

果蔬酚酸生物合成及代谢调控研究进展

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摘要: 酚酸类物质是高等植物体内广泛分布的一类重要的次生代谢产物, 具有抗氧化、抗炎、抗癌、抑菌、提高免疫力等多种生物活性。近年来, 大量的研究表明酚酸与植物生长发育及抗逆性、食品质量和人体健康密切相关, 有关植物酚酸的分离鉴定及生物合成途径已有广泛研究。本文综述了果蔬中酚酸的生物合成途径和酚酸与果蔬抗逆性及品质间的关系, 并对代谢组学在评价酚酸类物质分布规律中的应用进行了阐述, 以期酚酸类物质在果蔬中的开发利用提供有益参考。

关键词: 酚酸; 生物合成; 诱导性抗性; 果蔬品质; 代谢组学

Progress in Research on the Biosynthesis Pathway and Metabolic Regulation of Phenolic Acids

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Abstract: Phenolic acids, a class of plant secondary metabolites, are widely present in plants and have several bioactivities such as antioxidant, anti-inflammatory, anticancer, antibacterial, and immune-enhancing activities. In recent years, many studies have demonstrated that phenolic acids are closely related to plant development, induced resistance, food quality, and human health. The isolation, identification and biosynthesis pathway of phenolic acids have been investigated widely. Herein, the biosynthesis and metabolic regulation of phenolic acids, the influence of induced resistance on phenolic content, the relationship between phenolic acids and food quality, and the applications of metabolomics in studies on plant phenolics are reviewed, so as to provide a useful basis for the exploitation of phenolic acids in fruits and vegetables.

Keywords: phenolic acid; biosynthesis; induced resistance; quality of fruits and vegetables; metabolomics

DOI:10.7506/spkx1002-6630-201809043

中图分类号: TS201.2

文献标志码: A

文章编号: 1002-6630 (2018) 09-0286-08

引文格式:

高媛, 马帅, 代敏, 等. 果蔬酚酸生物合成及代谢调控研究进展[J]. 食品科学, 2018, 39(9): 286-293. DOI:10.7506/spkx1002-6630-201809043. <http://www.spkx.net.cn>

GAO Yuan, MA Shuai, DAI Min, et al. Progress in research on the biosynthesis pathway and metabolic regulation of phenolic acids[J]. Food Science, 2018, 39(9): 286-293. (in Chinese with English abstract) DOI:10.7506/spkx1002-6630-201809043. <http://www.spkx.net.cn>

酚酸类物质是植物体内广泛存在的重要次生代谢产物, 具有抗毒素、抗氧化、抗炎、抗癌、抑菌等多种生物活性^[1], 对于植物生长和繁殖起着非常重要的作用, 可以保护植物免受病原菌的侵扰^[2]。与类黄酮等其他多酚类物质相比, 对于酚酸类化合物活性的研究相对较少、较晚, 近年来才逐渐引起国内外学者的关注。研究

发现, 酚酸除具有清除自由基、抗氧化、抗肿瘤、抑菌作用外, 还可抑制肥胖、提高免疫力、改善情绪、促进人体肠道健康等, 此外还有一些酚酸可以作为信号分子在植物体内起重要作用, 如水杨酸可以作为信号分子参与机体的防御反应, 诱导植物对生物和非生物胁迫产生抗性^[3-5]。

收稿日期: 2017-04-24

基金项目: 国家农产品质量安全风险评估项目(GJFP2017003); 北京市农林科学院博士后科研基金项目

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动物和人自身不能合成酚酸,主要通过食物获得。水果、蔬菜、豆类、谷物等都是很好的酚酸来源,此外果汁、茶、啤酒、咖啡等饮品中酚酸含量也很丰富^[6-8],美国已有关于酚酸的每日推荐摄入量。酚酸与采后运输、贮藏及果实的色泽、风味等品质指标密切相关,是决定果蔬感官质量和营养质量的重要因素。本文对酚酸与果蔬品质间的关系、酚酸的生物合成途径、诱导性抗性对酚酸含量的影响进行了综述,以期对果蔬酚酸类物质的开发利用提供有益的参考。

