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燕麦皂苷合成积累的研究进展

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摘要:燕麦作为唯一同时积累三萜皂苷和甾体皂苷的禾谷类作物,具有多种药用功能和保健功能。本文通过系统概述国内外相关文献,对燕麦皂苷的相关研究进行综述。燕麦皂苷的构型及含量因器官组织和生长发育时期的不同而呈现出多样性,燕麦地下部分以三萜皂苷为主,而地上部分则以甾体皂苷为主。燕麦皂苷的合成和积累受品种基因型调控,同时也受环境因子和栽培措施的影响。通过梳理总结燕麦皂苷生物合成途径中的关键步骤,挖掘参与关键步骤的相关酶(如鲨烯环化酶、法尼基焦磷酸转移酶、糖基转移酶等),以促进燕麦的深度开发及利用。

关键词: 燕麦皂苷;合成;积累;调控

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Research Progress on Synthesis and Accumulation of Saponins in Oat

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Abstract: As the only cereal accumulating triterpenoid saponins and steroidal saponins, oat has many medicinal and health functions. In this review, the research on saponins in oat was reviewed by systematically summarizing the relevant literature. The configuration and content of saponins in oat varied among different organ tissues and growth stages. The underground part of oat mainly contains triterpenoid saponins, while the aboveground part dominantly contains steroid saponins. The synthesis and accumulation of oat saponins are regulated by genotype, and also influenced by environmental factors and cultivation measures. The key steps of oat saponin biosynthesis pathway were summarized, and related enzymes (such as squalene cyclase, farnesyl pyrophosphotransferase, glycosyltransferase and so on) involved in the key steps were mined to promote the deep development and utilization of oat.

Keywords: Saponin in oat; Synthesis; Accumulation; Regulation

皂苷(saponins)是广泛存在于植物体内的重要次生代谢产物之一^[1],通常分为三萜类皂苷和甾体类皂苷。作为药物、工业及食品加工业的原料^[2-3],除具有味道^[4-6]、起泡^[7]、乳化^[7]特性外,还

具有多种药理作用^[8]以及抗菌、化感、杀虫、杀软体动物^[9]和防御^[10]等生物活性。目前,关于皂苷的研究主要集中在蔬菜(山药、葱和芦笋等)以及中药材中,而日常食用的谷物通常缺乏皂苷类物

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质。

燕麦是唯一同时积累两类皂苷的禾本科谷类作物^[11],广泛分布于北纬 40°以北的北美、欧亚地区,是世界性一年生禾本科粮饲兼用栽培作物^[12],是发达国家最重要的谷类作物之一^[13]。早在 1997 年,FDA 就认定燕麦是营养平衡的功能性食物^[14],燕麦富含多酚^[4]、黄酮^[15-16]、生物碱^[17]、β-葡聚糖^[18]等多种活性成分,具有多种药用和保健功能,使其在食品领域和非食品领域(医药产品、洗涤用品、造纸、化妆品等)得到了广泛地应用^[11]。中国对于燕麦功能活性成分的挖掘起步相对较晚,目前研究较多的是 β-葡聚糖和生物碱等活性成分。对于燕麦皂苷的研究目前主要集中在结构与含量^[19-22]、提取工艺^[20-23]、生理活性^[24-25]及遗传^[26]等方面。

燕麦皂苷作为抗营养因子(anti-nutritional-factors, ANF)之一,是减少动植物产品中营养利用率和摄入量的化合物^[27],作为一种抗氧化活性重要成分,具有显著抗脂质氧化的作用^[24]。此外,它可以改善人体的部分肠胃功能^[28],对肠道线虫具有抗寄生虫活性作用^[29];还具有降低血清中胆固醇的效果^[30],预防骨骼疾病^[31];可作为天然乳化剂、表面活性剂、苦味剂^[32-33]和新型脂肪替

代物^[34]。因此,了解皂苷的结构类型、积累分配规律及合成途径,是充分利用和科学调控燕麦皂苷的关键,也是提高商业应用价值的主要途径。本文通过概述国内外对燕麦皂苷的研究进展,总结其结构类型及含量范围,归纳常见的测定方法,梳理生物合成途径中的关键步骤,分析有待进一步研究的问题,以期创制功能型燕麦品种、改变燕麦产品单一现状、提高燕麦产品附加值,深化燕麦资源开发、科学调控生物活性成分等方面提供理论参考。

1 燕麦中皂苷的结构及类型

依据皂苷类物质核心化学构造的不同,皂苷划分为三萜皂苷和甾体皂苷^[35],燕麦体内同时积累上述两类物质^[36]。从燕麦属植物根部获得的皂苷通常为三萜皂苷,属齐墩果烷型,称其为燕麦素(Avenacin)^[37],主要有以下 4 种:Avenacin A-1、Avenacin A-2、Avenacin B-1 和 Avenacin B-2,均具有三糖三萜烯骨架。其中,Avenacin A-1 和 Avenacin B-1 是 N-甲基邻氨基苯甲酸酯化,而 Avenacin A-2 和 Avenacin B-2 是苯甲酸酯化。也有研究表明,在商品型燕麦中同样测到了其它的三萜型皂苷^[38](表 1)。

