·综 述·

植物苯丙烷代谢及其对重金属胁迫的响应研究进展

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摘 要：苯丙烷代谢途径是植物中最重要的次生代谢途径之一，在植物抵抗重金属胁迫中直接或间接发挥了抗氧化作用，并能够提高植物对重金属离子的吸收与胁迫耐性。本文就苯丙烷代谢途径核心反应与关键酶系进行了总结，同时分析了木质素、类黄酮及原花青素等关键代谢产物的生物合成过程及相关机制，并以此为基础探讨了苯丙烷代谢途径关键产物响应重金属胁迫的相关机制。此外，结合当前研究现状，就苯丙烷代谢参与植物防御重金属胁迫的相关研究提出展望，以期为重金属污染环境的植物修复提供理论依据。
关键词：苯丙烷代谢途径；关键酶系；次生代谢物；重金属胁迫

Phenylpropanoid pathway in plants and its role in response to heavy metal stress: a review

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Abstract: Phenylpropanoid metabolic pathway is one of the most important secondary metabolic pathways in plants. It directly or indirectly plays an antioxidant role in plant resistance to heavy metal stress, and can improve the absorption and stress tolerance of plants to heavy metal ions. In this paper, the core reactions and key enzymes of the phenylpropanoid metabolic pathway were summarized, and the biosynthetic processes of key metabolites such as lignin, flavonoids and proanthocyanidins and relevant mechanisms were analyzed. Based on

this, the mechanisms of key products of phenylpropanoid metabolic pathway in response to heavy metal stress were discussed. The perspectives on the involvement of phenylpropanoid metabolism in plant defense against heavy metal stress provides a theoretical basis for improving the phytoremediation efficiency of heavy metal polluted environment.

Keywords: phenylpropanoid metabolic pathway; key enzymes; secondary metabolites; heavy metal stress

植物常受到干旱、盐碱、高温、寒冷及重金属等非生物胁迫，为了应对这些非生物胁迫和保证植物正常生长，植物进化出了次生代谢机制，以合成酚类、萜类及生物碱等次生代谢物[1]。在植物体内，次生代谢途径主要包括苯丙烷代谢途径、萜类代谢途径和生物碱代谢途径[2]。其中，苯丙烷代谢途径是植物中极为重要的次生代谢途径之一，受到了广泛关注和研究[3]。

植物在长期适应生存环境的进化过程中，通过基因复制和趋同进化等一系列策略促成了苯丙烷代谢途径的形成[4]。该途径最早形成于淡水藻，并在淡水藻陆地化过程中，进化出多个下游分支代谢途径，以合成木质素、黄酮、花青素及单宁等多种代谢物[3-4]。作为植物体内的重要防御系统，苯丙烷代谢途径在植物抵抗高盐、干旱、紫外辐射、低温及重金属等非生物胁迫中发挥了重要抗氧化作用[5-7]。本文针对苯丙烷代谢途径关键酶系和代谢产物进行分析，总结了苯丙烷代谢产物的生物合成过程，并结合已有及本课题组取得的研究就该途径对重金属胁迫的响应机制进行了总结，以期为从次生代谢途径增强植物重金属胁迫耐性提供理论依据。

1 苯丙烷代谢途径核心反应及其相关酶系

苯丙烷代谢途径由 1 个公共途径和若干个分支途径构成(图 1)，开始于莽草酸途径形成的苯丙氨酸[8]。苯丙烷代谢途径的前 3 个步骤构成公共代谢途径，是植物生长发育、重要次生代谢产物生物合成及胁迫防御的核心反应，位于初生代谢和次生代谢的交界处，为所有下游代谢物的生物合成提供前体[3,9]。公共代谢途径中的酶促反应由 3 种酶催化，分别为苯丙氨酸解氨酶(phenylalanine ammonialyase, PAL)、肉桂酸-4-羟化酶(cinnamic acid 4-hydroxylase, C4H)和 4-香豆酸辅酶 A 连接酶(4-coumarate-CoA ligase, 4CL)[10]，这些酶在植物适应逆境胁迫中调控次生代谢物合成具有关键作用。

1.1 苯丙氨酸解氨酶(PAL)

PAL 作为苯丙烷代谢途径的起点酶和限速酶，构成了初生代谢和苯丙烷代谢途径的枢纽，催化苯丙氨酸直接脱氨产生反式肉桂酸，是苯丙烷代谢途径的第一步反应[8,11-12]。PAL 由 Koukol & Conn 于 1961 年首次在大麦(*Hordeum vulgare* L.)中发现，广泛存在于除动物以外的真核生物和原核生物中[3,11]。PAL 在植物细胞分化、木质化过程以及抗逆等方面具有重要作用，是植物组织中重要的防卫反应酶[13-14]。

