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拟除虫菊酯类农药的微生物降解及其机制研究进展

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摘要:拟除虫菊酯被认为是有机磷农药的安全替代品,因此当有机磷农药被禁限使用时,其应用显著增加。目前,拟除虫菊酯销量约占世界杀虫剂总额的 20%。这类农药的长期、广泛使用既带来了经济效益,也造成了环境污染,危害人类及其他非靶标生物。针对这一问题,已开发出多项修复技术,其中微生物法高效环保、成本低廉,已成为修复拟除虫菊酯污染的最优方法。笔者综述了最新分离的拟除虫菊酯降解菌株及其特性;拟除虫菊酯降解酶及其基因;拟除虫菊酯及其代谢产物(间苯氧基苯甲酸等)的降解途径。此外,还提出了拟除虫菊酯类农药微生物降解研究的发展趋势和需要进一步解决的问题。

关键词:拟除虫菊酯;微生物降解;降解酶;降解途径;间苯氧基苯甲酸
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拟除虫菊酯类农药是人工合成的天然除虫菊酯的类似物[1],根据拟除虫菊酯分子中是否含有氰基,将其分为Ⅰ型和Ⅱ型,Ⅱ型具有氰基及更强的毒性[2,3]。

拟除虫菊酯通过开放钠离子通道,实现杀虫目的[4]。因其高效的杀虫能力,使其在农林业生产中发挥重要作用[5]。随着该类农药的大范围大量使用,其负面影响被不断报道。拟除虫菊酯及其代谢产物在环境及人体尿液、母乳中普遍检出,其对人体神经系统、生殖系统造成干扰,可能引起血液癌症、氧化应激及 DNA 损伤等危害已被证实[6 – 11]。因此,世界各国都制定了农产品中拟除虫菊酯类农药残留的限定标准[12 – 13]。

针对此环境问题,微生物降解是一种环境及经济友好的修复技术,目前研究者已在实验室获得大量研究成果,对这些研究成果的梳理,将有助于农药微生物降解技术的进一步发展和应用。

本文综述了已分离的拟除虫菊酯降解菌株,及其生理生化特性、关键功能基因和酶、拟除虫菊酯降解途径,并重点关注了其代谢产物间苯氧基苯甲酸(3 – phenoxybenzoic acid,简称 PBA)等的降解,以期为拟除虫菊酯的安全利用与污染修复提供参考。

1　降解菌株及其生理生化、降解特性

微生物可将有机污染物降解成更具安全性的产物,甚至完全矿化,广泛应用于环境污染物的降解中[10,14]。Kaufman 等最初描述了苄氯菊酯在土壤中的降解[15]。1988 年 Maloney 等从来自污水处理厂的样品中首次得到了能够有效降解拟除虫菊酯的菌株,共得到 3 个菌株,分别为荧光假单胞菌(*Pseudomonas fluorescens*) SM – 1、无色杆菌属(*Achromobacter* sp.) SM – 2、蜡样芽孢杆菌(*Bacillus cereus*) SM – 3[16]。自此,大量可以有效降解拟除虫菊酯的菌种被筛选鉴定。这些菌种大都能以某种拟除虫菊酯作为唯一碳源,进行生长代谢。笔者共整理了来自 45 个不同菌属的拟除虫菊酯降解菌,包括细菌 26 个菌属、真菌 14 个菌属、放线菌 5 个菌属,其生理生化、降解特性等详细信息见表 1。所有菌属中,芽孢杆菌属(*Bacillus*)、苍白杆菌属(*Ochrobactrum*)、假单胞菌属(*Pseudomonas*)、沙雷氏菌属(*Serratia*)及链霉菌属(*Streptomyces*)包含了较多菌株。大部分功能菌分离自污染环境,如污染土壤、污水、活性污泥等,亦有以茶叶、酒曲、动植物体,甚至来自大西洋的海绵等作为分离源的报道[17 – 22]。绝大多数菌株在温和环境(pH 值 = 7,30 ℃ 左右)中有较高活性。受益于拟除虫菊酯结