表 1 燕麦中其他三萜类皂苷构型^[38]
Table 1 Configuration of other triterpenoid saponins in oat^[38]

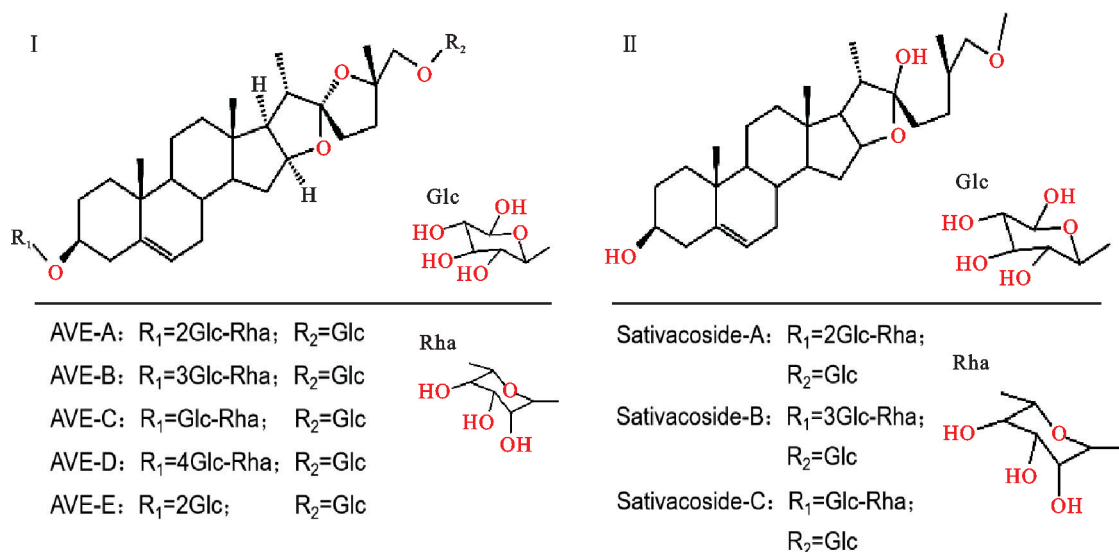
构型 Configuration	编号 No.	官能团 Functional group					
		R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
	1	OH	H	OH	OCH ₃	CHO	\
	2	OH	H	\	\	CHO	\
	3	OH	NHCH ₃	\	\	CH ₂ OH	\
	4	OH	CHO	NHCH ₃	H	H	OH
	5	OH	CH ₂ OH	NHCH ₃	H	H	OH
	6	OH	H	OH	OCH ₃	CH ₂ OH	H
	7	OH	H	H	H	CHO	OH
	8	OH	H	H	H	CHO	H

表格中 \ 代表此位置无任何官能团。

\ represents no functional group.

从燕麦植物地上部分获得的皂苷通常为甾体皂苷,称其为燕麦皂苷(Avenacoside, AVEs),常见的有燕麦皂苷 A(Avenacoside A, AVE-A)和燕麦皂苷 B(Avenacoside B, AVE-B)两种,均属变形螺旋甾烷醇类,其基础构造与螺旋甾烷醇类的组成一致^[39]。在 C-3 位置,燕麦皂苷 A 与一个三糖单位(包括一个鼠李糖和两个葡萄糖单位)以及 C-26 位置的一个葡萄糖单位发生了糖基化反应。同样,燕麦皂苷 B 在 C-3 位置与一个四糖(包括一个鼠李糖和三个葡萄糖单位)以及 C-26 位置

的一个葡萄糖单位发生了糖基化反应。此外,燕麦皂苷 B 苷元的 F 环是一个五元四氢呋喃环。在自然产物中,这种情况并不常见。陆灿^[22]在对燕麦中的皂苷进行分离鉴定发现,除了有燕麦皂苷 A 和燕麦皂苷 B,还从籽粒中提取出燕麦皂苷 C。此外,Yang 等^[37]从燕麦中发现了燕麦皂苷 D 和燕麦皂苷 E(图 1)。Hu 等^[38]通过使用基于全球天然产物协会(GNPS)特征的网络系统,在燕麦中除了已经发现的燕麦皂苷 A、B、C、D 和 E 外,还检索到一系列新的甾体皂苷(图 1)。



I. 燕麦皂苷中 AVE-A 和 AVE-B 是燕麦中最常见的成分, AVE-C、AVE-D 和 AVE-E 是燕麦产品或商业产品中新发现的成分^[22,37]; II. 基于全球天然产物协会(GNPS)特征网络系统发现了燕麦的新型甾体皂苷构型网络系统^[38]。

I. AVE-A and AVE-B are the most common ingredients in oat. AVE-C, AVE-D, and AVE-E are newly discovered ingredients in oat products or commercial products^[22,37]; II. The network system of neosteroidal saponin configuration of oat was discovered based on the characteristics of the Global Natural Products Society(GNPS)^[38].