PAL 位于细胞质和叶绿体、线粒体等膜细胞器中，其活性因植物种类或组织部位不同而有所差异，通常在幼嫩组织中具有较高活性[13,15]。同时，*PAL* 基因在植物中的表达也具有明显的组织特异性。大多数植物的 *PAL* 基因在成熟的花和根部表达量较高，其次是茎部，在成熟叶片中几乎不表达[16-17]。植物体内 *PAL* 基因普遍由小的多基因家族组成。在拟南芥中，活性 *PAL*
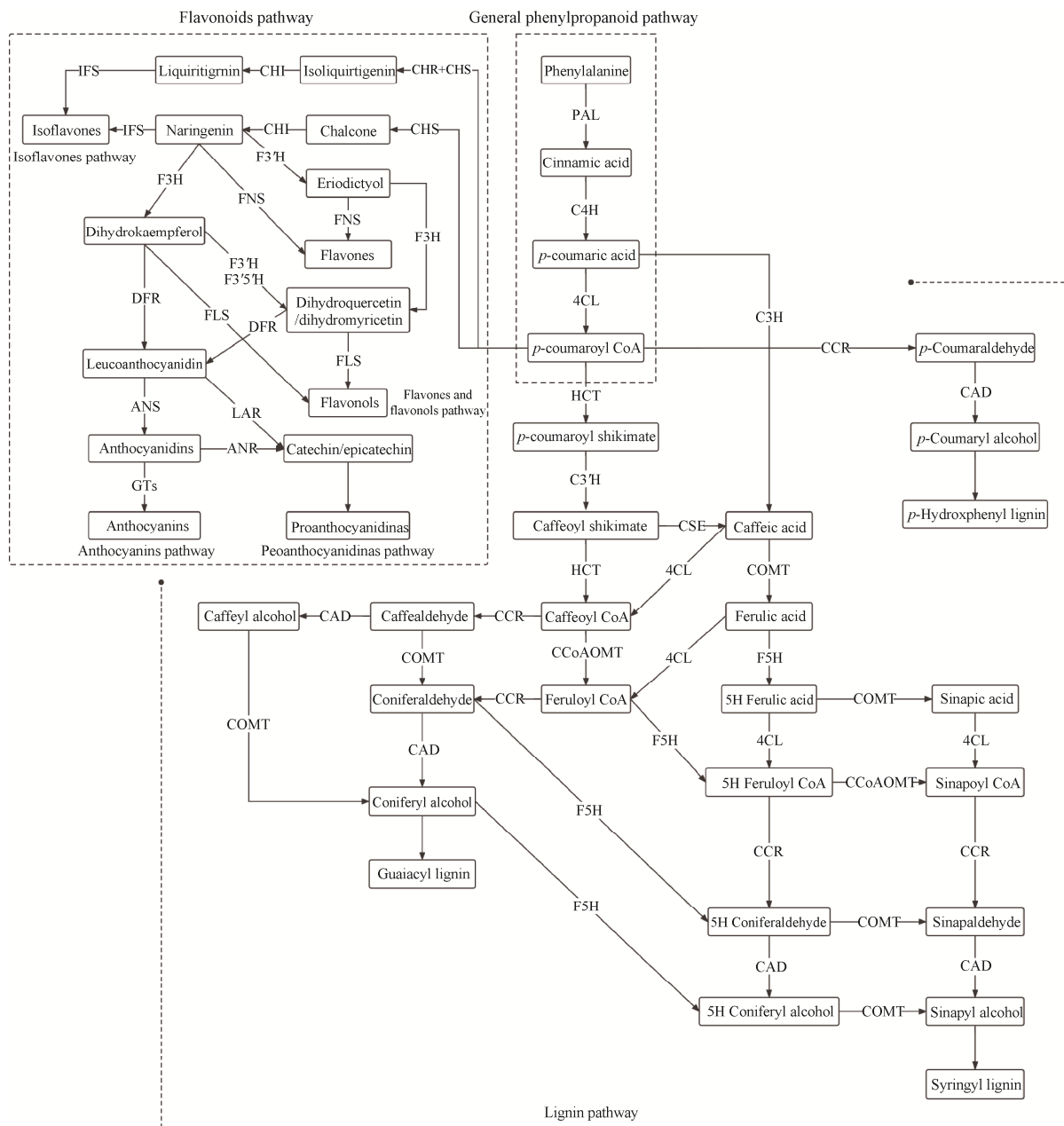
图 1　植物苯丙烷类代谢途径[3-4,7,11]

Figure 1　Etabolic pathways of plant phenylpropanes[3-4,7,11]. PAL: Phenylalanine ammonialyase; C4H: Cinnamic acid 4-hydroxylase; 4CL: 4-coumarate-CoA ligase; C3H: *p*-coumarate 3-hydroxylase; HCT: Hydroxycinnamoyl-CoA shikimate/quinate hydroxycinnamoyl transferase; C3′H: *p*-coumaroyl shikimate 3′ hydroxylase; CCR: Cinnamoyl-CoA reductase; CAD: Cinnamyl alcohol dehydrogenase; CSE: Caffeoyl shikimate esterase; COMT: Caffeate/5-hydroxyferulate 3-O-methyltransferase; CCoAOMT: Caffeoyl CoA 3-O-methyltransferase; F5H: Ferulate 5-hydroxylase; CHR: Chalcone reductase; CHS: Chalcone synthase; CHI: Chalcone isomerase; IFS: Isoflavone synthase; F3H: Flavanone 3-hydroxylase; FNS: Flavone synthase; F3′H: Flavonoid 3′-hydroxylase; F3′5′H: Flavonoid 3′5′-hydroxylase; DFR: Fihydroflavonol 4-reductase; FLS: Flavonol synthase; LAR: Leucoanthocyanidin reductase; ANS: Anthocyanin synthase; ANR: Anthocyanidin reductase; GTs: Glycosyl transferases.

