4)。

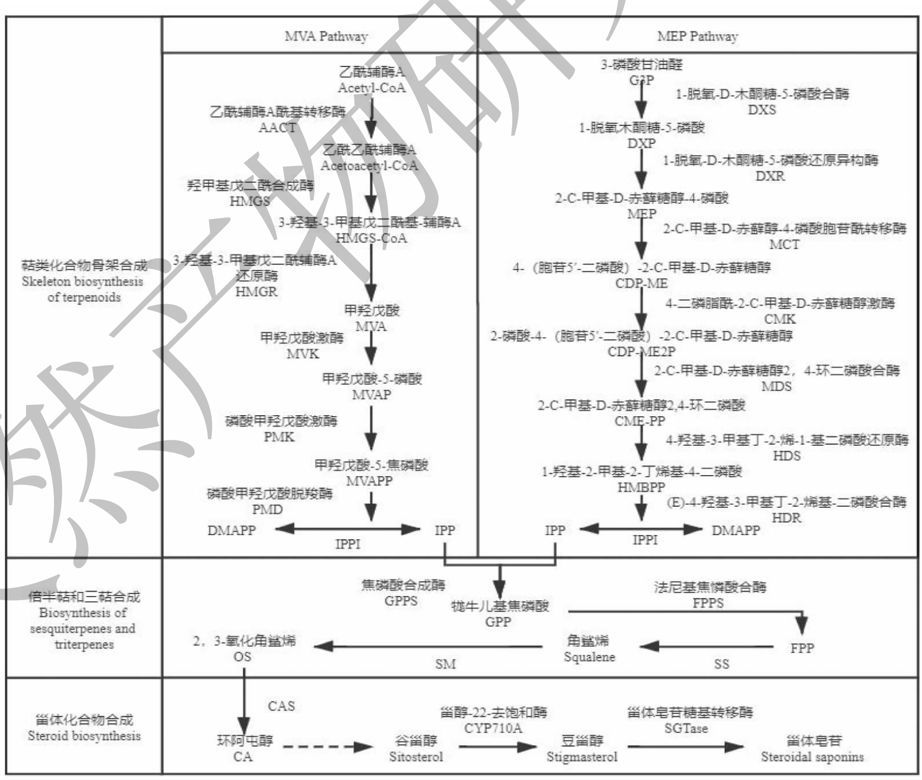

图4 黄精甾体皂苷的生物合成途径

Fig. 4 The biosynthetic pathway of steroidal saponin biosynthesis in *Polygonatum*

注:黑实线箭头代表已识别的酶反应;黑色虚线箭头代表省略的一系列合成步骤。Note:the solid black arrows represent identified enzyme reactions;The dotted black arrow represents a series of synthetic steps that have been omitted.

1.3　黄酮

黄酮类化合物广泛存在于植物体内,是指以 2-苯基色原酮为母核而衍生的一类色素。在 3 种黄精中分离得到了 20 种黄酮类化合物(化合物 **90** ~ **109**)[31,36-42],根据母核结构的不同,可分为 6 种,分别为高异黄酮类、异黄酮类、查耳酮类、二氢黄酮类、紫檀烷类和黄酮类(见图 5、表 2)。