图 1 燕麦甾体皂苷构型

Fig. 1 Configurations of Avenacoside in oat

2 燕麦中皂苷的测定

植物体生长发育是一个复杂动态生理过程,代谢产物的积累分配随着发育进程的改变而改变。研究表明,燕麦素作为一种高度特化植物防御性物质,只存在于根尖^[40],更具体地说,是在根表皮细胞的液泡中^[41]。它不但对土壤传播的病原体具有抗性作用,并且具有影响邻近植物发育的化感作用^[42]。燕麦素 A-1 是含量最丰富的燕麦根系皂苷,由于被 N-甲基氨基苯甲酸酯酰化,在紫外线照射下具有明亮的荧光反应,这一特性已被用于鉴定和分离参与燕麦素 A-1 生物合成的相应基因^[43]。燕麦素的生物合成似乎是由一个生物合成基因簇进行的,这意味着燕麦素的

合成、运输和分配都需要高度的协调,所有这些都必须在不同细胞器和细胞隔室之间精确地在时间和空间上进行协调^[44]。燕麦皂苷被发现在麸皮^[45]、籽粒(主要储存在燕麦籽粒的胚乳中)^[11]、叶片(叶中的甾体皂苷主要定位于液泡)中^[44],且不同器官中,燕麦甾体皂苷单体含量占比不同。Ute Laudenbach 等^[46]对燕麦皂苷 A 和 B 在绿苗和黄化苗中的积累进行了研究,发现它们与幼苗的生长密切相关,但是燕麦皂苷的积累与甾体发育不相关。

皂苷含量除了受到器官组织影响外,同样受测量方法敏感性和精确性的影响。通常,测定燕麦皂苷分为三个阶段:脱脂燕麦粉制备阶段、辅助提取阶段和比色阶段。传统的脱脂燕麦粉制备采

用索式提取抽提回流法提取燕麦皂苷^[21]但该方法提取率欠佳,后改为浸提法脱脂,但燕麦皂苷的含量因浸提溶液的不同而不同^[23-25],以正己烷最佳。辅助提取步骤的加入,大大提高了测定步骤中燕麦皂苷的含量,其中最为常见且使用最多的是超声辅助提取工艺^[20-22]。随着精量测定技术的发展,高效液相色谱技术(HPLC)和液质谱联用技术(HPLC-MS)开始应用到燕麦皂苷测定中,得到的皂苷含量一般在 0.200~0.500 g·kg⁻¹ 范围变化^[36-39],且品种不同,燕麦皂苷含量也不同^[38-39]。随着更精准的 UPLC-TQ-MS 方法的应用,测出的燕麦皂苷含量范围为 0.553~0.909 g·kg⁻¹,这些值高于以前报道的燕麦品种的燕麦皂苷含量,一方面可能是测定仪器更精确了,另一方面也可能与冷凉种植环境下,燕麦皂苷含量较高的原因^[47]。尽管方法不同,但通过测定发现,燕麦籽粒或麸皮中燕麦皂苷 A 含量最高,占总皂苷的 50%,燕麦皂苷 B 含量其次^[36,38,47]。

3 燕麦中皂苷的生物合成

目前,二倍体燕麦(*Avena strigosa*)的基因组序列草图已经完成绘制^[48],六倍体栽培裸燕麦“三分三”(Sanfensan, *A. sativa ssp. nuda*)参考基因组也完成了组装^[49],这些研究结果为探索燕麦中皂苷的生物合成创造了条件。通过系统整理

和归纳 NCBI (<https://www.ncbi.nlm.nih.gov/>)、Biocyc (<https://biocyc.org/>)、Pubchem (<https://pubchem.ncbi.nlm.nih.gov/>) 及 KEGG 数据库(<https://www.kegg.jp>)中关于二倍体燕麦中皂苷生物合成途径中功能明确的化合物及相关酶类,并结合其他植物中皂苷生物合成途径中已报道出的功能确定的物质、酶类和基因簇等信息,对燕麦中皂苷可能的生物合成途径进行综合分析及总结。

3.1 燕麦中皂苷生物合成的前体途径(上游途径)

皂苷的生物合成途径由上游途径(2,3-氧化鲨烯合成以前)和下游途径(苷元骨架的形成和结构修饰)共同组成。对于上游路径的探索已相当明确,它们合成了燕麦中皂苷所必需的骨架前体^[50]。