亚型由 *PAL1-4* 基因家族编码[18-19]。谷子[*Setaria italica* var. *germanica* (Mill.) Schred.]具有 11 个 *PAL* 基因，可分为 3 个亚家族。其中，*SiPAL2*、*SiPAL3* 及 *SiPAL11* 为一个家族；*SiPAL1*、*SiPAL6*、*SiPAL8*、*SiPAL9* 及 *SiPAL10* 为一个家族；*SiPAL7* 独自进化为一支，与其他家族成员基因同源性较低，基因结构差异也较大[20]。因此，*PAL* 可能具有多样化的转录调控过程。

1.2　肉桂酸-4-羟化酶(C4H)

C4H 是苯丙烷代谢途径中催化代谢物生物合成的第二个关键酶[21]，是植物细胞色素 P450 的单氧化酶复合物[8]。C4H 可以催化肉桂酸第 4 位上的羟基化，生成对香豆酸、阿魏酸、芥子酸及咖啡酸等多种代谢物[12]。目前，至少 50 多种植物的 *C4H* 基因已经被分离克隆，其基因数量因植物种类不同而不同，并具有较高的保守性结构域。C4H 的活性影响植物黄酮类化合物的生物合成过程[22]。Huang 等[23]克隆了莲雾[*Syzygium samarangense* (Blume) Merr. et Perry]的一个 *C4H* 基因 *SsC4H*，用 NO 处理抑制 *SsC4H* 的表达和 C4H 的活性后，木质素的生物合成延缓。Cheng 等[21]发现 UV-B、低温、水杨酸和脱落酸处理的银杏(*Ginkgo biloba* L.) *GbC4H* 的转录水平增加，表明 *GbC4H* 在响应胁迫和激素信号中发挥重要作用。*C4H* 基因的表达模式也因植物种类不同而有所变化。烟草(*Nicotiana tabacum* L.)中 *C4H* 在根、茎、叶、花、萼片中均有表达，以在茎木质部和韧皮部的表达量最高[24]，相似的结果也被发现于榅桲(*Cydonia oblonga* Mill.)[25]，表明 *C4H* 基因表达与植物木质化过程密切相关。花生 (*Arachis hypogaea* L.) *C4H* 基因编码区高度保守，在根、茎、叶、花、果实、种子中均有表达，而茎、叶中的表达量较低[26]。

1.3　4-香豆酸辅酶-A-连接酶(4CL)

4CL 位于苯丙烷公共代谢途径转向下游分

支代谢途径的交叉点，是参与木质素、黄酮类化合物的生物合成过程的关键酶，调控苯丙烷下游分支代谢途径的碳流方向[27-28]。不同的 4CL 同系物对不同的苯丙烷底物表现出不同的酶偏好性，同时 *4CL* 基因对羟基肉桂酸衍生物的偏好性及其表达模式也具有明显差异[3,29]。研究发现，拟南芥 *At4CL1* 和 *At4CL2* 参与木质素生物合成，*At4CL3* 参与类黄酮生物合成[30-31]。大豆中存在 4 个 4CL 同工酶，其中 Gm4CL1、Gm4CL2 参与植物生长发育，Gm4CL3、Gm4CL4 响应环境因子[32]。Chen 等[27]研究发现，*Fm4CL1* 基因不但参与木质素生物合成，而且还能催化其他苯丙类化合物与辅酶 A 的连接[29]。

2　苯丙烷代谢途径产物

苯丙烷代谢物的生物合成均始于苯丙烷公共代谢途径，其下游是苯丙烷代谢的多个分支途径，主要包括木质素合成途径、类黄酮合成途径以及原花青素特异合成途径[26]。

2.1　木质素

木质素是经由苯丙烷代谢途径合成木质素单体后,经过进一步运输和聚合形成的复杂酚类化合物，主要功能是为细胞壁提供结构和防御性屏障，与植物抗逆性密切相关[11,33]。木质素的 3 个基本单元是对-羟基苯基木质素(*p*-hydroxyphenyl lignin, H-木质素)、愈创木基木质素(guaiacyl lignin, G-木质素)和紫丁香基木质素(syringyl lignin, S-木质素)，分别由对香豆醇、松柏醇和芥子醇 3 种木质素单体合成[34]。其中，H-木质素的形成较为简单，由肉桂酰辅酶 A 还原酶(cinnamoyl-CoA reductase, CCR) 和肉桂醇脱氢酶 (cinnamyl alcohol dehydrogenase, CAD)两个关键酶将苯丙烷代谢公共途径生成的对香豆酰辅酶 A 直

接还原催化形成。G-木质素和 S-木质素的代谢途径则需要更多的酶参与反应。首先，羟基肉桂酰-CoA 莽草酸/奎宁酸羟基肉桂酰转移酶 (hydroxycinnamoyl-CoA shikimate/quinate hydroxycinnamoyl transferase, HCT)引导代谢通路从苯丙烷代谢公共途径进入木质素单体生物合成分支途径[3]，催化对香豆酰基转移到莽草酸酯[35]。其次，对香豆酰莽草酸 3′-羟化酶 (p-coumaroyl shikimate 3′ hydroxylase, C3′H)催化对香豆酰莽草酸形成咖啡酰莽草酸[36]，同时 HCT 能将部分咖啡酰莽草酸转移回辅酶 A[10]。对香豆酸-3-羟化酶(p-coumarate 3-hydroxylase, C3H)催化对香豆酸形成咖啡酸，由咖啡酸/5-羟基阿魏酸 O-甲基转移酶 (caffeate/5-hydroxyferulate 3-O-methyltransferase, COMT)催化成为阿魏酸[37]。阿魏-5-羟化酶(ferulate 5-hydroxylase, F5H)可催化多种苯丙烷代谢中间产物的 NADPH-和 O2-羟基化。阿魏酸通过 F5H 催化成为 5-羟基阿魏酸，再由 COMT 催化成芥子酸[38]。咖啡酸、阿魏酸、芥子酸在 4CL、COMT、F5H、咖啡酰辅酶 A 3-O-甲基转移酶 (caffeoyl CoA 3-O-methyltransferase, CCoAOMT)等关键酶的羟基化和甲基化下，活化成为各自的辅酶 A，然后通过 CCR 催化还原成咖啡醛、松柏醛、芥子醛，再由 CAD 完成最后一步催化，形成咖啡醇、松柏醇和芥子醇，进而形成 G-木质素和 H-木质素单体[3,7,11,39]。Vanholme 等[40]还发现咖啡酰莽草酸酯酶 (caffeoyl shikimate esterase, CSE)催化咖啡酰莽草酸生成的咖啡酸也是合成木质素的一个通路。