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构的相似性,筛选所得的菌株,往往具有对拟除虫菊酯类农药降解的广谱性,如乙酸钙不动杆菌(*Acinetobacter calcoaceticus*) MCm5[23]、类短短芽孢杆菌(*Brevibacillus parabrevis*) FCm9[23]、小链小杆菌属(*Catellibacterium* sp.) CC-5[24]等。

具有广谱、高效、高耐受性、降解彻底特性的菌株是研究者期待获得的菌株。虞云龙等分离得到具有农药降解广谱性的菌株产碱菌属(*Alcaligenes*) sp. YF11,能够同时降解部分拟除虫菊酯和一硫代磷酸酯[25]。陈锐等筛选出的草酸青霉(*Penicillium oxalicum*) SSCL-5,可在 24 h 内降解 97% 的氯氰菊酯(初始浓度 400 mg/L),具有较为突出的降解速率[26]。Chen 等从土壤中分离出的 *Bacillus* sp. DG-02,可耐受浓度高达 1 200 mg/L 的甲氰菊酯,能有效降解 7 种拟除虫菊酯,并在土壤修复中取得较好的效果,证明了其实际应用潜力[27],该研究组之后分离得到的菌株苏云金芽孢杆菌(*Bacillus thuringiensis*) ZS-19[28]、黄褐假单胞菌(*Pseudomonas fulva*) P31[14],亦有广谱、耐受性强及降解效果好的特点,其中 *Bacillus thuringiensis* ZS-19 对于 PBA 具有很好的降解效果[28]。研究者通过构建复合菌系协同降解的方式使矿化更为彻底,Zhao 等将地衣芽孢杆菌(*Bacillus licheniformis*) B-1 和米曲霉(*Aspergillus oryzae*) M-4 共同培养用于氯氰菊酯的降解[19],相较单一菌种的降解,提高了矿化程度。

拟除虫菊酯具有 1~3 个手型中心,2~8 个立体异构体[2-3],因此,菌株对于拟除虫菊酯的降解显示出结构选择性[29-30],Lee 等发现菌株弗氏耶尔森菌(*Yersinia frederiksenii*)、温和气单胞菌(*Aeromonas sobria*)、*Erwinia carotovora* 在降解苄氯菊酯过程中,反式异构体相对顺式异构体更易被降解[31]。

除去传统的富集培养筛选法,研究者也通过构建基因工程菌的方式获取菌株。Lan 等设计载体 pETDuet,用于同时表达 2 个目的基因。在共表达载体上克隆了黄杆菌属(*Flavobacterium* sp.)中的有机磷水解酶基因 *opd* 和来自尖音库蚊(*Culex pipiens*)的酯酶基因 *B1*,实现了单一微生物同时降解有机磷、氨基甲酸酯和拟除虫菊酯杀虫剂的目的[32],为复配农药的同时降解提供了新思路。