1 果蔬中的酚酸类物质

酚酸是一种非类黄酮类物质,按结构可分为羟基苯甲酸类和羟基肉桂酸类,大部分与糖、有机酸、醇等以酯化/结合态的形式存在于植物体中,少部分以游离态形式存在。大量流行病学研究显示,食用水果、蔬菜可有效降低多种疾病的发生率,果蔬中富含多酚类物质是重要原因,而酚酸约占总多酚含量的1/3。据估算,人体每天摄入的酚酸为25 mg到1 g不等,取决于食用果蔬的种类与质量^[9]。目前已有众多研究者对包括醋栗^[10]、山竹^[11]、柑橘类^[12]、果汁(苹果汁、葡萄汁、桃汁、橙汁)^[7-8]中的酚酸进行了研究。总体而言,能够检测到的酚酸种类包括羟基苯甲酸类(如没食子酸、原儿茶酸、龙胆酸、对羟基苯甲酸、香草酸、丁香酸、水杨酸)和羟基肉桂酸类(如绿原酸、咖啡酸、对香豆酸、阿魏酸、芥子酸、反式肉桂酸、鞣花酸)等。不同植物中酚酸种类和含量有所不同,如胡柚中绿原酸和阿魏酸是含量较高的2种酚酸,而肉桂酸、新绿原酸、香豆酸是甜樱桃中主要的酚酸类物质^[13-14]。有研究表明,很多浆果、水果及饮料是较好的酚酸类物质来源^[8-9]。邵亮亮等^[15]研究了葡萄汁、苹果汁、橙汁、西柚和胡萝卜汁5种果蔬汁中的酚酸含量,认为苹果汁中绿原酸含量最高,葡萄汁中酚酸种类最多且没食子酸含量最高,而橙汁中龙胆酸和对羟基肉桂酸含量较高。在植物不同组织、不同成熟期,酚酸的组成也有较大差别^[16-17],如对于柑橘果实,果肉中酚酸含量随成熟度的提高而减少,果皮中酚酸含量在半成熟期最高,且果皮中酚酸含量大大高于果肉。

2 酚酸的生物合成途径

植物多酚的前体物质来源于糖代谢的中间产物,经过莽草酸途径、苯丙烷代谢途径和类黄酮代谢途径合成多酚类物质。酚酸的生物合成途径在很多植物中已基本得到阐明(图1)。其中没食子酸是由莽草酸途径中间产物3-羟基莽草酸在相关酶的作用下经过2步反应合成的,其余大多数的酚酸类物质都是通过苯丙烷代谢途径合成

的。糖酵解(embden meyerhof parnas, EMP)途径生成的磷酸烯醇式丙酮酸和磷酸戊糖途径(pentose phosphate pathway, PPP)生成的赤藓糖-4-磷酸经过莽草酸途径生成苯丙氨酸,从而进入苯丙烷代谢途径。苯丙氨酸在苯丙氨酸解氨酶(phenylalanine ammonia lyase, PAL)和肉桂酸-4-羟化酶(cinnamate-4-hydroxylase, C4H)的作用下生成反式肉桂酸、苯甲酸、水杨酸、对香豆酸、咖啡酸、阿魏酸和芥子酸等酚酸类物质。这些酚酸在4-香豆酰辅酶A连接酶(4-coumarate-CoA ligase, 4CL)、甲基转移酶等的作用下,进一步转化为香豆素、绿原酸、咖啡酸等,也可以经过对香豆酰辅酶A生成4-羟基查尔酮,之后进入类黄酮代谢途径^[18]。此外,在一些植物体中还发现了其他途径,主要生成对羟基苯甲酸类酚酸:如水杨酸可以通过莽草酸途径产生的分支酸在异分支酸和酶、丙酮酸裂解酶催化下合成;对羟基肉桂酸类酚酸、类黄酮等可直接降解生成对羟基苯甲酸类酚酸,类似于脂肪酸的 β -氧化^[19]。