目前，参与木质素生物合成的多种基因功能得到了鉴定，其中 4CL、CCR、CAD、COMT、CCoAOMT、HCT 等基因的表达均可调控木质素的含量[33]。Gui 等[29]发现，抑制 Os4CL3 基因能够显著降低水稻植株的木质素含量。相似地，下调 CCR1 基因表达可有效降低牧草 (Paspalum dilatatum Poir.)木质素含量[41]。Lin 等[42]也发现，茶树 [Camellia sinensis (L.) O. Ktze.] CsCCoAOMT6 基因表达水平与叶片、茎部的木质素含量呈正相关。同时，木质素的特异性合成受植物 MYB 转录因子家族基因的调控。MYB58 和 MYB63 是拟南芥木质素特异性转录激活剂[43]，能够直接激活 PAL、C4H 和 4CL 等木质素生物合成基因。Geng 等[44]报道破坏拟南芥中的 MYB 转录因子 MYB20、MYB42、MYB43 和 MYB85，能抑制 PAL1、4CL1、C4H、CSE、HCT 和 CAD4 等木质素生物合成基因的转录水平，从而导致木质素含量降低。同时，NAC 转录因子家族的部分成员也可调控木质素的合成。抑制 NAC 结构域转录因子 SND1 和 NST1，拟南芥中木质素合成基因 4CL1、CCoAOMT 表达水平会降低，进而妨碍木质素生物合成[45]；过表达毛果杨(Populus trichocarpa Torr. & Gray)中的 PtrNAC128 不仅使所有木质素合成途径酶基因表达水平提高，还显著诱导 PtoMYB028、PtoMYB152、PtoMYB161、PtoMYB192、PtoNAC105、PtoNAC156 等转录因子的表达，从而促进木质素的生物合成[46]。

2.2 类黄酮

类黄酮是植物体内种类最多的酚类化合物之一，由 3 个碳(C 环)连接两个苯环(A 环、B 环)，从而形成 C6-C3-C6 结构[47]。其中，A 环通常由间苯二酚或间苯二酚通过乙酸途径产生，并在 5′-和 7′-位置羟基化；B 环来自莽草酸途径，在 4′-、3′4′-或 3′4′5′-位置发生羟基化[48]。根据 C 环的不同修饰，类黄酮化合物分为二氢黄酮、黄酮、黄酮醇、黄烷酮、异黄酮和花青素等[49]。

查尔酮合成酶(chalcone synthase, CHS)和查尔酮异构酶(chalcone isomerase, CHI)是类黄酮合成途径的两个限速酶。其中，CHS 是类黄酮生物合成的第一个关键酶，以对香豆酰辅酶 A 作为底物合成查尔酮，并将代谢通路导向类黄酮代谢。类黄酮生物合成的两个前体物质分别是对香豆酰辅酶 A、丙二酰辅酶 A。其中，对香豆酰辅酶 A 与 3 分子的丙二酰辅酶 A 在 CHS 作用下生成查尔酮，同时查尔酮在 CHI 催化作用下生成黄烷酮并向下延伸出不同的支链。黄烷酮在黄酮合成酶(flavone synthase, FNS)的作用下转变为黄酮，然后在黄烷酮 3-羟化酶(flavanone 3-hydroxylase, F3H)催化下合成二氢黄酮醇。作为黄酮醇和花色素苷生物合成的前体，二氢黄酮醇在一系列酶促反应下，最终生成花青素；黄酮烷在异黄酮合成酶(isoflavone synthase, IFS)催化下转变成为异黄酮[3,50-51]。

2.2.1 花青素

花青素合成代谢是类黄酮代谢中一个重要分支。花青素常以单体的形式出现，由于其酚羟基上连有糖苷，又称花青素苷，具有较强的抗氧化活性。CHS 催化对香豆酰辅酶 A 和丙二酰辅酶 A 合成黄色查尔酮，再经 CHI 和 F3H 催化形成二氢黄酮醇，然后二氢黄酮醇在类黄酮 3′-羟化酶(flavonoid 3′-hydroxylase, F3′H) 和类黄酮 3′,5′-羟化酶 (flavonoid 3′5′-hydroxylase, F3′5′H)的催化下形成合成花青素的前体——二氢槲皮素和二氢杨梅素。这两种前体物质经二氢黄酮醇-4-还原酶(fihydroflavonol 4-reductase, DFR)的作用形成无色花色素，并在花青素合成酶(anthocyanin synthase, ANS)的催化下形成有色花色素，最后花色素在糖苷转移酶(glycosyl transferases, GTs)的作用下形成不同颜色、稳定的花色素苷[52-53]。花青素的生物

合成过程需要多种结构基因酶的参与，并且受到多种调控基因及其他因子的影响[52]。其中，结构基因包括 *PAL*、*F3H*、*CHS*、*ANS*、*CHI* 和 *DFR* 等，其表达直接受控于 MYB、bHLH 和 WD40 转录因子形成的 MBW 复合体[54-55]。同时，*LBD* 基因家族、*microRNA*、外界环境因子以及植物激素对花青素的合成代谢过程具有调节作用[56]。