目前,所取得的成果多局限于实验室,在实际应用方面还缺少报道。构建具有优越特性的基因工程菌是值得探索的研究方向。

表 1　降解拟除虫菊酯的菌株基本信息

细菌属	微生物	来源	降解环境					降解率(%)	参考文献
			pH 值	温度(℃)	可降解拟除虫菊酯种类	降解时间(d)	初始浓度(mg/L)		
无色杆菌属	*A.* sp. SM-2	土壤和污泥	7.0	30	A	28	20	70.0~90.0	[16]
(*Achromobacter*)	*A.* sp. A-24	牛筋草	7.0	30	B	3	20	91.8	[18]
酸单胞菌属(*Acidomonas*)	*A.* sp.	土壤	7.0	37	C	7	5000	70.0	[33]
不动杆菌属(*Acinetobacter*)	*A. calcoaceticus* MCm5	污染土壤	7.0	30	B,D,E,F	B:10;D,E,F:7	100	B:84.7,D:78,E:61.5,F:72.7	[23]
	A. baumannii ZH-14	污泥	7.0	30	A	3	50	100	[34]
	A. junii LH-1-1	土壤	7.0	30	F	与肺炎克雷伯氏菌(*Klebsiella pneumoniae*) BPBA052 共培养 3 d 降解 94.25%(75 mg/L)			[35]
气单胞菌属(*Aeromonas*)	*A. sobria*	污染物	—	—	A	顺式异构体(20%),反式异构体(78%)半衰期分别为 56、45 h(200 mg/L)			[31]
产碱菌属(*Alcaligenes*)	*A.* sp. YF11	污泥	7.2	30	G,F,E,H,B,A	1 h	50.0	G:5.06,F:8.01,E:3.04,H:9.24,B:2,A:3.84(μmol/L)	[25]
固氮弧菌属(*Azoarcus*)	*A. indigens.* HZ5	污泥	7.0	30	B	3	50	70.0	[36]
芽孢杆菌属	*B. cereus* SM-3	土壤和污泥	7.0	30	A	28	20	50.0~90.0	[16]
(*Bacillus*)	*B.* sp. DG-02	污染环境	7.5	30	H,B,I,E,F,D,A	3	100	H:93.3,B:89.2,I:86,E:82.7,F:94.1,D:65.1,A:63.6	[27]

表 1(续)

细菌属	微生物	来源	降解环境					降解率(%)	参考文献
			pH 值	温度(℃)	可降解拟除虫菊酯种类	降解时间(d)	初始浓度(mg/L)		
	B. cereus ZH-3	污泥	7.5	28	B	3	50	78.4	[37]
	B. sp. ISTDS2	污水和污泥	7.0	30	G	180 h	50	100.0	[38]
	B. licheniformis B-1	土壤	7.0~7.5	30	B	3	100	50.0	[39]
	B. megaterium JCM2	污染土壤	7.0	30	B,D,E,F	B:10,D,E,F:7	100.0	B:86.6,E:75,E:10,F:83	[40]
	B. thuringiensis ZS-19	污泥	7.5	30	E,H,F,B,I,D	3	100.0	E:100,H:98,F:92.4,B:81,I:86,D:50.9	[28]
	B. sp. AKD1	污泥	8.0	37	B	7	100.0	86.0	[41]
	B. sp. SG2	污染土壤	7.0	32	B	15	50.0	82.0	[42]
	B. amyloliquefaciens AP01	污染土壤	7.0	30	B	5	50.0	45.0	[43]