上游路径分为两个部分:首先,乙酰辅酶 A 通过甲羟戊酸途径(MVA)进入细胞内部,然后丙酮酸通过甲基赤藓糖醇磷酸途径(MEP)进入细胞内部,从而形成并储存中间物,如法尼基焦磷酸(IPP)和二甲基烯丙基焦磷酸(DMAPP)。此外,通过 MEP 路线形成的 IPP 能够在 IPP 异构酶的影响下与 DMAPP 进行交替。上游途径中涉及到多种酶的持续作用,以生成鲨烯(表 2)。鲨烯环氧酶的参与使得鲨烯转变为 2,3-氧化鲨烯^[51]。至此,上游途径结束,进入下游苷元骨架合成及修饰途径。

表 2 燕麦中皂苷生物合成共性途径中关键酶及其功能
Table 2 Key enzymes and their functions in the common pathway of saponins in oat biosynthesis

关键酶 Key enzyme	缩写 Abbreviation	酶类型 Enzyme type	主要功能 Main function	参考文献 References
乙酰辅酶 A 转移酶 Acetyl-CoA transferase	AACT	转移酶 Transferase	催化形成乙酰乙酰辅酶 A Catalyze the formation of acetoacetyl-CoA	[48,50]
法尼基焦磷酸转移酶 Farnesyl diphosphate transferase	FDPs		催化 IPP 和 DMAPP 以 1-4 头尾连续缩合成 FPP Catalyze IPP and DMAPP to form FPP in 1-4 head and tail continuous condensation	[41,48,50]
HMG Co-A 还原酶 HMG Co-A reductase	HMGR		催化 HMG Co-A 还原形成 MVA Catalyze reduction of HMG Co-A to form MVA	[48]
DOXP 羧酸还原异构酶 DOXP reductoisomerase	DXR	还原酶 Reductase	催化 DOXP 生成 MEP Catalyze DOXP to form MEP	[41,48]
HMBPP 还原酶 HMBPP reductase	HMBPPR		催化前体物质生成 IPP Catalyze precursor substances to form IPP	[41,50]
HMG Co-A 合成酶 HMG Co-A synthase	HMGS		催化形成 HMG Co-A Catalyzed to form HMG Co-A	[51]
脱氧-D-木酮糖-5 磷酸酯合成酶 1-deoxy-D-xylulose-5-phosphate synthase	DXS	合成酶 Synthase	催化丙酮酸与 3-磷酸甘油酸缩合生成 DOXP Catalyze the condensation of pyruvate with 3-phosphoglyceric acid to form DOXP	[26-27]
鲨烯合酶 Squalene synthase	SS		位于内质网膜,催化 2 分子 FPP 缩合生成鲨烯 Located in the endoplasmic reticulum, it catalyzes the condensation of 2 molecules FPP to form squalene	[41,48,50-51]
甲羟戊酸激酶 Mevalonate kinase	MVK	激酶 Kinase	催化 MVA 形成 IPP Catalyze MVA to form IPP	[41]

3.2 燕麦中皂苷生物合成的后修饰过程(下游途径)

2,3-氧化鲨烯在不同环化酶的作用下生成不同的后续产物。苷元骨架侧链经过一系列氧化、羟基化和糖基化的结构修饰反应后,生成对应的皂苷物质储存在各个器官中,这一步是皂苷呈现多样性和复杂性的关键因素之一^[52],且有研究表明,该结构修饰步骤中的酶具有底物高度特异性,这也是各类皂苷产生生物活性的主要原因之一^[53](图 2)。该步骤中结构修饰酶主要包括细胞色素氧化酶 P450 家族^[54-55]、CAZY 家族中的 GT1 家族^[56]和 SCPL 家族^[57]等,这些酶主要负责苷元骨架的修饰步骤。此外,除上述类别的结构修饰酶外作为生物合成途径的候选酶,还需考虑如碳水化合物合成酶等其他类别的酶^[57]。相较于燕麦根系皂苷,燕麦甾体皂苷在构建基础苷元骨架后,关于苷元侧链的修饰步骤及具体的作用位点,目前尚未有系统具体的研究。