2.2.2 黄酮、黄酮醇

黄酮和黄酮醇广泛存在于植物根、茎、叶、花、果实、种子中，在植物生长发育和抵抗逆境胁迫中发挥了积极作用。黄酮和黄酮醇可作为花青素的辅色素，增强花色稳定性和多样性，吸引昆虫传粉，调控植物激素、促进侧根形成，并保护植物细胞免受干旱、盐碱、低温及紫外线等非生物胁迫诱发的氧化损伤[1,57-59]。黄酮以黄烷酮为底物，在 FNS 催化下形成。柚皮素在一种或多种 F3H、F3′H 或 F3′5′H 的催化下形成不同的二氢黄酮醇，包括二氢山奈酚、二氢槲皮素、二氢杨梅素等[59]。同时，二氢黄酮醇可以在黄酮醇合成酶(flavonol synthase, FLS)催化下氧化形成黄酮醇苷元，之后在 GTs 催化作用下发生糖基化修饰，从而形成稳定多样的黄酮醇衍生物[50,56]。黄酮醇生物合成也受到了 MYB、bHLH 及 WD40 等单一或多个转录因子复合体的调控[60]。

FLS、F3H、F3′H、F3′5′H 等是催化黄酮醇生物合成的关键酶。其中，*FLS*、*F3H* 的基因表达、酶活性和底物偏好性等关系到黄酮醇合成支路对代谢流的竞争能力，影响着该支路代谢流的强弱，从而调控黄酮醇的组成与含量[59]。Zhou 等[61]等发现，茶树(*C. sinensis*) *FLS* 基因在烟草(*Nicotiana tabacum* L.)中过量表达后，烟草中黄酮醇及其衍生物、总黄酮含量均显著升高。烟草中过表达玫瑰(*Rosa rugosa*

Thunb.)、桃(*Prunus persica* L.)、番茄(*Solanum lycopersicum* L.)等植物的 *FLS* 基因会产生相一致的结果[62-63]。然而，抑制烟草(*N. tabacum*)*F3H* 基因表达可使代谢流转向异黄酮和黄酮合成方向[64]。F3′H 和 F3′5′H 均属于细胞色素 P450 亚家族，它们催化依赖于NADPH和O_2的单加氧反应，决定了类黄酮化合物 B 环的羟基化模式[65]。

2.2.3　异黄酮

异黄酮类也是类黄酮生物合成代谢的最终产物之一。目前，已知异黄酮种类超过 1 000 种，在豆科植物中含量尤为丰富[66-67]。植物体内的异黄酮具有不同的生理功能活性，包括抵抗逆境胁迫、防御微生物侵染、促进根瘤菌趋化、生长繁殖、根瘤发育和固氮等[67]。在异黄酮代谢支路中，对香豆酰辅酶 A 由 CHS 和查尔酮还原酶(chalcone reductase, CHR)催化形成柚皮素查尔酮或异甘草素，然后在 CHI 的催化作用下形成柚皮素或甘草素，最后在 IFS 的催化作用下形成异黄酮苷元(包括染料木黄酮、黄豆苷元和黄豆黄素)。这些游离苷元在尿苷二磷酸葡萄糖基转移酶(UDP-ducuronosyltranskrase, UGT)、乙酰基转移酶(acetyl transferase, AT)和丙二酰基转移酶(malonyl transferase, MT)的催化下形成各种异黄酮[68-69]。

IFS 是苯丙烷途径中异黄酮代谢支路的入口酶。目前，相关学者从大豆[*Glycine max* (L.) Merr.]中克隆出 *IFS1* 和 *IFS2* 两个异黄酮还原酶基因，两者具有高度同源性[70]。其中，*IFS1* 主要在根和种皮中表达，*IFS2* 主要在胚芽和豆荚中表达[71]。Liu 等[72]发现，将大豆(*G. max*) *IFS* 引入拟南芥能够明显提高木黄酮含量。因此，*IFS* 可能是异黄酮合成过程中的限制因子。

2.3　原花青素

原花青素又叫缩合单宁，是植物色素成分之一，具有消除自由基、防止细胞过氧化和抗突变等功能，是植物应对生物和非生物胁迫的一种防御手段[73]。原花青素由黄烷-3-醇单体通过不同类型黄烷键连接聚合组成。根据聚合单体连接键数目的不同，可以分为 A 型和 B 型两类。其中，A 型原花青素有两个连接键，而 B 型只有一个内黄烷键[74]。

原花青素前体的合成与花青素由苯丙氨酸到无色花青素的代谢途径一致。无色花青素还原酶(leucoanthocyanidin reductase, LAR)、花青素还原酶(anthocyanidin reductase, ANR)是原花青素生物合成过程中的关键酶。其中，LAR 催化无色花青素生成儿茶素，然后缩合成原花青素。ANR 是原花青素代谢途径中的关键酶，催化花青素转化为表儿茶素，进一步向液泡转运聚合成为花青素[26]。该酶首先在拟南芥中被发现，同时 *AtANR* 基因在种皮中表达，编码 ANR 催化花青素生成黄烷-3-醇[75]。上述两种酶分别参与的 LAR 途径、ANR 途径是原花青素合成途径中的关键通路[73]。宋杨等[76]克隆了越橘(*Vaccinium corymbosum* L.)原花青素合成基因 *VcLAR*、*VcANR*，发现水杨酸可促进这两种基因的表达，同时 *VcANR* 基因转入拟南芥株系能够显著提高原花青素含量。

3　植物苯丙烷代谢途径对重金属胁迫的响应

随着工农业的发展，大量重金属离子流失到环境中，对土壤和水体造成不同程度的污染。重金属是指密度大于 4.5 g/cm^3 的金属。重金属的高毒性和高生物富集性使其成为重要的环境污染物，且无法通过分子降解消失，需要通过一定途径才能从环境中分离。多种重金属是植物所必需的营养元素，在植物生长发育过程中发挥重要作用，如锌(Zn)、铜(Cu)、铁(Fe)等。当这些重金属元素超过一定浓度范围，会对植