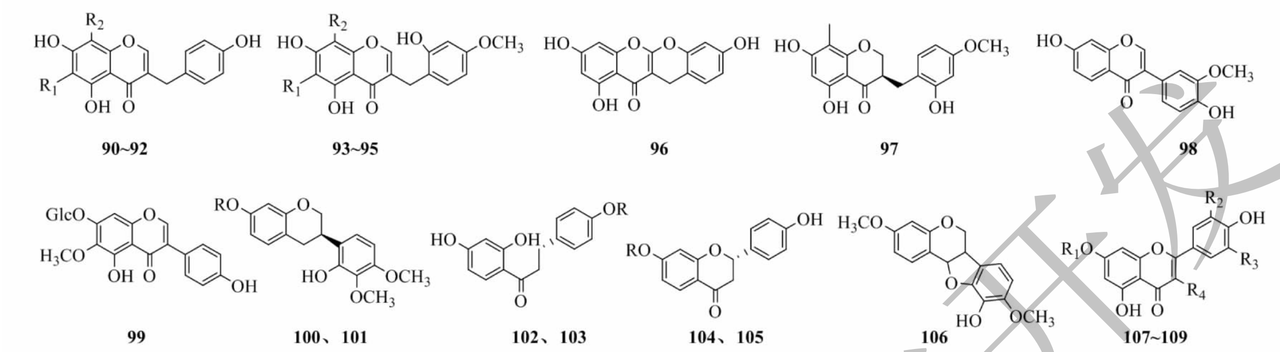

图 5　3 种黄精中黄酮化合物的结构

Fig. 5　Structures of flavonoids in three kinds of *Polygonatum*

表 2　3 种黄精分离得到的黄酮类化合物

Table 2　Flavonoids isolated from three kinds of three kinds of *Polygonatum*

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
高异黄酮类亚型 Homoisoflavones				
90	4′,5,7-三羟基-6,8-二甲基高异黄酮 4′,5,7-Trihydroxy-6,8-dimethyl-homoisoflavanon	$R_1 = R_2 = CH_3$	PS	31
91	4′,5,7-三羟基高异黄酮 4′,5,7-Trihydroxy-homoisoflavanon	$R_1 = R_2 = H$	PS	31
92	4′,5,7-三羟基-6-甲基高异黄酮 4′,5,7-Trihydroxy-6-methyl-homoisoflavanon	$R_1 = CH_3$, $R_2 = H$	PS	31
93	2′,5,7-三羟基-4′-甲氧基-6,8-二甲基高异黄酮 2′,5,7-Trihydroxy-4′-methoxy-6,8-dimethyl-homoisoflvanaone	$R_1 = R_2 = CH_3$	PS	31
94	2′,5,7-三羟基-4′-甲氧基高异黄酮 2′,5,7-Trihydroxy-4′-methoxyl-homoisoflvanaone	$R_1 = R_2 = H$	PS	31
95	2′,5,7-三羟基-4′-甲氧基-8-甲基高异黄酮 2′,5,7-Trihydroxy-4′-methoxyl-8-methyl-homoisoflvanaone	$R_1 = CH_3$, $R_2 = H$	PS	31
96	Disporopsin	–	PK	38
97	(3*R*)-5,7-Dihydroxy-8-methyl-3-(2′-hydroxy-4′-methoxybenzyl)-chroman-4-one	–	PC	36
异黄酮类亚型 Isoflavones				
98	4′,7-二羟基-3′-甲氧基异黄酮 4′,7-Dihydroxy-3′-methoxyisoflavone	–	PK	39
99	鸢尾苷 Tectoridin	–	PS	40
100	2′,7-二羟基-3′,4′-二甲氧基异黄烷苷 2′,7-Dihydroxy-3′,4′-dimethoxyisoflavanoside	R = -Glc	PK	37
101	2′,7-二羟基-3′,4′-二甲氧基异黄烷 2′,7-Dihydroxy-3′,4′-dimethoxyisoflavan	R = H	PK	37
查耳酮类亚型 Chalcones				
102	异甘草素 Isoliquiritigenin	R = H	PK	37

续表 2(Continued Tab. 2)

序号 No.	化合物名称 Compound name	取代基 Substituent	来源 Source	文献 Ref.
103	新异甘草苷 Neoisoliquiritigenin	R = -Glc	PK	39
二氢黄酮类亚型 Dihydroflavones				
104	新甘草苷 Liquiritin	R = -Glc	PK	37
105	甘草素 Liquiritigenin	R = H	PK	39
紫檀烷类亚型 Rosandalanes				
106	(6a*R*,11a*R*)-10-羟基-3,9-二甲氧基紫檀烷 (6a*R*,11a*R*)-10-Hydroxy-3,9-dimethoxypterane	–	PK	37
黄酮类亚型 Flavones				
107	芹菜素 7-*O*-*β*-*D*-葡萄糖苷 Apigenin-7-*O*-*β*-*D*-glucoside	R_1 = -Glc, R_2 = R_3 = R_4 = H	PS	42
108	山奈酚 Kaempferol	R_1 = R_2 = R_3 = H, R_4 = OH	PS	42
109	杨梅素 Myricetin	R_1 = H, R_2 = R_3 = R_4 = OH	PS	42

注:PS:黄精;PC:多花黄精;PK:滇黄精。
Note:PS:*Polygonatum sibiricum*;PC:*P. cyrtonema*;PK: *P. kingianum*.