3.2.1 燕麦地下部燕麦素生物合成的下游途径

燕麦素生物合成过程首先是 2,3-氧化鲨烯

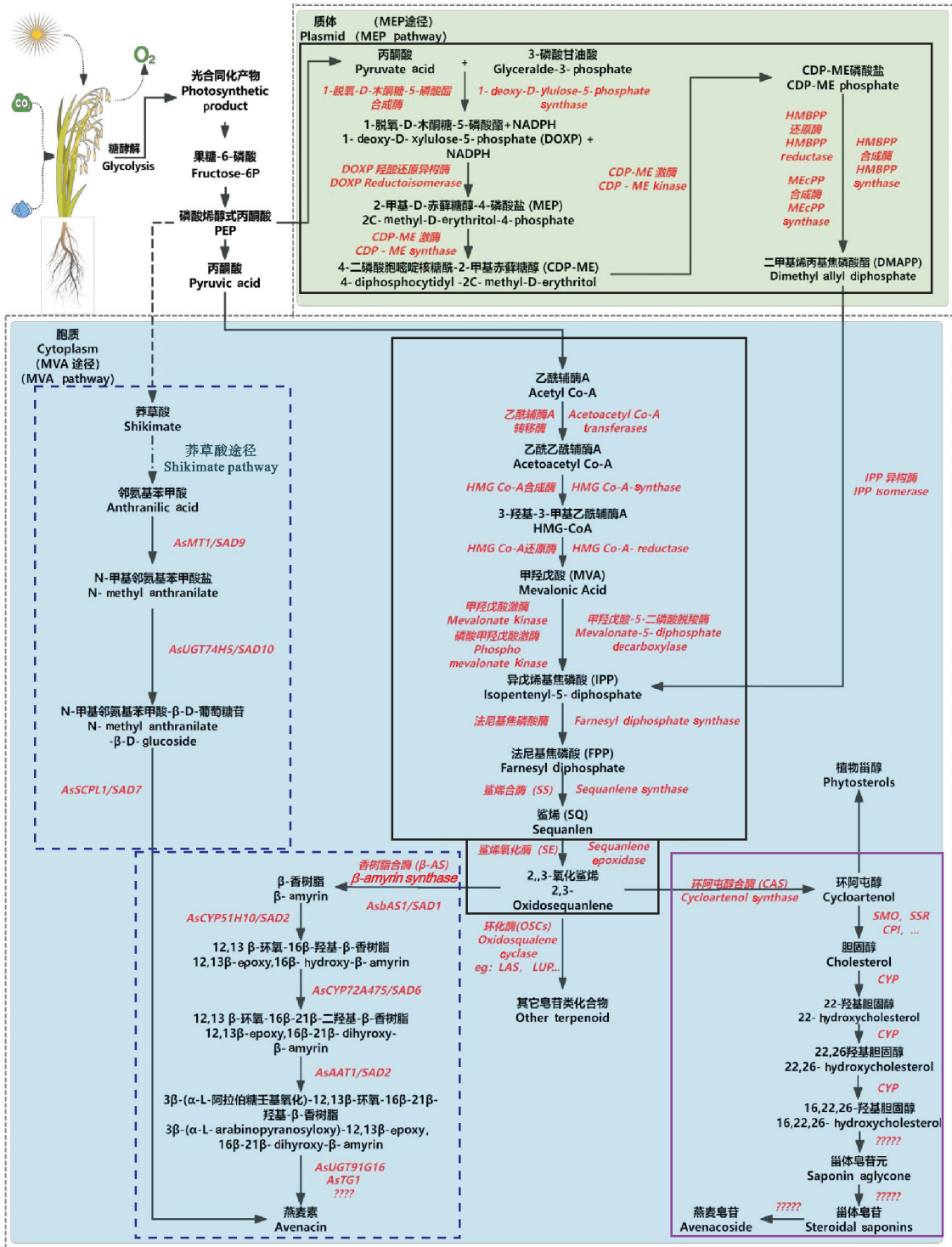
在 β -香树脂合成酶的作用下环化,生成 β -香树脂(图 2)^[58]。然后,在单加氧酶的影响下, β -香树脂经历羟基化和环氧化,最终形成 12,13 β -环氧-16 β -羟基- β -香树脂^[55]。在羟化酶的作用下,产生 C-21 β 氧化燕麦素中间体,然后该产物在 C-23 位被细胞色素 P450 酶进一步催化,并在 C-3 位置通过阿拉伯糖基转移酶和其它具体功能未定的糖基转移酶依次糖基化^[52]。

然后,该产物在 C-30 位被另一种细胞色素 P450 酶氧化并运输到液泡,在液泡中进一步被转糖苷酶家族成员糖基化。由莽草酸途径产生的邻氨基苯酸被甲基转移酶甲基化,并在细胞质中被糖基转移酶糖基化,得到 N-甲基邻氨基苯酸葡萄糖苷^[59],紧接着被运送到液泡,在液泡中作为丝氨酸羧基肽酶类酰基转移酶的激活酰基供体,并在酰基转移酶的催化下使脱氧酰基燕麦素最终转化为燕麦素^[55]。表 3 中是参与燕麦素合成途径的相关酶。

表 3 燕麦素生物合成下游途径中关键酶及其功能

Table 3 Key enzymes and their functions in the downstream pathway of avenacin biosynthesis