物产生毒害作用。而镉(Cd)、铅(Pb)、汞(Hg)等重金属元素对植物生长没有作用，低浓度下就可对植物体产生毒害。过量重金属会抑制植物种子萌发、妨碍幼苗生长。同时诱导活性氧和自由基在细胞中大量积累，破坏细胞质膜透性、诱导蛋白酶失活变性、妨碍水分和矿质营养吸收、抑制光合与呼吸作用等[34,77-80]。为了减缓重金属植物毒性，植物在长期进化过程中形成了规避和耐受两种保护机制。其中，规避机制即植物可通过分泌根系分泌物等方式减少对重金属的吸收，或通过外排作用将有毒的重金属排出体外，降低体内的重金属浓度[1,80-81]。内部耐受机制是植物通过自身的区室化作用、螯合作用、渗透调节及抗氧化系统等生理生化适应机制，减轻重金属的毒害作用[1,82-83]。

　　苯丙烷途径的代谢产物可以清除活性氧自由基，减缓膜质过氧化，在植物抵御重金属胁迫中发挥了重要抗氧化作用[84-86]。在逆境条件下，该途径代谢物的生物合成受 PAL、C4H、4CL 及 CHS 等关键酶系的调控[87]。研究表明，*PAL*、*C4H* 及 *4CL* 等基因的上调表达能够促进木质素、黄酮类及酚酸类化合物的生物合成，有利于增强植物对重金属胁迫的耐受性[85,88-90]。杞柳(*Salix integra* Thunb.)[91]、马蔺[*Iris lactea* var. *Chinensis* (Fisch.) Koidz.][92]及梭鱼草(*Pontederia cordata* L.)[93]等多种植物体内的苯丙烷代谢途径参与响应重金属胁迫，并在植物应对重金属胁迫中发挥了重要防御作用。

3.1　木质素对重金属胁迫的响应

　　细胞壁是植物储藏重金属离子的关键部位，同时也是植物吸收和运输重金属离子的第一道屏障[33,94]。木质素作为植物细胞次生壁的主要成分之一，在重金属离子固定中具有重要作用。植物可利用活性氧(reactive oxygen species, ROS)依赖的木质化作用,通过重金属离子与木质素羧基、酚基及醛基等官能团结合，将重金属离子固定在细胞壁中，降低其在植物体内的迁移能力，抑制重金属离子进入细胞质，从而增强植物对重金属胁迫的耐受性。

　　木质素的合成与积累是植物对重金属胁迫的常见反应[94-97]。过量铜条件下，拟南芥编码木质素合成的 *OsCCoAOMT1*、*CCoAOMT20* 基因与 CCoAOMT 活性均明显上调，诱导木质素含量的增加，相似的结果也被发现于铜胁迫下的水稻[98]，这有利于降低植物细胞原生质中 Cu^{2+} 浓度，意味着木质素合成与积累可能是植物缓解 Cu^{2+} 毒性的一种适应性策略。Xia 等[97]发现，*VsCCoAOMT* 基因过表达拟南芥能够促进镉胁迫下木质素含量的增加。这在镉胁迫下的芦苇[*Phragmites australis* (Cav.) Trin. ex Steud.][99]、大豆(*G. max*)[100]中得到了证实。Elobeid 等[101]发现，镉胁迫能够明显提高生长素酰胺合成酶活性，导致生长素被大量消耗，从而将代谢转向增强木质素的生物合成，表明镉胁迫下植物生长素含量与木质素生物合成之间存在着负反馈调节关系。然而，本课题组前期研究发现，Cd^{2+}胁迫会诱导梭鱼草(*P. cordata*)叶片木质素含量下降[93]，表明苯丙烷途径在叶片应对 Cd^{2+}胁迫中的物理防御能力下降，可能与 *4CL*、*CAD* 及 *POD* 基因的下调表达有关[102]。

　　Li 和 Ge[103]发现，从木质素中获得的重金属离子吸附剂具有较好的稳定性、生物相容性和吸附性，因此可以将木质素及其衍生物转化为重金属离子吸附剂进行环境治理。Wang 等[104]报道施用木质素提高了小麦(*Triticum aestivum* L.)的生长速度，降低了小麦(*T. aestivum*)中重金属的积累，可能是因为木质素的应用增加了土壤有机质的含量，有效吸附土壤溶液中的游离阳离子，降低了土壤中重金

属的流动性和生物利用度。造纸工业会产生大量副产品木质素，可以作为农用地微型肥料，是一种很有前途的替代污水排放的方法。

3.2　类黄酮对重金属胁迫的响应

类黄酮主要通过 2 种途径发挥抗氧化作用：(1) 作为防御性抗氧化剂，具有很强的自由基清除能力和抗氧化活性，其能够以自由基接受体的形式阻碍自由基连锁反应；(2) 与重金属离子螯合，减缓氧化损伤[105]。低浓度 Cu^{2+} 胁迫能够诱导胡卢巴(*Trigonella foenum-graecum* L.)根系黄酮类物质含量明显增加，其在清除细胞过量 ROS (如 H_2O_2)过程中表现出强效抗氧化性[106]。研究认为，类黄酮物质因酚羟基上的氢原子可与过氧化自由基结合生成黄酮自由基，进而与其他自由基反应，从而终止自由基链式反应。作为自由基的还原剂，类黄酮在极性水相中以单电子转移机制起作用，在非极性介质(如脂质)中与羟基氢的氢原子转移作用[107-108]。李建等[109]研究发现，类黄酮能够促进白骨壤[*Avicennia marina* (Forsk.) Vierh.]根系对 Cd^{2+} 的吸收和富集，抑制根系阳离子通道对 Cd^{2+} 的吸收，同时能够促进根系对必需元素的吸收，表明类黄酮类物质在增强植物 Cd^{2+} 胁迫耐性中具有重要作用。