1.4 生物碱及蒽醌类化合物

生物碱类化合物在黄精属植物中含量较低。Kun 等[43]从黄精中分离得到了腺苷(**112**),Sun 等[44]从黄精中共分离得到 polygonatine A(**110**)和 polygonatine B(**111**)。Sun 等[41]还从黄精中分离得到一种神经鞘苷类同系物,黄精神经鞘苷 A ~ C(**117**)。Wang[45]从黄精中分离出 11 种生物碱,其中有 3 种化合物是第一次从天然植物中分离得到。滇黄精中分离得到的生物碱类有 kingaone(**123**)、*N*-*trans*-*p*-coumaroyloctopamine(**116**)[38,46]。Ren 等[47]从多花黄精生品及酒制品中共鉴定 6 种生物碱(见图 6、表 3)。

多花黄精中还含有毛地黄精苷和吖啶-2-羧酸等蒽醌类化合物,且这类化合物与抗病毒、抗菌、免疫调节等生物活性相关[48]。

1.5 木脂素

木脂素是植物的次级代谢产物,广泛存在于植物体中,一般由两分子苯丙素氧化聚合而成的。2001 年,Sun[41]第一次分离得到了 4 个黄精木脂素化合物分别为右旋松脂醇-*O*-*β*-*D*-吡喃葡萄糖基(6→1)-*β*-*D*-吡喃葡萄糖苷、右旋丁香脂素、鹅掌楸碱和右旋丁香脂素-*O*-*β*-*D*-吡喃葡萄糖苷;直到 2020 年,Chen 等[49]从黄精中分离出 1 个新型苯骈呋喃型木脂素,并将其命名为黄精新木脂素苷 A。