关键酶名称 Key enzyme name	酶类型 Enzyme type	编码基因簇 Coding gene cluster	主要功能 Main function	参考文献 References
AsbAS1	环化酶 Cyclase	SAD1	使 2,3-氧化鲨烯环化形成 β -香树脂 The 2, 3-oxidized squalene was cyclized to form β -aromatic resin	[58]
AsCYP51H10	氧化酶 Oxidase	SAD2	进一步催化 β -香树脂环氧化和羟基化 Further catalyze epoxidation and hydroxylation of β -aromatic resin	[55,58]
AsCYP72A475	羟化酶 Hydroxylase	SAD6	负责在支架 C-16 位置氧化,C-21 位置羟基化 Oxidation at the C-16 position of the scaffold and hydroxylation at the C-21 position	[54]
AsUGT99D1		SAD3	C-3 位置添加 L-阿拉伯糖寡糖链中催化第一个糖加成 C-3 position addition catalyzes the first sugar addition in the oligosaccharide chain of L-arabinose	[53]
AsUGT74H5		SAD10	在细胞质中催化 N-甲基邻氨基苯甲酸甲酯甲基化,得到 N-甲基邻氨基苯酸葡萄糖苷,并在合成的最后步骤中为 AsSCPL1 的激活提供酰基供体 N-methyl-O-aminobenzoate methyl ester is catalyzed in the cytoplasm to obtain N-methyl-O-aminobenzoate glucoside and provides acyl donors for the activation of AsSCPL1 in the final step of synthesis	[57]
AsUGT74H6	糖基转移酶 Glycosyl transferase	\	在细胞质中催化 N-甲基邻氨基苯甲酸甲酯甲基化,得到 N-甲基邻氨基苯酸葡萄糖苷,并在合成的最后步骤中为 AsSCPL1 的激活提供酰基供体 N-methyl-O-aminobenzoate methyl ester is catalyzed in the cytoplasm to obtain n-methyl-O-aminobenzoate glucoside and provides acyl donors for the activation of AsSCPL1 in the final step of synthesis	[59]
AsUGT91G16		\	在胞质中将 1,2-D-葡萄糖连接到 L-阿拉伯糖中 1, 2-D-glucose is connected to L-arabinose in the cytoplasm	[56]
AsTG1		SAD3	添加 1,4-D-葡萄糖 Add 1, 4-D-glucose	[52,54]
AsSCPL1	酰基转移酶 Acyltransferase	SAD7	催化 C-21 位置被 N-甲基邻氨基苯甲酸甲酯酰化 Catalyzed the acylation of the C-21 site by N-methyl-anthranilate methyl ester	[54,57]
AsMT1	N-甲基转移酶 N-methyltransferase	SAD9	催化莽草酸途径产生的邻氨基苯酸甲基化 Catalytic methylation of O-aminobenzoic acid produced by the shikimic acid pathway	[52]



图中绿色部分是质体中 MEP 途径;蓝色部分是胞质中 MVA 途径;黑色实线框部分为燕麦中皂苷生物合成的共性途径;蓝色虚线框是燕麦地下部皂苷(燕麦素)合成途径;紫色实线框是燕麦地上部甾体皂苷(燕麦皂苷)合成途径。图中红色斜体字体为反应所需酶;红色问号为有待进一步研究的酶。

The green part of the figure is the MEP pathway in the plasmid; The blue part is the MVA pathway in the cytoplasm; The solid black frame part is the common pathway of saponin biosynthesis in oat; The blue dotted box is the synthetic pathway of Avenacin; The orange dotted box is the synthetic pathway of Avenacoside. The red italic font in the figure shows the enzyme required for the reaction; The question mark in red indicates the enzyme to be studied.

图 2 燕麦体内皂苷生物合成途径

Fig. 2 Avenacin and Avenacoside biosynthesis pathways in oat

然而,燕麦素合成途径中糖基化步骤的酶及其在生物合成序列中的确切位置大多仍未可知。研究表明,不完全糖基化的燕麦素毒性较小,在抵御微生物攻击方面效率会变低^[56],而具有去糖基化能力的真菌更容易入侵燕麦植物^[59]。所以,充分了解燕麦素骨架上正确且完全糖基化位置对了解其作为植物天然防御性物质的生物活性是非常重要的。

3.2.2 燕麦地上部燕麦皂苷生物合成的下游途径

2,3-氧化鲨烯在环阿屯醇合酶(CAS)催化下形成环阿屯醇,这是甾体皂苷元骨架形成的基础^[60-61]。在多种酶的协同作用下(表 4),形成胆固醇^[58]。

在对燕麦甾体皂苷元骨架修饰步骤中,低聚糖链是由单糖基按一定次序通过一系列酶的作用连接到苷元分子。后修饰步骤中结构修饰酶如表 5 所示,这些酶主要负责苷元骨架的结构修饰步骤^[58,60,62],这些研究结果为寻找调控燕麦甾体皂苷合成的同源基因提供了可能。目前已经确定了燕麦甾体皂苷生物合成后修饰过程中的结构修饰酶,除了 UDP-GluTase,其他的研究并未报道。同时,在燕麦甾体皂苷基本结构骨架形成后,苷元的氧化、取代和糖苷化作用的顺序和位置尚未有明确的研究结果。

