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李果实酚类物质及其生物活性研究进展

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摘 要：李果实中含有丰富的矿物质、类胡萝卜素、果胶和酚类物质，因其果实中富含酚类物质而具有抗氧化、抗炎、抗肿瘤等功能和极高的营养价值。本文对李果实中酚类物质组成、含量及其生物活性的研究进行综述。主要包括李果实中酚类物质组成，不同种质、不同时期李果实中主要酚类物质含量；李果实酚类物质在抗氧化、抗炎、改善认知、防治心血管疾病和骨骼健康等方面的生物活性。旨在通过综述李果实酚类物质组成、含量及其生物活性的报道，为李果实酚类物质评价体系的建立、李果实酚类物质开发利用和高酚李品种的选育提供信息。

关键词：李；果实；酚类物质；生物活性

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Advances in the research of phenolic compounds and their bioactivities in plum fruits

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Abstract: Plum is a drupe belonging to the subgenus *Prunus* (family Rosaceae), and one of the most important stone fruits in the world. Around the world there are about 30 species of plums, and in China there are 8 species, including *Prunus salicina*, *P. domestica*, *P. simonii*, *P. ussuriensis*, *P. cerasifera*, *P. americana*, *P. nigra* and *P. spinosa*. *P. salicina* plums are mainly for fresh consumption, while *P. domestica* plums are used for the production of prunes. Each species displays great diversity in shape, size, taste and appearance. Plum fruits are, from a nutritive and dietary point of view, a valuable component of the human diet due to their content in minerals, carotenoids, vitamins, fibre and phenolic compounds. Phenolic compounds are the most important group of secondary metabolites widely distributed in plants, playing important roles in diverse physiological processes such as coloring, flavor formation and stress resistance. In generally, phenolic compounds in plum fruits are determined and characterized by HPLC, using diode array detector (DAD), photoelectric secondary array (PDA), ultraviolet detector (UV), fluorescence detector (FLD), etc, and then combined with mass spectrometry (HPLC - MS) for primary structure identification. The commonly used is electrosprayionization mass spectrometry (ESI/MS). The phenolic compounds can be grouped into 4 classes, phenolic acids, flavonols, flavanols and anthocyanins. The phenolic acids detected include neochlorogenic acid, cis-3-caffeoylquinic acid 3-*O*-p-coumaroylquinic acid, 3-*O*-p-feruloylquinic acid, cryptochlorogenic acid, 4-*O*-p-coumaroylquinic acid, n-chlorogenic acid, caffeoyl-glucoses methyl 3-caffeoylquinate, methyl 4-caffeoylquinate, methyl 5-caf-