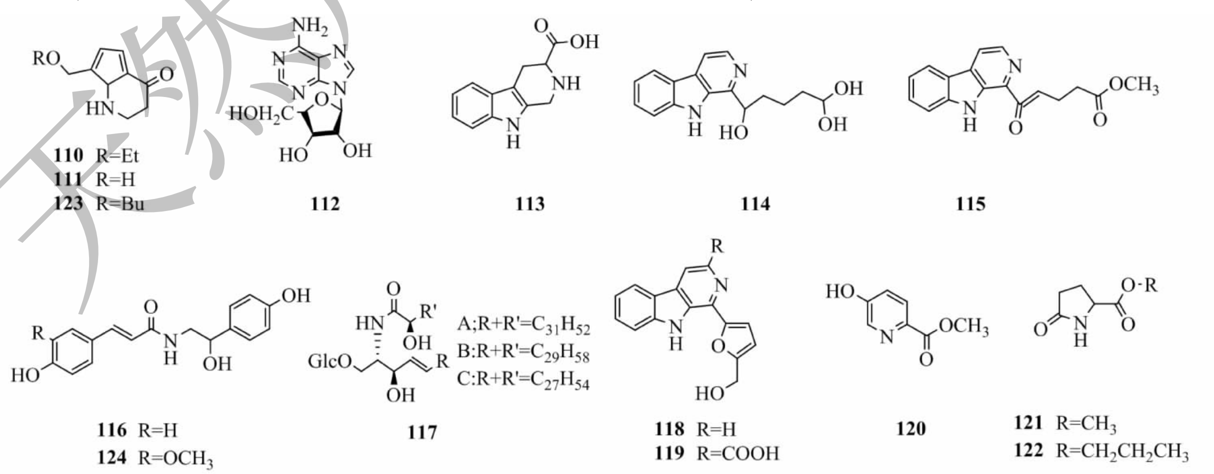

图 6 3 种黄精生物碱的结构
Fig. 6 Structures of alkaloids in 3 kinds of *Polygonatum*

表 3　3 种黄精中的生物碱

Table 3　Alkaloids in 3 kinds of *Polygonatum*

序号 No.	化合物名称 Compound name	来源 Source	文献 Ref.
110	Polygonatine A	PS、PK	38,44
111	Polygonatine B	PS、PK	38,44
112	腺苷 Adenosine	PS	43
113	2,3,4,6-Tetrahydro-1H-*β*-carboline-3-carboxylic acid	PS、PC	45,49
114	5-(9H-*β*-carbolin-1-yl)-pentane-1,2,5-triol	PS、PC	45,49
115	4-(9H-*β*-carbolin-1-yl)-4-oxo-but-2-enoic acid methyl ester	PS、PC	45,49
116	*N-trans-p*-coumaroyloctopamine	PK	38
117	黄精神经鞘苷 A ~ C Sibiricumcerebroside A-C	PS	41
118	1-(5-Hydroxymethyl-2-furyl)-9H-pyrido[3,4-b]indole	PS	45
119	l-(5-Hydroxym-ethyl-tetrahydro-furan-2-yl)-9H-*β*-carboline-3-carboxylic acid	PS	45
120	5-Hydroxy-pyridine-2-carboxylate	PS	45
121	5-Oxo-pyrrolidine-2-carboxylic acid methyl ester	PS	45
122	5-Oxo-pyrrolidine-2-carboxylic acid butyl ester	PS	45
123	Kingaone	PK	46
124	*N*-阿魏酰真蛸胺 *N*-feruloyloctopamine	PC	47

注:PS:黄精;PC:多花黄精;PK:滇黄精。

Note:PS:*Polygonatum sibiricum*;PC:*P. cyrtonema*;PK: *P. kingianum*.

1.6　挥发性物质

黄精中的挥发性物质研究较少,目前只在多花黄精根状茎中发现具有精油成分,占总挥发油的 95.97%,并通实验鉴定出 16 种化合物,如正癸烷、乳酸正丁酯和正十二烷等[50]。

1.7　植物甾醇

植物甾醇通常指的是植物固醇,广泛存在于各种植物的细胞膜中。黄精和滇黄精中发现了 4 种植物甾醇类化合物,分别为 *β*-谷甾醇、棕榈酸-3*β* 谷甾醇酯、胡萝卜苷、(22*S*)-cholest-5-ene-1*β*,3*β*,16*β*,22-tetrol 1-*O*-*α*-*L*-rhamnopyranosyl16-*O*-*β*-*D*-glucopyranoside[37,51]。

1.8　氨基酸和微量元素

黄精属植物中还存在大量氨基酸和微量元素。研究表明测得黄精根茎及其须根中均含有 14 种微量元素,以及 4 种常量元素(K、Ga、Mg、P),与此同时,还发现根茎中有 16 种氨基酸[52]。此外,Wang 等[53]发现黄精中丙氨酸和苏氨酸较为丰富。Li[54]在对黄精游离氨基酸成分分析中发现,黄精中富含 11 种游离氨基酸,其中含有赖氨酸、苯丙氨酸、组氨酸、缬氨酸、亮氨酸、异亮氨酸 6 种人体必需氨基酸。

2　黄精的药理作用

2.1　降血糖作用

目前,黄精对糖尿病及其并发症有明显的改善作用的活性成分为多糖、皂苷和总黄酮,其中,黄精多糖研究最广泛。Wang[55]发现 PKP 和 PSP 均对 *α*-葡萄糖苷酶有抑制作用,且 PSP 的抑制作用强于 PKP,随后作者利用 PSP 对链脲佐菌素(STZ)诱导的患病小鼠实施了体内降血糖实验,结果发现使用 PSP 后,小鼠饮水量、饮食量、血糖无变化,体重稍微升高,糖化血清蛋白含量降低,血清胰岛素升高。Shu 等[56]发现黄精总黄酮(TFP)对 1 型和 2 型糖尿病都有明显的降血糖作用,与对照组相比,100 和 200 mg/kg TFP 对 STZ 诱导的 T1DM 小鼠的降血糖作用与 20 mg/kg 阿卡波糖相似。在四氧嘧啶和高脂饮食诱导的 T2DM 小鼠中,200 mg/kg 的 TFP 具有与 15 mg/kg 的格列齐特相似的降血糖作用。

Wang 等[57]发现黄精多糖可降低 STZ 诱导的糖尿病小鼠血浆中的空腹血糖和糖化血红蛋白水平,升高其血浆胰岛素和 C 肽水平,同时增加了血浆中

丙二醛含量及降低超氧化物歧化酶活性，因此黄精多糖可能通过降低血糖和抑制氧化应激反应以减轻了视网膜血管病变。黄精多糖通过降低细胞凋亡蛋白 Bax、表皮生长因子 EGF、血管内皮生长因子 VEGF、转化生长因子 TGF-β 和 p38 MAPK 的信号转导作用，对糖尿病性视网膜损伤具有保护作用[58]。此外，还有研究发现黄精皂苷能够通过抑制 Wnt/β-catenin 信号通路激活而保护肾脏[59]。