4 燕麦中皂苷研究展望

随着中国大食物观的践行以及健康中国战略的推进,农业发展开始进入营养型时代。越来越多药食同源的作物成为研究热点,营养健康和营养强化成为新的研究主题。系统性了解植物天然营养成分的遗传因素、结构类型、积累分配及生物合成途径,是其充分开发利用的前提条件。燕麦中皂苷与其它植物天然成分一样,它的合成和积累是基因和环境互作的结果,同样也受栽培措施和外源调控的影响。形成过程复杂,涉及因素较多,需要针对调控燕麦皂苷合成积累的诸多因素进行研究。

4.1 充分了解燕麦中皂苷的积累分配规律,是开发利用的基础

研究表明,皂苷在植物界分布广泛,类型不同,含量不一,功效各异^[59-60,64],且分配和积累的部位具有高度的特异性。燕麦根皂苷含量最多的为 Avenacin A-1,但含量未知。而 Avenacoside A 和 Avenacoside B 作为燕麦甾体皂苷的主要成分,在籽粒中分别占籽粒总皂苷含量的 41.9%~60.6%和 35.8%~55.2%,在麸皮中分别占麸皮总皂苷含量的 37.1%~57.7%和 13.8%~49.0%^[14]。虽然有报道指出,燕麦叶中也含有燕麦甾体皂苷^[31],

表 4 燕麦甾体皂苷生物合成下游途径关键酶及其功能

Table 4 Key enzymes and their functions in downstream pathway of Avenacosides biosynthesis

关键酶名称 Key enzyme name	关键酶缩写 Key enzyme abbreviation	酶类型 Enzyme type	主要功能 Main function	参考文献 References
环阿屯醇合酶 Cycloartenol synthase	CAS	合成酶 Synthase	催化 2,3 氧化鲨烯环化生成环阿屯醇 Catalyze 2,3 oxidation of squalene cyclization to cycloartenol	[60-61]
甾醇 C-24 甲基转移酶 Sterol C-24 methyltransferase	SMT	转移酶 Transferase	催化胆固醇侧链生成甾体皂苷元骨架 Catalyze cholesterol side chain to form steroid saponin skeleton	[58,61]
环丙基甾醇异构酶 Cyclopropyl sterol isomerase	CPI	异构酶 Isomerase	催化胆固醇结构变化生成不同甾体皂苷元骨架 Catalyze the change of cholesterol structure to produce different steroidal saponin skeleton	[58]
甾醇脱甲基酶 Sterol demethylase	CYP	脱甲基酶 Demethylase	催化胆固醇侧链生成甾体皂苷元骨架 Catalyze cholesterol side chain to form steroid saponin skeleton	[58,60-61]
固醇甲基氧化酶 Sterol methyl oxidase	SMO	氧化酶 Oxidase	催化胆固醇侧链氧化生成甾体皂苷元骨架 Catalyze side chain oxidation of cholesterol to form steroid saponin skeleton	[58,60]
侧链氧化酶 Side chain oxidase	SDR		催化胆固醇侧链生成甾体皂苷元骨架 Catalyze cholesterol side chain to form steroid saponin skeleton	[58]
固醇侧链还原酶 Sterol side chain reductase	SSR	还原酶 Reductase	催化胆固醇侧链生成甾体皂苷元骨架 Catalyze cholesterol side chain to form steroid saponin skeleton	[58,61]
甾醇还原酶 Sterol reductase	DHCR			[58]

表 5 燕麦甾体皂苷生物合成下游途径结构修饰步骤中关键酶及其功能

Table 5 Key enzymes and their functions in structural modification steps of downstream pathway of avenacosides biosynthesis

关键酶名称 Key enzyme name	关键酶缩写 Key enzyme abbreviation	酶类型 Enzyme type	主要功能 Main function	参考文献 References
UDP-谷氨酸转移酶 UDP-glutamate transferase	UDP-GluTase	转移酶 Transferase	结构修饰形成甾体皂苷 Structurally modified form steroid saponins	[64]
β -糖苷酶 β -glycosidase	F26G	\	催化呋甾烷醇-26(27)-葡萄糖苷水解成环形成螺甾烷型皂苷 Catalyzed the hydrolysis of furanostanol-26 (27)-glucoside into rings to form spirostane-type saponins	[66-67]
UDP-葡萄糖甾体糖基转移酶 UDP-glucosteroid glycosyltransferase	UDPG-SGTas		在甾体皂苷元 C-3 的羟基位置引入糖基 A sugar group is introduced into the hydroxyl position of steroid sapogenin C-3	[62]
UDP-葡萄糖糖基转移酶 UDP-glucose glycosyltransferase	UDPG-GlcTase	糖基转移酶 glycosyl transferase		[63]
尿苷二磷酸葡萄糖醛酸基转移酶 Uridine diphosphate glucuronide transferase	UGT		结构修饰形成甾体皂苷 Structurally modified form steroid saponins	[62]
糖基转移酶 glycosyl transferase	SaGT4A		催化甾体皂苷元的 3-O-糖基化 Catalyze 3-O-glycosylation of steroid saponins	[65]
糖基转移酶 glycosyl transferase	StSGT			[65]

