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生氰糖苷类物质的结构和代谢途径研究进展

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摘　要:生氰糖苷类成分作为多种植物的防御物质被广泛研究。随着对其研究的深入,发现在细菌、真菌、节肢动物和鳞翅目昆虫体内也存在该类物质,生氰糖苷具有防御和性信息素等作用。本文对该类物质的结构、合成和降解途径等方面进行了综述,为新农药先导化合物的发现提供理论依据。

关键词:生氰糖苷;化学结构;代谢途径
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Advances in Research on Chemical Constituents and Metabolic Pathways of Cyanogentic Glycosides

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Abstract: Cyanogenic glycosides are found in a wide range of taxa including ferns, woody and herbaceous plants, as well as some bacteria, fungus, arthropod and insects. Cyanogenic glucosides play several important roles in addition to defense. The transfer of a nuptial gift of cyanogenic glucosides during mating of Zygaena has been demonstrated as well as the possible involvement of hydrogen cyanide in male assessment and nitrogen metabolism. Researches on the cyanogenic glucosides are reviewed from the aspects of their structure, synthesis and degradation.

Key words: cyanogentic glycoside; chemical constituent; metabolic pathways

生氰糖苷(Cyanogentic glycosides)亦称氰苷,作为具有防御功能的次生代谢产物已在包括蕨类,裸子植物和被子植物在内的2500多种植物中被发现,它们储存于液泡中,当植物组织遭到破坏,如食草动物侵袭或病原体入侵,生氰糖苷与降解酶相接触,释放有毒物质HCN和酮(或醛)类物质,提供植物一个立即的防御对抗。在对橡胶产胶量的研究中,发现植物中的生氰糖苷还具有转运、存储氮元素的作用。在4亿多年植物和动物共同进化的过程中,动物可以从外界获取或是自身合成该类化合物为己所用[1],因此在动物界,主要在一些节肢动物和昆虫中存在生氰糖苷,这类物质既可作为化学防御物质,也可作为性信息素,在择偶和交配期起到重要作用[2-4]。本文对该类物质的结构类型、合成和降解途径等方面进行综述,为深入研究该类化合物在植物和动物中的作用提供资料。

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1　生氰糖苷的结构

生氰糖苷是氰醇衍生物的羟基和D-葡萄糖缩合形成的糖苷(图1),根据取代基不同主要分为脂肪族生氰苷和芳香族生氰苷。该类化合物主要由三种脂肪族蛋白质氨基酸(L-valine, L-isoleucine, L-leucine),两种芳香族氨基酸(L-phenylalanine, L-tyrosine)以及一种脂肪族非蛋白质氨基酸(2-(2′-Cyclopentenyl)-glycine)衍生而来[5],结构综述如下(图2,3)