类黄酮也能够与植物细胞膜中的膜磷脂相互作用，阻碍毒性小分子物质进入到磷脂双分子层的疏水区域，从而保护植物细胞膜的完整性。在较高浓度 Cd^{2+} 胁迫下，拟南芥幼苗体内类黄酮、花色素苷含量显著增加，相似结果也被发现于重金属胁迫下的大麦(*H. sativum*)[110]、羽扇豆(*Lupinus luteus* L.)[111]、秋茄树(*Kandelia obovata* Sheue et al.)[112]、狗头七[*Gynura pseudochina* (L.) DC.][113]和刺槐(*Robinia pseudoacacia* L.)[85]等多种植物。这可能是因为重金属胁迫能够诱导苯丙烷公共代谢

途径 *PAL*、*C4H*、*CHS* 基因和下游分支代谢途径 *FLS*、*F3H*、*MOMT3*、*ANS*、*CCoAOMT* 基因等上调表达[102,114-115]。

3.2.1　花青素对重金属胁迫的响应

花青素是一类重要的次生代谢产物，其生物合成过程易受环境因子诱导。研究表明，重金属胁迫能够诱导芥菜 [*Brassica juncea* (Linnaeus) Czernajew][116]、拟南芥[117-119]、莴苣(*Lactuca sativa* L.)[120]、八仙花 [*Hydrangea macrophylla* (Thunb.) Ser.][121]及玉米(*Zea mays* L.)[122]等多种植物体内花青素含量的增加。这可能是因为重金属胁迫能够诱导 CHS、DFR 结构基因的上调表达，从而增强编码 ANS 的活性[123]。同时，重金属还能够诱导苯丙烷途径 *PAL*、*CHS*、*F3H* 和转录因子 *MYBL* 等基因表达增强，从而促进花青素含量增加[124-127]。

作为植物细胞中的一种强抗氧化剂，花青素在植物应对重金属胁迫中具有重要的保护作用。花青素中含有多个酚羟基供体，能够与自由基反应生成较为稳定的半醌式自由基，抑制自由基链式反应，进而清除活性氧自由基[128]。Xu 等[88]认为，ROS 与花青素积累之间存在交叉调控作用。在重金属胁迫下，矮牵牛[*Petunia hybrida* (J. D. Hooker) Vilmorin]中超氧化物歧化酶(superoxide dismutase, SOD)、过氧化物酶(peroxidase, POD*)*及过氧化氢酶(catalase, CAT)的基因表达量增加，与调控花青素生物合成的转录因子 *RsMYB1* 表达水平之间表现出明显的正相关[129]。这在重金属胁迫下的红球甘蓝(*Brassica oleracea* var. *rubrum* L.)[130]和芥菜(*B. juncea*)[127]等多种植物上也得到了证明。同时，外源喷施花青素可增强水稻叶片 SOD、POD、CAT 和抗坏血酸过氧化物酶(aseorbateperoxidase, PAX)活性，并明显提高谷胱甘肽、抗坏血酸、非蛋白硫醇及植物螯合素

含量[131]。这意味着花青素能够激发植物内源酶类抗氧化系统活性，并提高非酶抗氧化剂含量，从而有利于降低细胞中活性氧与自由基含量，进而缓解重金属植物毒性[132]。其次，花青素与金属离子的螯合能力取决于类黄酮骨架 B 环中的 3′,4′-O-二羟基，其可以降低细胞内自由金属离子的浓度，从而减轻重金属毒性[133]。Hale 等[134]研究发现，花青素能与重金属钼(Mo)结合形成 Mo-花青素化合物，然后转运至液泡中，从而减轻钼胁迫的毒害作用。

3.2.2　黄酮、黄酮醇和异黄酮对重金属胁迫的响应

黄酮主要包括黄芩素、芹菜素等化合物，黄酮醇主要由槲皮素、芦丁等化合物组成。研究表明，铜处理能够诱导药蜀葵 (*Althaea officinalis* L.)体内槲皮素、芦丁等酚类化合物含量的增加[135]。这些化合物不但能够与活性氧自由基直接反应，而且还可以与重金属离子螯合以降低细胞中有效态金属离子含量，从而减缓重金属胁迫诱发的氧化损伤[104]。Keilig 和 Ludwig-Müller[136]发现，外源黄酮醇能够激活核黄素、吡咯素、抗坏血酸及谷胱甘肽等抗氧化解毒系统，从而改善铅胁迫下拟南芥的生长状态。同时，Mira 等[137]研究发现，黄酮、黄酮醇类化合物对 Cu^{2+} 具有很强的螯合能力。通过对芦丁、槲皮素、3-羟基黄酮等金属-类黄酮配合物的研究发现，这些化合物 C 环中的 3-羟基或 5-羟基、4-碳基是与金属离子相互作用的主要络合域[105]。此外，改良 *FLS* 基因能够提高植物合成黄酮醇的能力，从而增强植物对铅的耐性[138]。

Dowling 等[139]认为，异黄酮中的生物香黄素 A 和染料木素的 4-酮、5-OH 位点能够与 Cu^{2+} 螯合，并且异黄酮的金属螯合物具有更强的自由基清除能力，可作为有效的抗氧化剂。研究发现，铅处理诱导羽扇豆根部染料木素