但是具体含量多少尚未可知,且常用作饲料的茎秆中是否含有燕麦皂苷,作为抗营养因子,它对于动物的消化吸收有哪些影响?不同生育阶段中燕麦根系、茎秆、叶片、圆锥花序(穗)以及籽粒等器官中总皂苷的原生分配积累规律是什么?燕麦籽粒皂苷积累是否存在基因型差异?遗传多样性如何?是否与环境型有关?它们的互作效应对皂苷积累是否有影响?旗叶、茎秆和叶鞘中是否有皂苷物质输出?对籽粒皂苷的积累是否有贡献?若有,其贡献率是否随品种演替发生变化?籽粒皂苷积累与农艺性状之间是否存在相关性?在籽粒灌浆过程中,皂苷的积累与干物质积累是否相关?造成上述现象的分子机制是什么?明确上述问题,对选育新型功能性燕麦品种,改变燕麦产品单一的现状,提高种植农户的经济收益,提高燕麦副产品(如茎秆等)的利用率,增加燕麦产品附加值具有重要的现实意义。

4.2 加强探索燕麦中皂苷的生物合成途径,是开发利用的方向

虽然以燕麦二倍体为研究对象的燕麦根系皂苷研究已初见成效,在其合成途径的关键步骤中,起关键调控作用的酶和基因簇也逐渐被报道,但从 β -香树脂到转化为最后的燕麦根系皂苷需要在不同位点进行氧化、羟基化以及酰化的修饰,这些具体的位点,结构修饰需要的酶以及这些酶是否具有高度底物特异性还有待进一步研究。相较于

燕麦根系皂苷,燕麦地上部的甾体皂苷的生物合成的研究处于起步阶段,尤其是下游途径修饰阶段中涉及碳环骨架合成和糖基化修饰步骤中关键的酶和基因尚不明确。明确苷元骨架上连接糖链的位置、种类、数目如何受酶的调控以及关键酶的调控基因,对实现燕麦皂苷体外批量商业化生产具有重要的科学意义。

4.3 明晰调控燕麦中皂苷的外在因素,是开发利用的关键

目前,关于环境和栽培措施对燕麦中皂苷影响的研究较少。但植物中皂苷的产生、分配、积累通常因植物种类、遗传背景、环境因子(光质^[68-69]、光强^[70]、光周期^[71-72]、温度^[73-75]、非生物胁迫^[76-78]、土壤类型^[79-81]等)、人为因子(施肥^[82-84]、外源物质调控^[85-86]、生物强化因子^[87-89]等)、器官组织和生长发育时期的不同而呈现出种类和结构的多样性和特异性。研究表明,上述因素是通过影响皂苷生物合成途径中的酶、合成前体、酶反应底物、合成所需物质的识别、启动酶活力、还原当量等来影响最终皂苷的含量^[90-98]。目前,各类因素对于植物皂苷合成积累的影响研究主要集中在中药材上,土壤的类型和结构以及可利用的营养物质通过优化根系结构和养分吸收效率,促进干物质的积累和皂苷类物质的合成^[79]。大田栽培模式下,合理施肥尤其是调整 N、P、K 肥的合理配比也可以增加植物中皂苷类物质的含量^[82-85]。

除了影响皂苷总含量外,营养的供应也会影响合成途径中相关前体的含量。据报道,在苗圃条件下,较高的氮供应可以刺激萜类物质的生产^[83]。同时,皂苷类物质的生物合成生产也受到磷元素利用率的影响^[84,99]。生物营养强化技术也是调控天然植物活性成分的有效措施。硒、锌等微量元素作为外源强化元素被广泛用于农作物。研究表明,外源硒可以提高植物中皂苷类物质的含量^[87-89]。不同植物种类甚至是同一植物的不同品种对于硒的吸收转运有着基因型的差异,因此对于皂苷类物质的合成积累也存在差异。外在因素(如环境因子包括逆境胁迫下、栽培措施以及外源调控措施等)对燕麦体内皂苷分配积累规律、品种遗传多样性及合成积累影响机制等方面研究较少,且在贮藏加工过程中,燕麦皂苷的稳定性尚不明确。研究各项因子影响燕麦中皂苷合成积累的规律和可能的机制,对生产上调控燕麦皂苷的合成具有实践意义。

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