苯丙烷代谢途径是植物最重要的次生代谢途径之一,在细胞中有20%以上的代谢会通过这一途径进行。目前,已有大量研究证实PAL、C4H、4CL是苯丙烷类代谢途径的3个关键酶。其中,PAL催化L-苯丙氨酸生成反式肉桂酸,是苯丙烷类代谢途径的起始步骤,也是连接初生代谢和苯丙烷类代谢途径的枢纽,对植物具有非常重要的生理意义。1961年,Koukol等^[20]首次在大麦中发现PAL,并对其进行了纯化和相关酶学性质的研究。PAL存在范围广泛,已从多种高等植物如小麦、水稻、大豆、马铃薯等中分离纯化,在真菌中也发现了其存在^[21]。PAL是植物苯丙烷代谢的关键酶和限速酶,与木质素、黄酮、异黄酮、生物碱等重要的次生代谢产物的合成密切相关,在植物生长发育、遭受寒冷、机械损伤和抵御病菌侵害过程中起重要作用,其活性受多种因素的影响^[22-24]。由于PAL催化L-苯丙氨酸生成肉桂酸的反应是可逆的,目前工业上该酶已被固定化,用于工业生产苯丙氨酸。C4H是植物中第一个被克隆和鉴定的P450单加氧酶^[25]。C4H催化反式肉桂酸生成对香豆酸,其催化作用需要氧气且依赖还原型辅酶II,在植物生长发育中同样会受到光照、温度等的调节。苯丙烷代谢途径的终产物是对香豆酰辅酶A,4CL就是作用于苯丙烷代谢途径中的这一步反应。有研究表明对香豆酰辅酶A可以在一系列酶的作用下生成绿原酸、羟基肉桂酸等酚酸类物质,也可以作为重要的前体物质进入类黄酮代谢,进一步生成黄酮醇、黄烷醇、原花青素、芪类等多种多酚类化合物^[26]。

式,这种诱导的初衷是降低果蔬发病率。寡雄蛋白是一种类似于诱导激素类的蛋白质,研究表明,对番茄果实进行10 $\mu\text{g/mL}$ 寡雄蛋白处理,可显著降低灰霉病的发病率和严重程度,同时提高PAL、PPO、POD等与防御相关酶的活性^[52]。细菌过敏致病性蛋白能够引起过敏反应,从而诱导植物产生系统获得性抗性^[53]。其中甜瓜中一些由于过敏致病性蛋白诱导产生的防御反应也被认为是多酚类、类黄酮类等预成型的抗真菌物质的替代物引起的^[54-55]。壳聚糖和低聚壳聚糖(壳寡糖)处理也可以诱导PPO、POD和PAL活性显著增加^[56-58],研究表明,壳聚糖处理提高了酚酸类物质、黄酮类以及其他抗真菌物质的含量^[57]。罗伦隐球酵母和膜醭赤毕酵母处理可以降低梨^[59]、鲜食葡萄^[60]、桃子^[61]的发病率,这主要是通过提高几丁质酶、葡聚糖酶、PAL等的活性来实现的。Shivashankar等^[62]比较了易受瓜实蝇侵染的佛手瓜和对瓜实蝇有抗性的佛手瓜的酚酸含量及苯丙烷代谢介导合成的木质素的含量,结果表明对瓜实蝇有抗性的佛手瓜中积累了更多的木质素,且苯丙烷代谢相关酶类(如PAL)的活性更高,对香豆酸含量也较高,表明佛手瓜对瓜实蝇的抗性可能与苯丙烷代谢相关酶及代谢产物有一定的相关性。另外,研究表明,镰刀菌素菌丝体提取物也可以提高番茄根部细胞中阿魏酸、对羟基苯甲酸、对香豆酸及木质素的含量^[63]。

苯丙烷类化合物可以在植物体内形成和诱导产生物理、化学屏障,从而抵御真菌和细菌的感染,同时作为信号分子在植物发育和防御中发挥着重要作用^[64]。目前的研究中,关于低温胁迫、紫外辐射、外源激素诱导等因素对果实采后影响的研究较多,即通过诱导抗性对酚酸类物质含量产生影响,从而影响果蔬品质。因此,分析非生物和生物胁迫对采后果蔬中酚酸类物质积累的影响,可以为果实的贮藏及保证果实品质提供一定的理论依据。