	B. licheniformis B-1	土壤和酱油曲	—	30	B	与 *Aspergillus oryzae* M-4 共培养 3 d 降解 78.85%(100 mg/L)			[19]
	B. licheniformis B-1	土壤	—	35	B	与 *Streptomyces* sp. K-1 共培养 5 d 降解 85.7%(100 mg/L)			[44]
	B. subtilis 1D	污染土壤	7.0	32	B	15	20.0	81.6	[45]
	B. cereus BCC01	污水处理池	8.0	30	B	5	100.0	99.6	[46]
短芽孢杆菌属(*Brevibacillus*)	*B. parabrevis* FCm9	污染土壤	7.0	30	B,D,E,F	B:10,D,E,F:7	100.0	B:100,D:89,E:60.23,F:81.6	[23]
	B. parabrevis BCP-09	污泥	7.4	38.9	B	3	30.9	75.8	[47]
短杆菌属(*Brevibacterium*)	*B. aureum* DG-12	污泥	7.0	27	I,E,H,F,D,B	5	50.0	I:87.4,E:89.1,H:82.6,F:80.9,D:80.1,B:78.3	[48]
小链小杆菌属(*Catellibacterium*)	*C.* sp. CC-5	污染土壤	7.0	30	B,G,H,F,A,E	7	100.0	B:90,G:83,H:83,F:90,A:73,E:56	[24]
梭菌属(*Clostridium*)	*C.* sp. ZP3	污泥	7.5	35	H	12	100.0	12.6	[49]
产杆菌属(*Enterobacter*)	*E. aerogenes*	污泥	7.0	25~30	D,H,B	3	100.0	D:55.74,H:55.11,B:56.96	[50]
欧文氏菌属(*Erwinia*)	*E. carotovora*	污染物	—	—	A	顺式异构体(20%),反式异构体(78%)半衰期分别为 61,46 h(200 mg/L)			[31]
克雷伯菌属(*Klebsiella*)	*K. pneumoniae* BPBA052	土壤	7.0	30	F	与 *Acinetobacter junii* LH-1-1 共培养 3 d 降解 94.25%(75 mg/L)			[35]
库特氏菌属(*Kurthia*)	*K.* sp. LF-1	污染土壤	7.0	35	B	8	100.0	80.2	[51]
赖氨酸芽孢杆菌属(*Lysinibacillus*)	*L. sphaericus* FLQ-11-1	污泥	7.0	35	I	5	100.0	80.0	[52]
微球菌属(*Micrococcus*)	*M.* sp. CPN1	污染土壤	7.0	30	B	8	1 000.0	90.0	[53]
苍白杆菌属(*Ochrobactrum*)	*O. tritici* pyd-1	污染土壤	7.0	30	H,A,B,G,E,F,D	H:3,A,B,G,E,F,D:6	100.0	H:100,A:100,B:100,G:100,E:85,F:70,D:50	[54]
	O. lupini DG-S-01	污泥	7.0	30	B,I,H,E,F	5	50.0	B:90,I:80.8,H:74.4,E:56.2,F:43	[55]
	O. anthropi JCm1	污染土壤	7.0	30	B,D,E,F	B:10,D,E,F:7	100.0	B:90.5,D:70,E:39,F:65	[40]