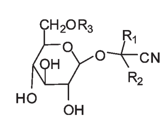

图1　生氰糖苷的基本结构式

Fig. 1　Basic chemical structure of cyanogentic glycosides

2　生氰糖苷的生物合成

生氰糖苷生物合成过程中涉及3大类酶,分别属于CYP79、CYP71家族的两种细胞色素CYP450(也称P450)及葡萄糖转移酶UGT8581。CYP450是

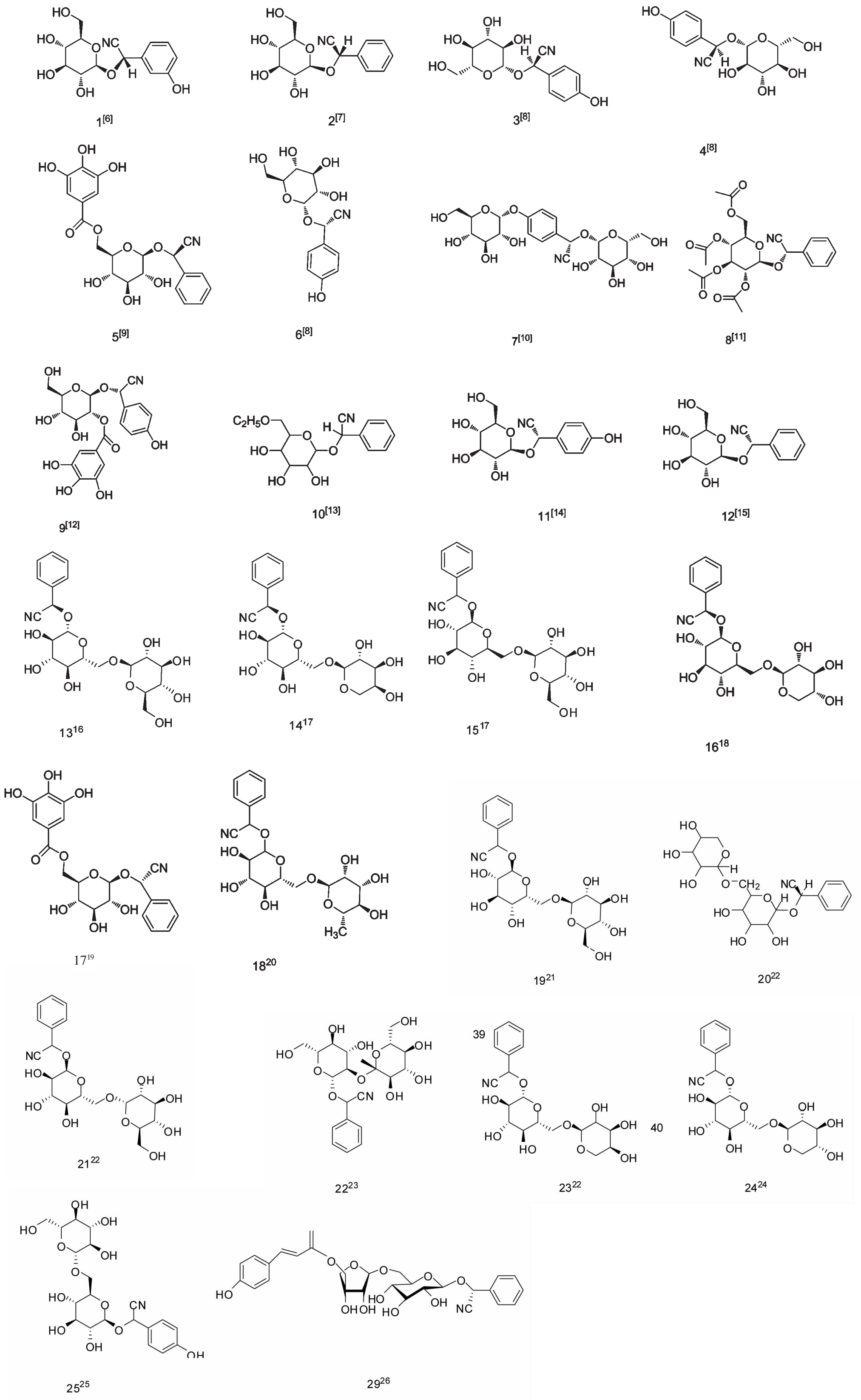

图 2 芳香族生氰糖苷的结构式

Fig. 2 Chemical structures of aromatic cyanogenic glycoside

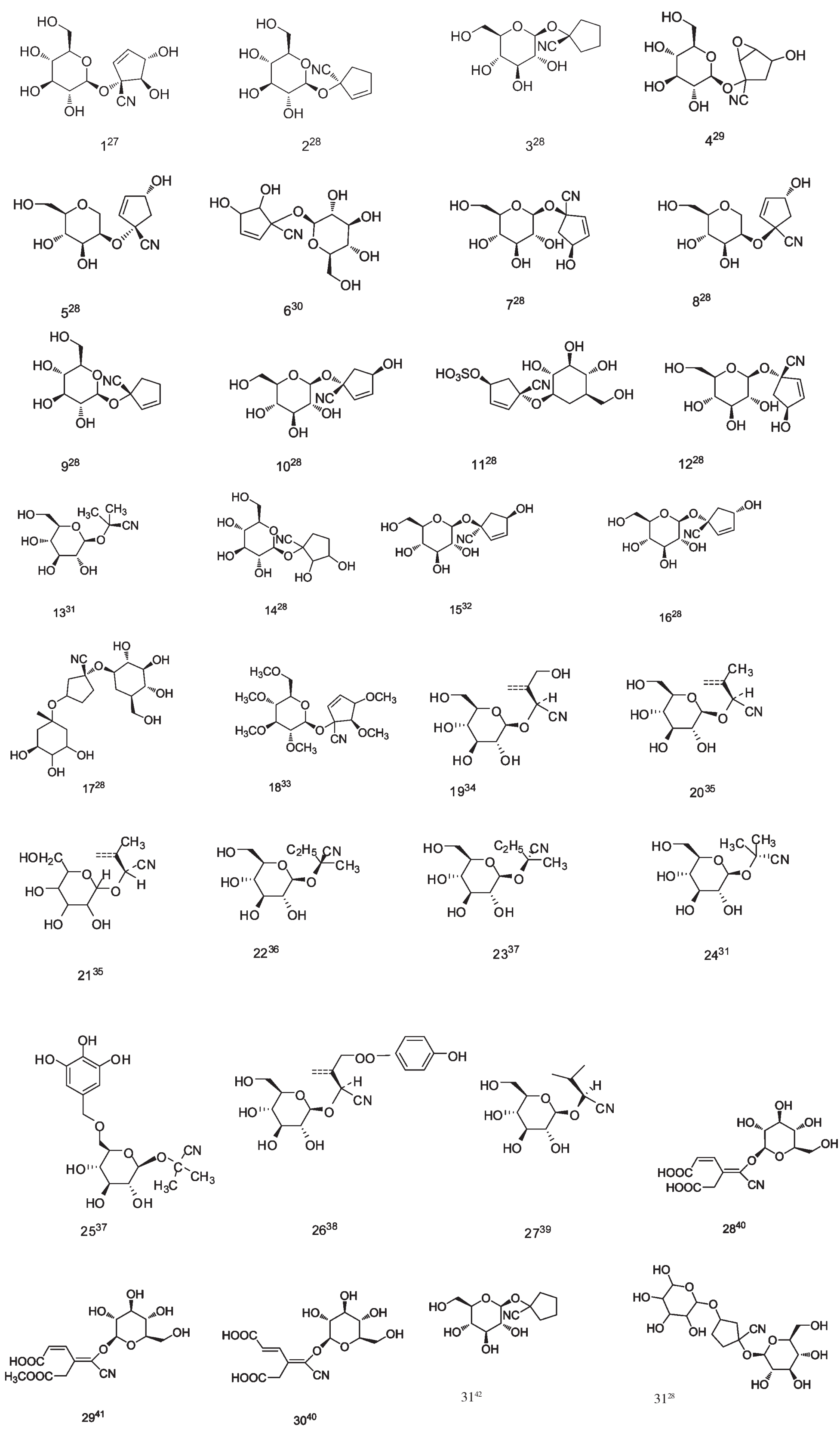

图 3　脂肪族生氰糖苷的结构式

Fig. 3　Chemical structures of aliphatic cyanogenic glycoside

一类以还原态与 CO 结合后在波长 450 nm 处有吸收峰的含血红素的单链蛋白质[43](图 4)。不同植物中合成生氰糖苷的部位有所差异,例如高粱 CYP79A1 主要表达于幼苗;日本百脉根 CYP79D3 主要表达在叶子,而 CYP79D4 在根组织上表达相对低,表明生氰糖苷的积累发生在顶端组织;在木薯中,生氰糖苷先在地上部分合成,随后运送到根部贮存,第一片展开的叶子和叶柄具有最高的生氰苷生物合成活性。高粱、利马豆、葡萄、苦杏仁、亚麻籽中的生氰苷类物质研究较多。在生氰苷中作用的第一个酶是细胞色素 P450,其生物合成途径是 α-氨基酸