3.2 酚酸与果蔬品质

酚酸类物质作为果实中重要的次生代谢产物,与果实色泽、风味、口感等感官指标密切相关。通常认为可溶性固形物、糖、酸等是衡量果品品质的重要指标,但在进行果品品质综合评价的过程中,还应特别注意对感官引起其他感官感受的物质含量的变化,如引起涩感的酚酸类物质。许多酚酸类物质是食品原料感官性状的重要贡献者,同时也可以作为抗氧化剂防止脂质氧化造成的酸败味道的产生。酚酸类物质可引起酸味、苦味和涩感^[65-66]。研究表明,对不同柠檬草浸剂进行消费者感官品评,当酚酸类化合物特别是对香豆酸含量较高时,柠檬草浸剂表现出更高的苦味^[67]。Duizer等^[68]研究了谷物中阿魏酸和香草酸引起的感官感受,认为香草酸比阿魏酸更酸,而阿魏酸则呈现出相对更高的苦味,且两者的

感官强度随浓度增大而增大,但两者引起的涩感差异不大。张李明等^[69]研究了滁菊提取物(其酚酸含量超过总酚含量的60%)对卷烟感官质量的影响,结果表明在卷烟中添加滁菊提取物0.4~0.6 g/kg时,可显著改善余味,降低刺激性,增加香气量。酚酸类物质还与食品原料的颜色有关。杨丽^[70]认为类胡萝卜素、总酚酸是枸杞子“变色”的物质基础,其外观颜色值与总酚酸含量成显著负相关。没食子酸本身虽不具有呈色作用,但可以在葡萄酒中起辅色作用,且与其颜色强度呈正相关^[71]。由于多酚类物质的种类和含量对水果的风味和品质具有重要影响,也逐渐成为评价和衡量果实风味品质的重要指标之一。

酚酸类化合物也是影响果汁质量的重要因素,与其口感、色泽、非生物稳定性密切相关^[72-74]。Hufnagel等^[75]的研究认为酚酸是一种收敛的涩感,而并非苦味,这种收敛的涩感与有机酸的含量呈正相关。Makila等^[74]的研究发现,在黑加仑果汁热加工和贮存过程中酚酸变化很大,因此他们认为低温贮藏对保证果汁原始品质非常必要。酚酸作为一类重要的抗氧化物质,能参与多种褐变和氧化还原反应,进而影响食品的感官品质,如羟基肉桂酸类酚酸是多酚氧化酶的最适底物,对果汁颜色稳定性有重要影响。Yawadio等^[76]向黑米汁中添加对香豆酸、芥子酸、阿魏酸、单宁酸及硫辛酸,发现这些有机酸均能不同程度地对花色苷起到增色和提高稳定性的作用。近年来的研究发现,羟基肉桂酸类物质对葡萄与葡萄酒的收敛性有一定贡献,葡萄和葡萄酒中的酚酸也会直接或通过辅色作用间接影响其色泽、风味、感官品质和营养价值^[77-78]。

此外,植物酚酸类物质也可以作为外源添加物(如防腐剂、保鲜剂、增香剂等)应用于食品中,从而影响食品的色、香、味。没食子酸衍生物如没食子酸丙酯、没食子酸辛酯等常用作抗氧化剂添加到食品中,而由阿魏酸或香草酸生成的香兰素因其浓郁的奶香味也被广泛应用于香料中。

4 代谢组学在评价酚酸类物质分布规律中的应用

植物代谢组学是以高通量、高灵敏度的现代分析仪器为硬件基础,研究生命个体在特定时间和条件下(包括外源性物质的刺激、环境变化或遗传修饰等)作出的所有代谢应答,并对这种应答产生的所有小分子代谢物进行定性及定量分析,从而定量描述生物内源性代谢物质的整体及其对内因和外因变化的应答规律。代谢组学技术已广泛应用于毒理学、营养、食品、中药、环境等的研究中^[79-80],所依托的分析技术包括核磁共振(nuclear magnetic resonance, NMR)、气相色谱-质谱联用(gas

chromatograph-mass spectrometer, GC-MS)、液相色谱-质谱联用(liquid chromatograph-mass spectrometer, LC-MS)等。代谢组学研究的关键问题在于对庞大的数据信息进行充分解读,由于代谢组学原始谱图极为复杂,需要进行数据降维和信息挖掘,包括谱图的预处理、分析模式的识别等。