明显增加[111,140-141]，相似的结果也被发现于重金属胁迫下的蒺藜苜蓿(*Medicago truncatula* Gaertn.)[142]、大豆(*G. max*)[143]、染料木(*Genista tinctoria* L.)[144]、黄芪[*Astragalus membranaceus* var. *mongholicus* (Bunge) P.K.Hsiao][145]及紫花苜蓿(*Medicago sativa* L.)[146]等多种植物。这可能是因为重金属胁迫能够诱导植物体内 *IFS*、*PAL*、*C4H*、*4CL*、*CHS*、*CHI* 及 *CHR* 基因的上调表达，从而有利于提高异黄酮生物合成酶的活性[102,143,147-148]。

3.3　原花青素对重金属胁迫的响应

作为一种酚类物质，原花青素不但具有很强的抗氧化性，而且对 Cu^{2+}、Pb^{2+} 等二价金属离子具有很强的螯合作用[149]。研究表明，重金属胁迫能够诱导蜈蚣草(*Pteris vittata* L.)[150]、秋茄树(*Kandelia obovata* Sheue et al.)[112]等植物根、叶中原花青素含量增加，其可能参与重金属离子的螯合，有利于增强植物抗性。外源添加原花青素能促进紫花苜蓿种子在酸铜胁迫下的发芽势、发芽率、发芽指数和活力指数等萌发指标和根长、根系表面积等根系性状指标，且各项指标随原花青素浓度的增加而增加[151]。这种改善效应也被发现于镉胁迫下的大麻 (*Cannabis sativa* L.)[152-153]。

研究表明，原花青素结构单元的芳香环具有多个邻、间位活性酚羟基，其容易释放质子给各类自由基，并终止自由基链式反应，从而防止氧化[112]。同时，原花青素由一个或多个儿茶素或表儿茶素聚合而成，聚合度越大，抗氧化性越强，清除自由基的能力也越强[154]。其次，原花青素还能够提高植物体内 SOD、POD 活性和 GSH 含量，从而缓解重金属胁迫诱发的氧化损伤[153]。Chen 等[155]曾报道水杉(*Metasequoia glyptostroboides* Hu & W. C. Cheng)中总原花青素含量与自由基清除或抗氧化活性之间的

关系最为显著。在锌胁迫下，樟子松(*Pinus sylvestris* L.)幼苗器官中乙醇提取物的抗氧化能力显著增加，这是由于(+)-儿茶素和原花青素的总含量增加所致，表明儿茶素和原花青素在樟子松幼苗抗氧化状态中的重要性[156]。尹明[153]发现，外源原花青素与Cd^{2+}能够同时作用于 *EDS1* 基因，诱导大麻(*C. sativa*)内源水杨酸的合成与积累，从而通过光合作用、次生代谢物与抗氧化剂的生物合成等途径缓解镉胁迫。

4 总结与展望

作为植物体内重要的次生代谢途径之一，苯丙烷代谢途径在植物应对重金属胁迫过程中发挥了重要的防御作用。苯丙烷代谢途径中大量的关键酶及其基因已被发掘鉴定。众多研究克隆了植物体内 *PAL*、*C4H*、*4CL*、*F3H*、*FLS*、*CHS* 等苯丙烷代谢途径的相关基因并进一步验证其功能，但主要应用于品种改良、医药、工农业生产等，在植物重金属胁迫耐性方面的相关研究较少。本课题组前期研究了苯丙烷代谢途径参与梭鱼草(*P. cordata*)防御重金属镉胁迫的作用机制，发现总黄酮含量显著增加，其能够直接或间接地发挥抗氧化作用[93]；同时，通过转录组测序，挖掘出 26 个与苯丙烷代谢途径相关的差异表达基因，分别编码苯丙烷代谢公共途径的 3 个关键酶、5 个木质素合成关键酶以及 7 个类黄酮合成关键酶，其中 *C4H*、*ANS*、*CCoAOMT* 等基因在防御镉胁迫中发挥了重要作用[102]，为今后进一步研究苯丙烷代谢途径在梭鱼草(*P. cordata*)抵御重金属胁迫中的作用及相关机制提供了理论依据。但是，苯丙烷途径在植物应对重金属胁迫中的代谢机理以及分子机制并未得到较全面的解析。同时，该途径在重金属污染环境的植物修复过程中的潜在作用也值得进一步研究。今后，针对植物苯丙烷代谢途径响应重金属胁迫的相关研究可从如下 3 个方面展开。

(1) 植物苯丙烷代谢受到转录、翻译和表观遗传等多方面的调控[3]。通过将转录组学、代谢组学、蛋白质组学相结合，揭示重金属胁迫下关键基因的表达与代谢通量的分配规律，有助于更清晰地认知植物的苯丙烷代谢，为提高植物重金属胁迫耐性提供科学依据。

(2) 以往苯丙烷代谢相关的基因工程研究集中于改良植物产量及品质，以满足园艺、工农业的生产应用需求[11,157-158]，在提高植物重金属胁迫耐性方面的研究较少。因此，今后可以挖掘重金属胁迫下植物体内苯丙烷代谢相关的耐性基因，并通过基因工程技术进一步提高植物对重金属胁迫的耐受性，从而为提高重金属污染环境的植物修复效率提供理论支撑。

(3) 研究表明，通过外源添加酚类化合物能够有效提高植物抗逆性，但多数研究侧重于室内试验[131-132,159-161]。因此，今后可以室内理论研究为基础，在野外开展外源酚类化合物增强植物重金属胁迫耐性的相关研究，为提高重金属污染土壤或水体的植物修复效率奠定理论基础。

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