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feoylquinate, 5-*O*-p-coumaroylquinic acid, 5-*O*-p-feruloylquinic acid, caffeic acid, caffeoylshikimic acid, p-coumaric acid, 3-p-coumaroylquinic acid, *cis*-3-p-coumaroylquinic acid, 4-p-coumaroylquinic acid, *cis*-4-p-coumaroylquinic acid, p-coumaroyl-glucoses, methyl 3-p-coumaroylquinate, feruloylquinic acid, feruloyl-glucoses, 3-p-methoxycinnamoylquinic acid, vanillic acid-glucoses 3,4-dihydroxybenzoyl- glucoses, and esculin. The flavonols are isoquercitrin, rutin, hyperoside, quercetin 3- rhamnoside, quercetin- pentoside, quercetin, quercetin- pentoside- rhamnoside, isorhamnetin- rutinoside, myricetin, and avicularin. The flavanols include catechin, epicatechin, procyanidin B1, procyanidin B2, procyanidin B4, procyanidin B7. The anthocyanins were cyanidin 3-glucoside, cyanidin 3-rutinoside, peonidin 3-glucoside, and peonidin 3-rutinoside. The content of phenolic compounds in plum fruit is usually quantified by mg·kg^{-1} (fresh weight basis), and has been shown to vary significantly among different varieties, environmental conditions and test methods. The results of previous studies showed that the content of the same substances varied significantly between different varieties and different periods. For example, a study showed that neochlorogenic acid varied in a range of 0-985.6 mg·kg^{-1}; chorogenic acid 0-57.2 mg·kg^{-1}; coumaroylquinic acid 0-151.6 mg·kg^{-1}; catechin 0-224.7 mg·kg^{-1}; epicatechin 0-97.1 mg·kg^{-1}; rutin 0-119.4 mg·kg^{-1}; procyanidin B1 22.5-328.6 mg·kg^{-1}; procyanidin B2 7.6-101.8 mg·kg^{-1}; cyanidin 3-glucoside 0-730 mg·kg^{-1}, and cyanidin 3-rutinoside 0-2 610 mg·kg^{-1}. The content of anthocyanins gradually increases in the peel and flesh as the fruit matures, and procyanidins reach a highest value in both skin and flesh during the stone hardening phase. In addition, phenolics have several pharmacological activities including antioxidant, anticancer, antimutagenic, antidiabetic, anti-inflammatory, and anti-HIV activities. The increased interest in plum research has been attributed to its high phenolic content, mostly the anthocyanins, which are known to be natural antioxidants. The effect of immature plum extract on *in vitro* cancer cells, eg. human hepatocellular carcinoma HepG2 cells, Kato III gastric cancer cells, HeLa human cervical carcinoma cells and U937 leukaemia cells, has been studied and the results show that the extract is effective in inhibiting growth of the cancer cells. Based on these results, the immature plum with its active compound, epicatechin, is expected to be a natural resource for developing novel therapeutic agents for cancer prevention and treatment. After taking the Queen Garnet (a high anthocyanin and high antioxidant plum) plum juice, there was a threefold increase in hippuric acid excretion (a potential biomarker for total polyphenols intake and metabolite), an increase in urinary antioxidant capacity and a reduction in malondialdehyde, which is a biomarker of oxidative stress. Chlorogenic acid from plum can decrease in anxiety-related behaviors (anxiolytic-like effect) and protect the granulocytes from oxidative stress in mice. Dringking plum juice can also decrease the levels of angiotensin II in plasma and its receptor Agtr1 in heart tissues, suggesting a role of plum polyphenols as peroxisome proliferator- activated receptor-γ agonists, and cardioprotective effects can be achieved by replacing drinks high in sugar content with fruit juice rich in polyphenols in a diet. Meanwhile, polyphenols in dried plums are beneficial to bone health. In this review, we summarize recent research progress on phenolic compounds and their bioactivities in plum fruit in order to provide useful information for the development and utilization of plum fruits and breeding of high-phenolic varieties.

Key words: Plum; Fruit; Phenolic compounds; Bioactivities

酚类物质是植物主要的次生代谢产物之一，广泛分布于蔬菜、水果、谷物等中[1]。在植物界已知的酚类物质有8 000种以上，主要由类黄酮、酚酸和单宁3类物质构成，各类又由许多亚类物质组成（图1）[2]。类黄酮是2个具有酚羟基的苯环通过中央三碳原子相互连接形成的一系列化合物[3]。酚酸按其碳骨架结构的不同可以分为2类：苯甲酸型（hydrobenzoic）和苯乙烯型（hydrocinnamic）[4]。单宁分为