2.2 降血脂作用

黄精可以调节与脂质代谢相关的相应基因和蛋白质的表达水平，对高脂血症、肥胖和脂肪肝的预防起到至关重要的作用。滇黄精多糖通过增加短链脂肪酸（SCFAs）的产生调控肠道微生物群落的相对丰度和多样性，促进肠道通透性屏障恢复，抑制 LPS（脂多糖）进入循环系统，减轻炎症反应，最终预防脂质代谢紊乱[60]。

Kong 等[61]研究表明，与对照组相比，黄精多糖组小鼠体内血清 TC（总胆固醇）、TG（甘油三酯）、LDL-C（低密度脂蛋白-胆固醇）的含量明显降低，HDL-C（高密度脂蛋白胆固醇）的含量显著增加；肝脏中的 PPAR-γ（过氧化物酶体增殖物激活受体-γ）、SREBP-1c（胆固醇调节元件结合蛋白 1c）、IL-6（白介素-6）和 TNF-α（肿瘤坏死因子-α）的表达下调，PPAR-α（过氧化物酶体增殖物激活受体-α）表达上调，因此多糖对脂类代谢相关因子具有调节作用，并能抑制肝脏脂质氧化，从而预防高脂血症。滇黄精可通过调节脂类代谢因子、降低氧化应激反应以及抑制细胞凋亡等发挥抗非酒精性脂肪肝的作用[62]。

2.3 抗肿瘤

Li 等[9]分离纯化得到 4 种多花黄精多糖，进一步研究了其是否抑制宫颈癌 Hela 细胞抑生长，结果表明 4 种多糖都具有诱导凋亡、抑制癌细胞增殖的效果。Long 等[63]发现黄精多糖可以激活 TLR4 信号通路，尤其是选择性上调 MyD88 依赖通路，引起 TRAF6（肿瘤坏死因子受体相关蛋白 6）增加，并诱导下游 MAPK/NF-κB 信号通路发挥其抗癌作用；在此过程中，白介素 IL-6、IL-1β、IL-12p70 和肿瘤 TNFα 等细胞因子的分泌被强烈诱导。此外，多花黄精凝集素（PCL）诱导细胞凋亡和自噬的机理是通过调节 Bax 和 Bcl-2 蛋白，引起线粒体去极化，细胞色素 c 释放和胱天蛋白酶激活，随后 PCL 能够终止谷胱甘肽抗氧化系统并诱导线粒体产生活性氧积累，从而导致 p38-p53 活化[64]。

2.4 抑菌抗炎作用

Cao 等[65]发现黄精多糖对金黄色葡萄球菌、大肠杆菌、枯草芽孢杆菌等都有明显的抑制作用。Debnath 等[66]发现黄精水提取物能够降低小鼠巨噬细胞系中的 NO，并抑制了 iNOS（诱导型一氧化氮合酶）和 TNF-α 蛋白的表达，以证实抗药作用。

2.5 免疫调节

Yelithao 等[67]利用 RAW264.7 细胞和 NK 细胞评估黄精多糖硫酸化和水解衍生物的免疫刺激作用，并发现 RAW264.7 细胞通过 MR（甘露糖受体）和 TLR4（Toll 样受体）介导的信号通路激活，CR3（β 葡聚糖受体）和 TRL2 在刺激 NK 细胞中起主要作用。Yong[68]通过 MTT 实验分析多花黄精多糖 PCP-1 的免疫调节作用，结果发现 PCP-1 浓度在 25-400 ug/mL 之间，不仅对巨噬细胞 RAW264.7 的生长无害，且有利于它的生长；随后，通过中性红实验发现 PCP-1 能够明显加强细胞吞噬，PCP-1 还能使巨噬细胞 RAW264.7 产生 NO。