代谢组学方法的诞生为评价果蔬中酚酸类物质的分布规律及其对机体的影响等方面提供了新的视角^[81]。基于GC-MS或气相色谱-飞行时间质谱数据的代谢组学分析在人参根部^[82]、草本植物^[83]等酚酸研究中得到应用,GC-MS可以通过检索数据库进行代谢物结构鉴定,但更适用于分析易挥发性物质,而酚酸类物质作为不易挥发的次生代谢产物,其代谢组学的应用多依托于LC-MS技术^[84-86]。LC-MS技术灵敏度高、无需衍生化,尤其是超高效液相色谱-飞行时间质谱能够更好地用于代谢物和同分异构体的鉴定。代谢组学技术已应用于果蔬品种特征及成熟期变化规律的研究。Moco等^[87]采用液相色谱-飞行时间质谱对不同品种、不同成熟期的番茄代谢产物(包括类胡萝卜素、类黄酮、酚酸等)进行了比较,发现尽管不同品种番茄基因型有所差别,但这些代谢产物的整体趋势类似,而对于同一品种而言,这些代谢产物仅在特定的发育时期积累。Choi等^[88]利用液相色谱技术研究了不同贮藏时间对陈皮中酚酸类物质变化的影响,结果表明长期贮藏的陈皮中酚酸类物质总量更高,且主成分分析可以将不同贮藏时期的陈皮根据检测到的11种酚酸类物质的含量进行较好地区分。近年来,基于NMR技术的代谢组学方法在鉴定植物次生代谢产物、果蔬酚酸类物质变化、酚酸对机体影响的评价等方面得到了发展^[89-91]。Francini等^[92]利用¹H NMR技术结合主成分分析,研究了不同品种苹果干中的多酚成分,发现不同品种的苹果干可以根据其化学组分(如儿茶素、表儿茶素、绿原酸)以及抗氧化活性进行区分。施孝活^[93]利用基于NMR的代谢组学方法结合临床血液生化和组织病理学手段,系统研究了5种酚酸类物质(包括没食子酸、香草酸、咖啡酸、阿魏酸和姜黄素)的长期饮食干预对正常大鼠机体代谢的影响;同时,利用代谢组学的方法研究了5种酚酸类物质间的构效关系,拓展了代谢组学的研究领域。代谢组学的方法还可以应用于研究某一特定过程中代谢产物的动态变化。Ku等^[94]利用¹H NMR耦合GC-MS技术,结合代谢组学研究绿茶的发酵特征,结果表明绿茶发酵过程中表儿茶素、奎宁酸等的质量分数不断下降,而没食子酸的质量分数不断增加。代谢组学技术也可以作为果蔬成熟过程、采摘后水果生理变化状况的评估工具,为水果贮存方式的选择和营销策略提供依据^[88,95]。

5 结 语

苯丙烷代谢途径是植物次生代谢的重要途径之一,与酚酸、类黄酮等多种次生代谢产物的合成有关,目前已成功克隆了部分与酚酸合成相关的关键酶基因,对植物酚酸合成途径的研究已取得了较大进展。但关于酚酸的生物合成较为复杂,同一种酚酸可以由多条途径或不同的底物合成,有些酚酸的代谢途径还不够明确(如绿原酸),且仍有部分酚酸及其相关酶学特性还有待进一步研究,如对香豆酸-3-羟化酶是咖啡酸生物合成途径的关键酶,但关于该酶的本质特征还未彻底阐述清楚。酚酸生物合成的复杂性导致对其代谢调控的研究也变得相对复杂,尽管酚酸作为小分子次生代谢产物,在参与防御反应及植物抗逆性方面发挥了重要作用,但对于其发挥作用的方式与防御机制还有待深入研究。

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