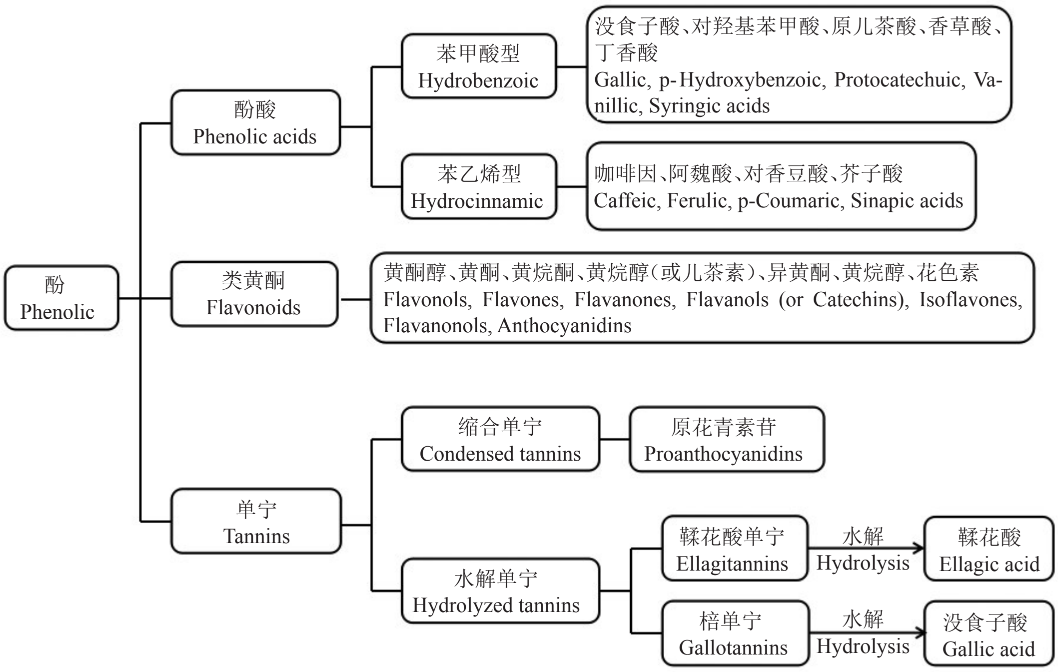

图1 酚类化合物分类

Fig. 1 Classification of phenolic compounds

水解单宁（hydrolyzed tannins）和缩合单宁（condensed tannins）2种类型[5]。酚类物质对植物的色泽、品质和风味等有一定的影响，其抗氧化功能更是引起广泛关注[6-7]，酚类物质还具有多种生物学功能，如植物抗毒素和拒食素[8]。这些生物活性对于植物生长和繁殖起着非常重要的作用，它们保护植物免于病原菌的侵扰[9]，研究报道天然来源的多酚成分作为食品防腐剂效果显著，此外还具有抗氧化、抗癌、抗辐射、降血压、预防心脑血管疾病等多种功能活性[10-12]。

李为蔷薇科（Rosaceae）李属（*Prunus*）植物。全世界李属植物约有30余个种，目前我国保存的李资源有8个种，分别为中国李（*P. salicina* L.）、欧洲李（*P. domestica* L.）、杏李（*P. simonii* Carr.）、乌苏里李（*P. ussuriensis* Kov.et Kost.）、樱桃李（*P. cerasifera* Ehrhart.）、美洲李（*P. americana* Marsh.）、加拿大李（*P. nigra* Ait.）和黑刺李（*P. spinosa* L.）。李的生产栽培品种主要为中国李和欧洲李，中国李主要供于鲜食市场，而欧洲李主要用于加工。李果实富含维生素、纤维素和酚类物质，人们对李研究兴趣的提高主要是因其高酚含量和高花青素含量，且酚类物质对维持健康具有重要意义[13]。众所周知，在众多水果中，李果实通常含有较高浓度的酚类化合物[7, 14]。且酚类物质具有许多药理活性，如抗氧化活性[14]、抗癌[15-16]、抗诱变[17]、抗糖尿病[18]、抗炎[19]、抗HIV[20]等。已有研究表明，李果实酚类化合物对健康有益，包括抗乳腺癌细胞增殖活性[21]、免疫活性[22]、降血糖活性[23]、减轻与年龄相关的认知衰退[24]、抵抗致癌物的防癌活性等[25]。本文重点围绕李果实酚类物质及其生物活性进行综述。

1 李果实中酚类物质

目前已从李果实中分离鉴定出的酚类主要为酚酸、黄烷醇、黄酮醇和花青苷4类（表1）。新绿原酸和绿原酸是主要的酚酸类物质[26-28]，儿茶素和表儿茶素是主要的黄烷醇类物质[28]；芦丁是主要的黄酮醇类物质[28-29]；矢车菊素-3-葡萄糖苷、矢车菊素-3-芸香糖苷，芍药素-3-葡萄糖苷和芍药素-3-芸香糖苷是主要的花青苷物质[28, 30-31]。

1.1 李果实酚类物质检测方法

李果实酚类物质的检测通常采用高效液相色谱法（HPLC），HPLC大多使用二极管阵列检测器（Diode arraydetector，DAD）、光电二级阵列（Photodiode-array detector，PDA）、紫外检测器（UV-VIS Detector，UV）、荧光检测器（Fluorescence Detection，FLD）等，之后又结合质谱（HPLC-MS）对酚类物质进行初步结构鉴定。表2中详细列出了李果实酚类物质测定的方法、提取剂和流动相以及鉴定分析的物质类