2.6 抗氧化及抗衰老

Li 等[69]通过清除 ABTS 和 DPPH 自由基和总还原力等测定，表明多花黄精多糖具有一定的抗氧化作用，多糖对四种革兰氏阴性均具有抑菌作用，对枯草芽孢杆菌（*B. subtilis*）抑制作用最强。Yong[68]通过体外抗氧化实验验证多花黄精多糖 PCP-1 具有抗氧化和清除自由基的功能，PCP-1 清除 DPPH 能力随着 PCP-1 值升高而升高。Jiang 等[70]通过对黄精多糖进行动物实验验证，得知黄精粗多糖对 CCl_4 引发的大鼠肝氧化损伤具有一定抑制作用。

2.7 抗阿尔兹海默病

学习记忆能力衰退是阿尔兹海默症（AD）的主要特征之一，黄精水煎剂可明显缩短 β-淀粉样蛋白诱导的 AD 模型大鼠的逃避潜伏期，并通过降低 CA1 区在 Thr231 位点 tau 蛋白的磷酸化改善海马病理损伤，增强大鼠学习记忆能力，最终预防阿尔兹海默病[71]。

2.8 抗动脉粥样硬化

Yang 等[72]通过建立兔子动脉粥样硬化模型，结果表明多糖的抗动脉硬化作用可支持其低脂活动，改善大动脉形态，减少动脉粥样硬化兔模型中泡沫细胞数量和内皮细胞损伤。

2.9 心肌保护作用

Zhu 等[73]研究黄精多糖对大鼠急性心力衰竭

的保护作用,通过检测大鼠心率、左室收缩压、超氧化物歧化酶、丙二醛含量等指标,可知多糖可预防阿霉素所致急性心力衰竭。

2.10 抗骨质疏松作用

研究表明多糖在不影响 BMP(骨形态发生蛋白)信号通路的情况下,可抑制骨质疏松;多糖通过增加成骨细胞分化因子的表达或者碱性磷酸酶的活性以增强骨髓间充质干细胞(BMSCs)的成骨分化[74,75]。

2.11 其他作用

此外,黄精还具有促进睡眠、抗疲劳及抗 HIV 等多方面的药理活性。黄精根部的水提物促进睡眠的作用与 NREM(非快速眼动睡眠)的延伸以及 $GABA_A$-R2(G 氨基丁酸 A 型受体 2)和 5-HT1A(5-羟色胺受体)的上调相关,并通过与脊椎动物模型中的 $GABA_A$ 受体结合而被介导[75]。而多花黄精鲜品可以通过增加肌糖原和肝糖原含量,降低乳酸含量,从而起到抗疲劳作用,提高小鼠游泳时间[77]。另外多花黄精凝集素是一种新型抗 HIV 甘露糖结合凝集素[78]。

3 黄精产品应用

《食疗本草》曾记载:“黄精根、叶、花、实,皆可食之。”黄精除了药用外,还可作为食物食用。此外黄精也被列入在“药食同源”名录中[79]。随着人们对健康食品的要求升高,黄精被广泛的应用在保健食品的开发中,目前,黄精保健产品有 450 种,包括黄精酒、黄精糖、黄精茶、黄精固体饮料、黄精果脯、黄精豆腐等[80-82]。黄精中还含有多种天然美容活性成分,具有抗氧化、防辐射、亮泽容颜、乌须黑发等美容功能,黄精保健化妆品 10 种,有洗发水、护发素、沐浴露、洗面奶等;此外,现代研发的黄精中成药处方有 204 种,如三蛇药酒、丹田降脂丸、养胃舒颗粒;市场上黄精药品有 10 种,黄精赞育胶囊、黄精养阴糖浆、益元黄精糖浆、黄精丸等[83]。

4 展望

黄精作为我国传统中药材,具有非常高的药用价值和医疗保健功效。然而,就 2020 版《中国药典》规定的 3 种黄精,化学成分和药理作用方面的研究主要集中在黄精和滇黄精,而对多花黄精的研究较少;黄精的化学成分研究也主要集中在多糖、皂苷和黄酮,对其他微量成分研究甚少;其药理作用的研究也只集中在药用部位和简单的药效验证,并未做出深入的药理作用机制研究。因此,应该从黄精单个化学成分及其结构入手,研究其深入的作用机制,寻找其药物作用靶点,阐明其药效基础,为黄精药品、保健食品、化妆品的进一步开发利用提供基础。

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