植物单宁对微生物的抑制作用及其机制

阮志平[1,2]，向　平[1]

(1. 厦门大学 生命科学学院，福建 厦门　361002；2. 厦门市园林植物园，福建 厦门　361003)

摘要：通过植物单宁对植物病原和非病原物的作用机制的综述，单宁对微生物的抑制作用主要是因为单宁能与主要蛋白质如酶等形成氢键作用；其中单宁聚合体的分子大小是决定单宁对微生物毒性的重要因子，因为低聚体的体积足够以蛋白质形成氢键，又能够插入微生物的敏感部位，所以，低聚体对微生物有最强的抑制作用，而在实践中单宁的毒性是动态过程，单体的聚合作用也可以产生毒性，而低聚体的聚合使得单宁的毒性反而降低。

关键词：植物单宁；微生物；单体；低聚体；毒性

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Antimicrobial Activity of Tannic Compounds

RUAN Zhi-ping[1,2]，XIANG Ping[1]

(1. Life Science College of Xiamen Vniversity，Xiamen　361002，China；
2. Xiamen Botanical Garden，Xiamen　361003，China)

Abstract：The view that tannic compounds have the main function against the microbes including plant pathogenic microbes and non pathogenic microbes，The important factors that influence that ability of tannic compounds to microorganisms is the tannin polymer size. In practice，the toxicity of tannins is always dynamic. The tannin monomers polymerization can improve the toxification，while the tannin oligomers polymerization can lead to the detoxification.

Key words：Tannic；Microbes；Monomers；Oligomers；Toxicity

植物单宁以苯酚为最基本的骨架，以苯环的多烃基取代为特征，从低分子量的简单酚类到分子量为数千的鞣质类，包括苯酪类、酚酸类、烃基苯丙烯酸类、香豆素类、黄酮类和木脂素类等。植物多酚具有在植物界中分布的广泛性、分子结构和生物活性的多样性以及来源的丰富三大特点，多年来，人们通过它们在生理、生态和演变中所起作用的研究表明，植物产生的单宁能够储藏超值的代谢、调节植物光合作用和植物生长，辨认共生菌调整基因功能，优化条件提高土壤质量和营养的功能，防止水分蒸发和防御植物病原物及植物害虫的功能[1~9]；研究还表明植物单宁具有保护植物免受各种病原物侵染和昆虫危害的作用[2,5]，Zucker基于假设性的结构和功能的关系把单宁划分成抗病原单宁和抗虫单宁[9]，其中抗病单宁主要表现在它具有抑制细菌、真菌、病毒和酶的作用。

1　单宁对病原物的作用

1.1　单宁对细菌的抑制作用

单宁对不同类型的细菌表现出不同的作用趋势，通过同种单宁对多种细菌 *Nitrifying bacteria*，*Azotobacter vinelandii*，*Escherichia coli*，*Bacillus subtilis*，*Methanogenic bacteria* 等抑制作用的试验表明，革蓝氏阳性细菌比革蓝氏阴性细菌对单宁更敏感[10]，说明革蓝氏阴性细菌的胞外膜能够抵抗单宁的抑制作用。不同种类的单宁对细菌的作用效果也不一样，没子酸鞣质对产烷细菌的活性比对五倍子酸更大[11,12]，又如五倍子酸对各种革蓝氏阳性细菌的抑制的最低浓度大约是单宁酸的20倍[10]，通过不同的单宁分子类型的研究，要使单宁具有抑制细菌的

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作者简介：阮志平(1969－)，男，福建莆田人，农艺师，农学硕士，主要从事植物学和植物病理学研究工作。

特性，至少要使用分子量为 500 Da 以上的单宁，因为其分子量的大小刚好和二聚体大小一致，它代表交联效应的最小聚合度。

1.2 单宁对真菌的抑制作用

很多研究表明，单宁对真菌的孢子萌发和菌丝的生长均有抑制作用，但单宁对真菌的孢子萌发的抑制作用比对菌丝的生长抑制作用更大[13]。

1.3 单宁对病毒的抑制作用

多酚对植物病毒也有很好的抑制作用，植物组织中的多酚对植物病毒的特性有长期的阻隔作用[14]。水解单宁和缩合单宁都能抑制很多病毒的侵染[15,16]，例如没子酸和鞣花酸鞣质能够对疱疹、恐犬病、天花等侵染人体的病毒和其他病毒起抑制作用[16,17]，3-Methoxyflavone 对小核糖核酸病毒也有很大的活性[18]，氧化聚合的咖啡酸衍生物对 Herpes 具有活性作用[19]，没子酸鞣质能抑制疱疹、HIV 的感染，各种天然和合成的多酚 Chalcone 衍生物对鼻病毒具有抑制作用[20]，越来越多的事实证明，简单的多酚对防止昆虫的病原病毒侵染起重要作用。