表1 李果实酚类组成

Table 1 Composition of phenolic compounds in plum fruit

类别 Class	酚类名称 Phenolic compound names	参考文献 Reference
酚酸 Phenolic acid	3-*O*-咖啡酰奎尼酸(新绿原酸)、顺式-3-咖啡酰奎尼酸、3-*O*-p-香豆酰奎尼酸、3-*O*-p-阿魏酰奎尼酸、4-*O*-咖啡酰奎尼酸(隐绿原酸)、4-*O*-p-香豆酰奎尼酸、5-*O*-咖啡酰奎尼酸(绿原酸)、咖啡酰-葡萄糖、甲基3-咖啡酰奎尼酸、甲基4-咖啡酰奎尼酸、甲基5-咖啡酰奎尼酸、5-*O*-p-香豆酰奎尼酸、5-*O*-p-阿魏酰奎尼酸、咖啡酸、咖啡酰莽草酸、p-香豆酸、3-p-香豆酰奎尼酸、顺式-3-p-香豆酰奎尼酸、4-p-香豆酰奎尼酸、顺式-4-p-香豆酰奎尼酸、p-香豆酰葡萄糖、甲基3-p-香豆酰奎尼酸、阿魏酰奎尼酸、阿魏酰-葡萄糖、3-p-甲氧基肉桂酰奎尼酸、香草酸-葡萄糖、3,4-二羟基苯甲酰葡萄糖、七叶苷 3-*O*-Caffeoylquinic acid (Neochlorogenic acid), *cis*-3-Caffeoylquinic acid, 3-*O*-p-Coumaroylquinic acid, 3-*O*-p-Feruloylquinic acid, 4-*O*-Caffeoylquinic acid (Cryptochlorogenic acid), 4-*O*-p-Coumaroylquinic acid, 5-*O*-Caffeoylquinic acid (n-Chlorogenic acid), Caffeoyl-glucoses, methyl 3-Caffeoylquinate, methyl 4-Caffeoylquinate, methyl 5-Caffeoylquinate, 5-*O*-p-Coumaroylquinic acid, 5-*O*-p-Feruloylquinic acid, Caffeic acid, Caffeoylshikimic acid, p-Coumaric acid, 3-p-Coumaroylquinic acid, *cis*-3-p-Coumaroylquinic acid, 4-p-Coumaroylquinic acid, *cis*-4-p-Coumaroylquinic acid, p-Coumaroyl-glucoses, methyl 3-p-Coumaroylquinate, Feruloylquinic acid, Feruloyl-glucoses, 3-p-Methoxycinnamoylquinic acid, Vanillic acid-glucoses, 3, 4-Dihydroxybenzoyl-glucoses, Esculin	[26-28,30,32-34]
酮醇 Flavonols	槲皮素3-葡萄糖苷(异槲皮苷)、槲皮素3-芸香糖苷(芦丁)、槲皮素3-半乳糖苷(金丝桃苷)、槲皮素3-鼠李糖苷、槲皮素-戊糖苷、槲皮素、槲皮素-戊糖苷-鼠李糖苷、异鼠李素芸香糖苷、杨梅素、广寄生苷 Quercetin 3-glucoside (Isoquercitrin), Quercetin 3-rutinoside (Rutin), Quercetin 3-galactoside (Hyperoside), Quercetin 3-rhamnoside, Quercetin-pentoside, Quercetin, Quercetin-pentoside-rhamnoside, Isorhamnetin-rutinoside, Myricetin, Avicularin	[26-28,30,33-34]
花色苷 Anthocyanins	矢车菊素3-葡萄糖苷、矢车菊素3-芸香糖苷、芍药素3-葡萄糖苷芍药素3-芸香糖苷 Cyanidin 3-glucoside, Cyanidin 3-rutinoside, Peonidin 3-glucoside, Peonidin 3-rutinoside	[27-28,30-31]
黄烷醇 Flavanols	儿茶素、表儿茶素、原花青素B1、原花青素B2、原花青素B4、原花青素B7 Catechin, Epicatechin, Procyanidin B1, Procyanidin B2, Procyanidin B4, Procyanidin B7	[26-27,33]

型。根据检测方法的不同,一般检测物类型为酚酸、黄酮醇、黄烷醇、花色苷4类。

1.2 不同李种质酚类组成和含量

果实酚类物质含量通常以mg·kg^{-1}度量(以鲜质量计),各酚含量差异显著,且不同品种、环境条件和测试方法对酚含量均有影响。研究发现,新绿原酸、绿原酸、隐绿原酸、儿茶素、表儿茶素、芦丁、原花青素B1、原花青素B2、矢车菊素-3-*O*-葡萄糖苷和矢车菊素-3-*O*-芸香糖苷等是李果实中的主要酚类物质(表3)。Treutter等[28]对不同种李资源果皮酚类物质进行了分析,发现酚酸和花色苷含量方面均表现为欧洲李(*P. domestica* L.)>黑刺李(*P. spinosa* L.)>中国李(*P. salicina* L.)>樱桃李(*P. cerasifera* Ehrhart.),欧洲李品种'President'的矢车菊素-3-葡萄糖苷和矢车菊素-3-芸香糖苷含量最高,分别为274.2 mg·kg^{-1}和793.4 mg·kg^{-1};在樱桃李品种'Späte Myrobalane'中未检到花色苷物存在,酚酸物质中仅检测到少量绿原酸存在。