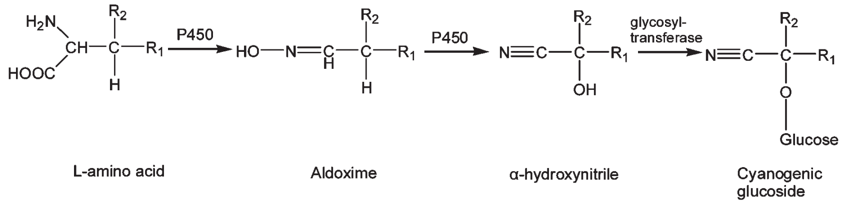

图 4　生氰糖苷生物合成途径

Fig. 4　Biosynthetic pathway of cyanogenic glycoside

羟基化形成 N-羟基氨基酸,然后形成醛肟,进一步形成腈。生氰糖苷生物合成的最后一步是由糖基转移酶催化的半氰醇的糖基化反应。

3　生氰糖苷的降解

生氰糖苷本身不呈现毒性,在正常植物体内生氰糖苷和(-葡萄糖苷酶并不会相遇,当草食动物或病原体损伤生氰植物组织时,组织内的 β-葡萄糖苷酶(β-Glucosidase)与生氰糖苷相遇,对其进行降解,随后 α-羟腈酶(α-Hydroxynitrile lyase)降解细胞内的生氰类化合物,生成并释放出有毒的氰化氢以及葡萄糖和醛或酮,即产生化学防御反应(图 5)。正常情况下,植物体内产生的极少量 HCN 可通过体内不同的途径进行脱毒反应,转化为无毒化合物(图6)。

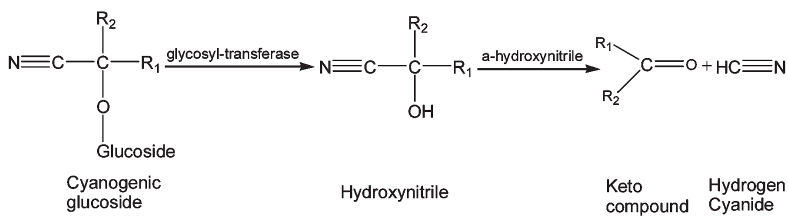

图 5　生氰苷降解途径

Fig. 5　degradation pathway of cyanogenic glycoside

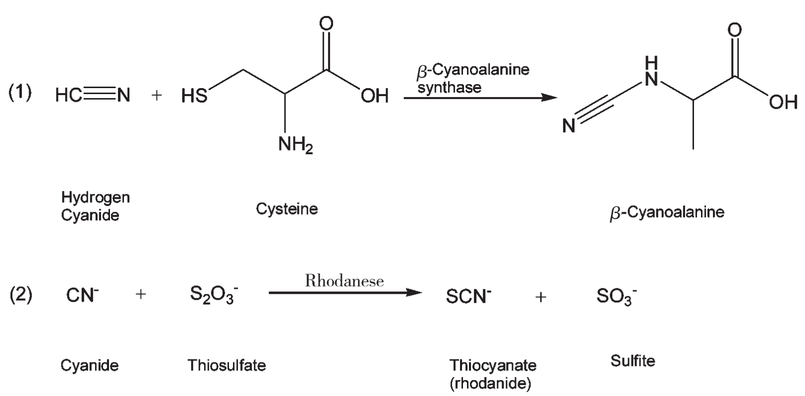

图 6　HCN 在体内不同的脱毒反应途径

Fig. 6　Detoxification pathway of HCN *in vivo*

4 结语

目前已发现2000多种植物,多种细菌、真菌以及鳞翅目昆虫体内含有生氰糖苷类物质,这类物质的结构类型变化较少,主要是脂肪族、芳香族取代的单糖或二糖类的生氰糖苷。迄今为止,国内外对生氰糖苷类物质的研究,多限于该类物质的分离和鉴定方面,对生氰糖苷的代谢途径的研究仅限于木薯、高粱、百脉根等少数植物。因此,对含氰植物体内生氰糖苷的生物合成途径以及抗虫抗病机理的深入研究,将为其作为基因资源增强农作物抗病虫害能力具有重要意义,同时有助于人为地调控生成途径中的基因,从而干扰其毒性物质的产生,对提高含氰植物的食用安全性,同样具有重要意义。

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