2 单宁和病原物的作用机制

2.1 单宁对多种酶有抑制作用

单宁对代谢酶的抑制作用已有深入的研究，单宁对酶的作用随着酶的种类、浓度的不同而有变化，其抑制作用主要是当有很多的烃基从分子中延伸出来和蛋白质形成交联，单宁的苯环和蛋白质多肽碳酰基之间便形成氢键，因此，单个单体苯环与蛋白质和聚酰胺之间形成的亲和力比较低，但是，单宁通常是寡聚体，所以，能最大限度地形成交联效应[21,22]。随着分子量从二聚体到寡聚体的增加，单宁与蛋白质的反应不断增加，所以，在通常情况下单宁对酶的抑制作用比单体有效得多，这已通过聚合单宁和水解单宁与代谢酶[23]和胞外酶[21,24~26]的作用来论证。

2.2 单宁的自氧化和聚合作用

植物抗病的一个重要机制是当细胞受到损害时，能够在植物多酚氧化物的作用下，快速从简单的单体酚类化合物氧化成具有毒性单宁[24,26,28,29]，植物病原真菌主要是通过单宁的氧化作用来抑制孢子的生长和(或)萌发[2,28]。一些多酚通过多酚氧化酶对植物病毒产生有效作用，单体多酚的氧化作用能够对病毒和其他病原产生的杀害作用，很可能是通常的诱导作用来实现的。没有毒性的单宁单体在多酚氧化酶或自氧化的作用下，能够提高其对酶[24,26,28]、真菌[28,29]、病毒[30]和产烷微生物细菌[31~33]的抑制活性。在微酸性或中性条件下，单宁和植物病原物之间可通过亲水键和疏水键的活性来相互作用[34]，当 pH< 5 时植物病原真菌的孢子萌发就会受到抑制，但在 pH> 8 时，单宁的毒力就会丧失[13]。

2.3 单宁能结合细菌的酶和毒性蛋白

单宁通过结合细菌的酶和毒性蛋白而使酶和蛋白质失去活性[35~37]。当植物受到侵染时，能够在木质部产生阻止真菌和细菌等植物病原传输的单宁物质[38]。

2.4 单宁的甲基化作用

通常，单宁甲基化后才具有毒性，在病菌和多酚相互作用中，完整的、无甲基化的多酚多聚体很难侵入细胞膜，这可能是因为甲基化后，有更多的亲脂性分子进入和跨过细胞膜，从而进入病原物的细胞内[39]，所以，水解单宁比多聚水解单宁或缩合单宁或没有甲基化的单宁单体更容易进入细胞膜。

2.5 聚合作用对单宁毒性的影响

具有高度苯环烃基的物质很容易被氧化聚合成分子量大的化合物[40~43]，单宁及其相关化合物发生聚合反应，单宁的聚合作用对单宁的毒性具有许多实际意义，在单宁的毒性中，聚合程度起到很重要的作用[31,44]。当单宁单聚体聚合成寡聚体时，它们和蛋白质之间的交联能力提高，也就是说这些单宁化合物的毒性提高。另一方面，如果寡聚化合物又聚合成高分子量的腐殖质化合物，那么就会降低抑制作用的活性，如单宁的聚合作用对酶[24,45]、对真菌的降解[46]、真菌的生长[47]和产烷微生物细菌的活性。由于代谢酶和其它功能性蛋白质位于细胞内或与细胞膜紧密相连，所以单宁的毒性受到其穿透能力的限制[31,43,48,49]，以革蓝氏阴性细菌细胞外膜为例，分子量为 600~9 000 Da 的都可以主动渗透进入[50~52]，能够进入产烷细菌细胞膜内的单宁的最大分子量大约为 3 000 Da[43,49]，当单宁聚合成高分子量时，它们对细胞没有毒性，但是仍然能对胞外酶起反应。根据 Jones 等单宁对蛋白质的反应数据可以看出，当单宁的分子量超过 20 000 Da 时，单宁对可溶性蛋白质的反应能力降低[53]。如果单宁的分子量太大，那么蛋白质的反应形成氢键过程中，烃基在聚合体中埋的太深，因此，单宁对胞外酶就失去毒性。当聚合到一定程度时就形成腐质沉淀化合物，

在这种情况下解毒是由于单宁从溶液中移走[54]。寡聚单宁对微生物的作用效果最好,因为它们足够大与蛋白质形成交联的氢键,同时也足够小使得能够穿过细胞膜到达微生物的蛋白质。

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