张静茹等[35]分析了13份野生樱桃李(*P. cerasifera* Ehrhart.)和1个中国李(*P. salicina* L.)资源的11种酚类物质,包括绿原酸、原花青素B1、儿茶素、原花青素B2、表儿茶素、原花青素C、芦丁、槲皮素-半乳糖、槲皮素-葡萄糖、槲皮素-木糖醇、槲皮素-吡喃阿拉伯糖,在栽培品种'晚熟红李'中未检测到儿茶素、原花青素B2、表儿茶素和原花青素C,13份野生李资源中仅1份资源中不含原花青素C和槲皮素-半乳糖,其他野生资源中均含有11种酚类物质。在对11个李品种(系)的14种酚类物质[酚酸类:新绿原酸、绿原酸和p-香豆酰奎尼酸;花青苷类:矢车菊素-3-*O*-半乳糖苷、矢车菊素-3-*O*葡萄糖苷和矢车菊素-3-*O*-芸香糖苷;黄酮醇类:芦丁、槲皮素戊糖-己糖苷、槲皮素-3-*O*葡萄糖苷、槲皮素-3-*O*-木糖苷、槲皮素戊糖-戊糖苷、槲皮素-3-*O*阿拉伯糖苷(呋喃)、槲皮素-3-*O*-鼠李糖苷和槲皮素-乙酰己糖苷;黄烷-3-醇类:儿茶素、表儿茶素、原花青素B1和原花青素B2]的研究中,'Sun Breeze'中未检测到花青苷类物质,'Sapphire'中未检测到酚酸类物质,所有品种(系)均含有黄烷-3-醇类物质,矢车菊素-3-*O*-半乳糖苷仅在'Laetitia'品种中检测到[34,36]。对178个李品种(系)果实花青苷含量进行分析比较,发现'Hohenheim breed 4894'的矢车菊素-3-芸香糖苷含量比其他品种(系)均高,高达2 610 mg·kg^{-1}[37]。