表 1(续)

细菌属	微生物	来源	降解环境					降解率(%)	参考文献
			pH 值	温度(℃)	可降解拟除虫菊酯种类	降解时间(d)	初始浓度(mg/L)		
	O. haematophilum JCm7	污染土壤	7.0	30	B	10	100.0	78.0	[40]
假单胞菌属	*P. fluorescens* SM-1	土壤和污泥	7.0	30	A	28	20.0	20.0~55.0	[16]
(*Pseudomonas*)	*P. stutzeri* S1	污染土壤	7.0	28	I	8	50.0	94.0	[56]
	P. aeruginosa CH7	污泥	7.0	29.4	B	12	100.0	90.0	[57]
	P. viridoflava	污染土壤	6.2~7.0	—	G	8	500.0	52.2	[58]
	P. aeruginosa JCm8	污染土壤	7.0	30	B	10	100.0	46.0	[40]
	P. aeruginosa JQ-41	污染土壤	7.0	30	H,B,F,D,E	7	50.0	H:91.7,B:87.2,F:90.4,D:70.1,E:74.8	[59]
	P. fulva P31	污泥	7.3	29.5	J	3	50	100.0	[14]
拉乌尔菌属(*Raoultella*)	*R. ornithinolytica*-ZK4	污染土壤	6.3	37	I,F	—	-	-	[60]
沙雷氏菌属	*S.* spp. JC1	污泥	7.6	31	B	10	100.0	92.0	[61]
(*Serratia*)	*S.* spp. JCN13	污泥	8.0	34	B	8	100.0	100.0	[61]
	S. marcescens DeI-1	污染土壤	7.2	30	F	10	50.0	88.3	[62]
	S. marcescens DeI-2	污染土壤	7.2	30	F	10	50.0	82.8	[62]
	S. nematodiphila CB2	污染土壤	7.0	30	B	7	100.0	98.0	[63]
鞘脂菌属(*Sphingobium*)	*S.* sp. JZ-2	污泥	7.0	30	H,B,A,G,F,E	5	50.0	H:100,B:90,A:90,G:90,F:90,E:70	[64]
鞘氨醇单胞菌属(*Sphingomonas*)	*S.* sp. RCm6	污染土壤	7.0	30	B,D,E,F	B:10,D,E,F:7	100.0	B:91.8,D:82.5,E:58.26,F:70.2	[23]
	S. sp. JCm3	污染土壤	7.0	30	B	10	100.0	34.2	[40]
中华根瘤菌属(*Sinorhizobium*)	*S.* sp. CY 22-7	污染土壤	—	30	B	6	100.0	60.0	[65]
寡养单胞菌属(*Stenotrophomonas*)	*S.* sp. ZS-S-01	污泥	7.0	30	G,F,B,I,E	G:6,F,B,I,E:5	50.0	G:100,F:100,B:86.7,I:85,E:60.3	[66]
	S. acidaminiphila	污染物	—	—	D	100h	100.0	80.0	[31]
耶尔森氏菌属(*Yersinia*)	*Y. frederiksenii*	污染物	—	—	A	顺式异构体(20%),反式异构体(78%)半衰期分别为 80,37 h (200 mg/L)			[31]
					真菌				
枝顶孢属(*Acremonium*)	*A.* sp. CBMAI 1676	海绵	—	30	K	14	100.0	35.2	[22]
曲霉属	*A. niger*	—	6.5	28	I	30	5.0	20.0	[67]
(*Aspergillus*)	*A. terricola*	—	6.5	28	I	30	5.0	25.0	[67]
	A. terreus	污泥	7.0	30	B	5	100.0	84.5	[68]
	A. oryzae M-4	土壤和酱油曲	—	30	B	与 *Bacillus licheniformis* B-1 共培养 3 d 降解 78.85% (100 mg/L)			[19]
假丝酵母属(*Candida*)	*C. pelliculosa* ZS-02	污泥	7.5	32	D,I,F,G,B,H	5	D:100,I,F,G,B,H:50	D:100,I:94.8,F:93.4,G:93,B:87.7,H:51	[69]
枝孢属(*Cladosporium*)	*C.* sp. HU	污泥	7.2	26	G,H,B,F,D,A	5	G:400,H,B,F,D,A:100	G:100,H:100,B:100,F:94.6,D:92.1,A:91.6	[70]
小克银汉霉属(*Cunninghamella*)	*C.* elegans DSM1908	—	—	28	E	—	—	—	[71]

表 1(续)