1.3 不同时期李果实酚类物质含量

'安哥诺'李果皮酚酸类和花青苷类物质含量随着果实成熟而升高,相应在果肉中含量逐渐降低,黄烷-3-醇和黄酮苷类物质含量在果皮和果肉中均增

表2　李果实酚类物质测定方法

Table 2 The methods for determination of phenolic compounds in plum fruit

方法 Method	提取剂 Solvent/(*V/V*)	流动相 Mobile phase/(*V/V*)	检测物类型 Analytes	参考文献 Reference
HPLC-DAD HPLC-MS	甲醇/水(80∶20) Methanol/H_2O(80∶20)	A. 甲醇/水(5∶95)；B. 甲醇/水(12∶88); C. 甲醇/水(80∶20); D. 甲醇 A. Methanol/water (5∶95); B. Methanol/water (12∶88); C. Methanol/water (80∶20); D. Methanol	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[27]
LC/MS/MS HPLC-DAD	甲醇/水(80∶20) Methanol/H_2O (80∶20)	A. 水(5%甲酸)；B. 甲醇 A. Water (5% Formic acid); B. Methanol	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[38]
HPLC-PDA	甲醇/水(80∶20) Methanol/H_2O (80∶20)	A. 50 mmol· L^{-1}磷酸氢铵；B. 乙腈/50 mmol· L^{-1}磷酸氢铵(80∶20)；C. 200 mmol· L^{-1}磷酸 A. 50 mmol· L^{-1} Ammonium phosphate monobasic; B. Acetonitrile/50 mmol · L^{-1} Ammonium phosphate monobasic(80∶20); C. 200 mmol· L^{-1} Phosphoric acid	酚酸，黄酮醇，花色苷 Phenolic acid, Flavonols, Anthocyanins	[39]
HPLC-DAD	甲醇（1%盐酸和1% 2,6-二叔丁基-4-甲基苯酚） Methanol（1% HCl and 1% 2.6-di-tert-butyl-4-methylphenol）	A. 水(0.01 mol· L^{-1}磷酸)；B. 甲醇 A. Water (0.01 mol· L^{-1} Phosphoric acid）; B. Methanol	酚酸，黄酮醇，花色苷 Phenolic acid, Flavonols, Anthocyanins	[40]
HPLC LC/MS-QTOF	甲醇（0.5%三氟乙酸） Methanol (0.5%TFA)	A. 水(0.05%三氟乙酸）；B. 乙腈（0.05% 三氟乙酸） A. Water (0.05% TFA); B. Acetonitrile (0.05% TFA)	酚酸，黄酮醇，花色苷 Phenolic acid, Flavonols, Anthocyanins	[30]
HPLC-DAD	甲醇/水（50∶50） Methanol/H_2O（50∶50）	A. 超纯水（2 mol· L^{-1}盐酸调节pH为2.3）；B. 乙腈 A. Nanopure water adjustedto pH 2.3 with 2 mol· L^{-1} HCl; B. Acetonitrile	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[21]
HPLC-DAD TLC-UV	甲醇/甲酸（95∶5） Methanol /formic acid (95∶5)	A. 5%甲酸；B. 甲醇 A. 5% Formic acid; B. Methanol	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[28]
HPLC-DAD		A. 水（2 mol· L^{-1}甲酸）；B. 乙腈(2 mol· L^{-1}甲酸） A. Water（2 mol· L^{-1}formic acid）; B. Acetonitrile（2 mol· L^{-1} formic acid）	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[41]
HPLC-DAD	甲醇（1% 2,6- 二叔丁基-4- 甲基苯酚和3% 甲酸) Methanol(1% 2,6-di-tert-butyl-4-methylphenol and 3% formic acid)	A. 水（1% 甲酸）；B. 乙腈 A. Water (1% Formic acid); B. Acetonitrile	酚酸，黄酮醇，花色苷 Phenolic acid, Flavonols, Anthocyanins	[42]
HPLC-DAD	甲醇/乙酸(99.5∶0.5） Methanol/acetic acid (99.5∶0.5)	A. 水（2% 甲酸）；B. 乙腈 A. Water (2% Formic acid); B. Acetonitrile	酚酸，黄酮醇，黄烷醇 Phenolic acid, Flavonols, Flavanols	[43]
HPLC-DAD HPLC-MS	甲醇/水（70∶30） Methanol/water（70∶30）	A. 水/甲酸 (1 000∶0.05)；B. 甲醇 A. Water/formic acid (1 000∶0.05); B. Methanol	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[34]
HPLC-DAD-FLD HPLC-DAD-MS/ESI	甲醇 Methanol	A. 0.05%三氟乙酸；B. 乙腈 A. 0.05% TFA; B. Acetonitrile	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[44]
HPLC-DAD-FLD	甲醇 Methanol	A. 0.05%三氟乙酸；B. 乙腈 A. 0.05% TFA; B. Acetonitrile	酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[36]
GC-MS/MS	甲醇 / 水（ 80∶20） Methanol/H_2O(80∶20）		酚酸，黄酮醇，黄烷醇，花色苷 Phenolic acid, Flavonols, Flavanols, Anthocyanins	[45]
HPLC-DAD		A. 甲醇/乙酸/水（10∶2∶88）；B. 甲醇/乙酸/水（90∶2∶8） A. Methanol/acetic acid/water (10∶2∶88); B. Methanol/acetic acid/water (90∶2∶8)	酚酸，黄酮醇，黄烷醇 Phenolic acid, Flavonols, Flavanols	[46]
HPLC-UV	甲醇 Methanol	A. 水（2%乙酸）；B. 乙腈/水（70∶30） A. Water (2% acetic acid); B. Acetonitrile/water (70∶30)	酚酸，黄酮醇，黄烷醇 Phenolic acid, Flavonols, Flavanols	[47]
UPLC-DAD UPLC-MS/MS	丙酮/水（70∶30） Acetone/H_2O (70∶30)	A. 水/甲酸(99.95∶0.05)；B. 甲醇 A. Water/formic acid (99.95∶0.05); B. Methanol	酚酸，黄酮醇，黄烷醇 Phenolic acid, Flavonols, Flavanols	[48]

表3 李果实主要酚类的含量

Table 3 Concentrations of main phenolic compounds in plum fruit

类别 Class	酚类物质名称 Phenolic compound names	$w/(mg\cdot kg^{-1})$
酚酸 Phenolic acid	新绿原酸 Neochlorogenic acid	0~985.6
	绿原酸 Chorogenic acid	0~57.2
	隐绿原酸 Coumaroylquinic acid	0~151.6
黄酮醇 Flavonols	芦丁 Rutin	0~119.4
花色苷 Anthocyanins	矢车菊素3-葡萄糖苷 Cyanidin 3-glucoside	0~730
	矢车菊素3-芸香糖苷 Cyanidin 3-rutinoside	0~2 610
黄烷醇 Flavanols	儿茶素 Catechin	0~224.7
	表儿茶素 Epicatechin	0~97.1
	原花青素 B1 Procyanidin B1	22.5~328.6
	原花青素 B2 Procyanidin B2	7.6~101.8

加；‘Black Beaut’中酚酸类、花青苷类、黄烷-3-醇和黄酮苷类物质含量在果皮和果肉中随着果实成熟均增加[27]；Venter等[36]对10个李品种（系）研究发现，矢车菊素-3-葡萄糖苷和矢车菊素-3-芸香糖苷含量随着果实成熟均升高，芦丁含量随着果实成熟增加（‘PR04-35’除外），表儿茶素、儿茶素、原花青素B1和原花青素B2含量在大部分品种（系）中随着果实成熟而降低。González等[49]研究了4个李品种4个不同时期酚类物质含量发现，花青苷类物质含量随着果实成熟在果皮和果肉中逐渐增加，原花青素类物质含量在果皮和果肉中均在硬核期最高。

2 李果实酚类物质生物活性

2.1 抗氧化和抗炎

酚类物质是一种普遍存在于植物中的重要植物化学物质，具有高抗氧化能力和自由基清除能力，可以抑制负责活性氧产生的相关酶活性和减少高氧化性的活性氧产生[50]。李果实的抗氧化特性主要归因于其高酚含量[51-52]。Fu等[14]对62种水果总酚含量和抗氧化能力进行了比较，李果实中总酚含量排在第8位，抗氧化能力排在第6位。在对未成熟李果实提取物[酚类物质总量达10 g·kg^{-1}（干质量），表儿茶素和没食子儿茶素没食子酸酯分别占34.7%和28.6%]的体外抗氧化活性研究发现，提取物能有效抑制癌细胞的生长（人肝癌细胞HepG2、胃癌细胞Kato Ⅲ、人宫颈癌细胞 HeLa和血癌细胞U937），并且随着果实的成熟抑制作用降低，提取物中有效活化物表儿茶素也被认为是治疗和预防癌症的新型药物资源[53]。Noratto等[21]对红肉李‘Black Splendor’果实中起潜在化学预防或化学治疗作用的酚组分进行了鉴定，发现所有的成分对癌细胞系均具有抗氧化作用，且黄酮醇和原花青素类物质比酚酸和花青苷类物质更有效。Lea等[52]的研究也证实了这一结果，同时发现李总酚含量的协同效应能够显著的增加抗氧化能力。服用‘Queen Garnet’（高花青素含量、强抗氧化能力）李果汁后马尿酸（总酚摄取和代谢的潜在生物标志）排泄量增加3倍，尿的抗氧化能力增加，而丙二醛（氧化应激反应生物标志）排泄量降低[54]。研究发现李果实酚类物质可以引起Caco-2结肠癌细胞中碱性磷酸酶活性的增加，而在NCM460、HT29和SW1116结肠癌细胞中没有增加，但是，在四种细胞中蛋白合成均减少，且在诱导癌细胞凋亡的同时没有降低人体正常结肠纤维细胞的活细胞数量[54]。在乳腺癌细胞的研究中也发现了类似结果[21]。Ko等[51]研究结果表明，食用李果汁30分钟后，人血浆抗氧化能力显著增强，而Prior等[55]研究发现食用李汁对人血浆抗氧化能力并没有改变。

2.2 认知改善

李果实对认知改善尚未在人体中广泛研究，大部分依据源于动物上的研究，研究发现对认知的影响主要归因于李果实高酚含量。对添加5%李果实粉末饲喂高胆固醇饮食5个月小鼠的认知能力和脑神经退化相关蛋白表达进行调查，发现高胆固醇组（AIN-93M 饲料+5%胆固醇）血液和脑中的胆固醇含量显著高于对照组（AIN-93M 饲料）和添加李果实粉末组（AIN-93M 饲料+5%胆固醇+5%李果实粉末），高胆固醇组产生显著的认知缺陷，且伴有Cyp46、BACE1和羟化胆固醇 mRNA在大脑皮层和海马体中表达显著增加，然而，在添加李果实粉末组无显著增加现象[56]。Bouayed等[57]通过光/暗测试、高架十字迷宫测试和自由探索测试，检测发现李果实中绿原酸能降低小鼠的焦虑行为。

2.3 防治心血管疾病

Noratto等[58]对饲喂李果汁肥胖和消瘦大鼠体重增加量、量化心脏组织炎症和心血管疾病的生物化学标志物和分子标志物进行了调查，结果发现，由于李果汁中富含多酚物质，饲喂李果汁可以防止肥胖诱导的代谢紊乱，如高血糖症、胰岛素和瘦素抵抗、血脂异常和低密度脂蛋白氧化。同时有效的阻止体重增加，提高血浆中高密度脂蛋白胆固醇与总胆固

醇的比例。'Queen Garnet'李品种果汁比其他李品种果汁含有更高的花青素，能够有效地抑制由二磷酸腺苷、胶原蛋白和花生四酸引起的血小板凝结[59]。Bhaswant等[60]研究还发现，花青苷物质对大鼠的代谢综合征有一定效果。

2.4 骨骼健康的影响

已有一些关于李子对骨骼健康有益的研究。Bu等[61]进行了2组离体试验，研究李干中酚类物质对破骨细胞分化的影响，其中一组采用脂多糖（LPS）诱导发炎，另一组采用过氧化氢（H_2O_2）诱导脂质过氧化。研究发现，LPS诱导组在试验8 h检测到有一氧化氮产生，并在16 h进一步增加；然而，H_2O_2诱导组未产生一氧化氮。在8 h和16 h使用不同质量浓度（10、20、30 μg·mL^{-1}）的李多酚物质可以下调与LPS诱导相关的一氧化氮的产生。分析认为李干中酚类物质可通过下调活化T细胞核因子-1和炎症介质，降低成骨细胞活性进而直接抑制成骨细胞分化。在一些其他试验研究中也证实了这一研究结果，其中欧洲李李干中的高酚含量和强抗氧化能力有助于抵抗或逆转性激素缺失的大鼠和骨质疏松小鼠的骨流失[62-66]，其咖啡酸可以逆转氧化应激诱导的成骨细胞碱性磷酸化酶（ALP）和Ⅰ型胶原蛋白表达的减少和Runx2的磷酸化[67]。此外，研究还发现，李干中酚类物质对正常和发炎条件下的MC3T3-E1前成骨细胞的矿化过程和ALP活性有积极的影响[68]。离体试验中新绿原酸、绿原酸和咖啡酸可诱导原前成骨细胞增殖和抑制ALP活性，且与浓度成量效关系；体内试验中低绿原酸含量的李浓缩汁可以阻止5月龄大雌鼠雌激素缺乏引起的股骨矿物密度的降低，并能有效地恢复骨标记物骨钙素和脱氧吡啶啉的变化[69]。

3 问题与展望

大量研究证明，李果实酚类物质含量丰富，且食用李果实对健康大有益处。虽然目前有关李果实酚类物质的研究日渐增多，但仍有许多问题需要解决。

（1）我国有关李果实酚类物质的研究极少，且大部分研究集中在李果实总酚含量及其抗氧化能力方面[70-71]，相对于我国丰富的李资源而言，研究十分有限。因此，今后应开展更多李种质资源的研究，同时，纵向研究果实不同发育时期酚类物质，相关酶和环境等对李果实酚类物质的影响；分析李果实主要酚类物质，建立李果实酚类物质评价体系，为李果实酚类物质的开发利用和高酚李品种的选育提供信息。

（2）不同李种间和品种间酚类物质组成含量均存在显著差异，但目前酚类物质分析方法多样，精确度有差异，对各酚类含量进行横向比较相对较难；且大部分物质没有商业标准品，难以定性定量分析及开展后续研究。因此急需对测定方法和提取条件进行优化，建立适宜李果实酚类物质分离与鉴定的方法，对其进行更深入组分分析与鉴定。

（3）李果实酚类物质的合成与转运调控研究尚不明确。今后应在现有研究基础上，将分子生物学、转录组学和代谢组学相结合，构建从基因到代谢的网络，发掘目标代谢物相关基因簇及表达机制；进一步确定与李果实酚类物质的合成、转运、调控有关的基因及调控机制。

（4）迄今为止，虽然有大量的证据表明李果实酚类物质具有生物活性，且对一些疾病具有预防和治疗的作用。但是，许多研究不够深入，且大部分以动物为研究对象。因此，今后应深入研究李果实酚类物质代谢机制，并进行人体试验以证实研究效果。同时，对李果实鲜食和加工品的生物活性进行系统研究，并确定潜在的不良反应以及剂量对结果的影响，为慢性病预防和膳食指南提供基本信息。

总之，更多更深入的李果实酚类物质研究将有利于李的综合利用，为优质的李新品种培育提供基础，以推动李产业的可持续发展。

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