细菌属	微生物	来源	降解环境					降解率(%)	参考文献
			pH 值	温度(℃)	可降解拟除虫菊酯种类	降解时间(d)	初始浓度(mg/L)		
散囊菌属(*Eurotium*)	*E. cristatum* ET1	茯砖茶	—	30	B	8	50.0	57.9	[17]
镰孢菌属(*Fusarmm*)	*F.* sp. TS-203	污泥	7.0	30	B	5	100.0	94.5	[68]
Microsphaeropsis	*M.* sp. CBMAI1675	海绵	—	30	K	14	100.0	22.1	[22]
Monilochaetes	*M.* sp. TS-205	污泥	7.0	30	B	5	100.0	91.4	[68]
Paracoccus	*P.* acridae SCU-M53	植物	—	28	E	2	75.0	79.8	[20]
青霉素(*Penicillium*)	*P.* oxalicum SSCL-5	土壤	—	28	B	1	400.0	97.0	[26]
平革菌属(*Phanerocaete*)	*P.* chrysosporium	—	6.5	28	I	30	5.0	60.0	[67]
木霉属	T. viridae 5-2	—	6.5	28	*I*	10	5.0	80.0~83.0	[67]
(Trichoderma)	*T. viridae* 2211	—	6.5	28	I	30	5.0	60.0	[67]
Westerdykella	*W.* sp. CBNAI 1679	海绵	—	30	K	14	100.0	30.5	[22]
			放线菌						
戈登氏菌属(*Gordonia*)	*G.* sp.	污水处理池	7.0	30	B	7.5	100.0	52.3	[72]
诺卡氏菌属	*N.* sp. F20	污染土壤	—	28	B	—	—	—	[73]
(*Nocardia*)	*N.* sp. F21	污染土壤	—	28	B	—	—	—	[73]
红球菌属	*R.* sp. JCm5	污染土壤	7.0	30	B,D,E,F	B:10,D,E,F:7	100.0	B:100,D:93,E:65,F:85	[40]
(*Rhodococcus*)	*R. rhodochrous* L5	大曲	—	30	E	7	5.0	71.4	[21]
Streptomyces	*S.* sp. HU-S-01	污泥	7.5	30	B	24h	50.0	90.0	[74]
	S. sp. F9	污染土壤	—	28	B	—	—	—	[73]
	S. aureus HP-S-01	污泥	7.8	27	F,I,D,G,H,A	F:4,I,D,G,H,A:5	50.0	F:99%,I:100,D:100,G:100,H:95,A:87.4	[75]
			7.5	28	B	3	50.0	69.3	[76]
	S. sp. K-1	土壤	—	35	B	与 *Bacillus licheniformis* B-1 共培养 5 d 降解 94%(50 mg/L)			[44]
链轮丝菌属	*S.* sp. F1	污染土壤	—	28	B	—			[73]
(*Streptoverticillum*)	*S.* sp. F4	污染土壤	—	28	B	—			[73]
	S. sp. F13	污染土壤	—	28	B	—			[73]

注:A:苄氯菊酯;B:氯氰菊酯;C:丙烯菊酯;D:联苯菊酯;E:三氟氯氰菊酯;F:溴氰菊酯;G:氰戊菊酯;H:甲氰菊酯;I:氟氯氰菊酯;J:苯醚菊酯;K:高氰戊菊酯。表 2 同。

2　降解拟除虫菊酯的酶及基因

2.1　降解酶

在微生物降解有机污染物过程中,实际起作用的是微生物体内的各种酶。降解酶往往比产生这种酶的微生物细胞具有更强的抗逆性及降解效率,特别是在低农药浓度条件下[77]。早在 1993 年,Maloney 等通过层析技术从 *Bcillus cereus* SM3 中分离获得 1 种羧酸酯酶,命名为氯菊酯酶(permethrinase),并采用离子交换色谱法和凝胶过滤色谱法进行纯化,首次实现了通过无细胞的酶系统降解拟除虫菊酯[78]。类似的,从黑曲霉(*Aspergillus niger*) ZD11 细胞提取物中提取纯化的新型拟除虫菊酯水解酶,分子量为 56 ku、pI 值(等电点)为 5.4,当温度为 45 ℃、pH 值为 6.5 时酶活性最佳,该酶优先降解对于哺乳动物更具毒害作用的反式异构体拟除虫菊酯,人肝脏羧酸酯酶也存在这一特性[79-80]。1993 年至今,陆续有研究者对拟除虫菊酯降解酶进行纯化(部分酶信息见表 2),多为酯酶。其中大多数酶为胞内酶,而铜绿假单胞菌(*Pseudomonas aeruginosa*) GF31 降解氯氰菊酯过程中起催化作用的氨肽酶是一种胞外酶[81]。图 1 描

述了表 2 所列部分酶之间的进化关系(作图软件为 MEGA X 64 – bit,蛋白质序列来自:https://www.ncbi.nlm.nih.gov/protein)。2018 年,Gangola 等发现漆酶参与了氯氰菊酯降解过程,这是首次发现漆酶作用于拟除虫菊酯降解[45]。漆酶已被发现可用于多种有机污染的环境修复,白腐菌是常见的漆酶生产源,其在食用菌菌渣中也大量存在[82]。这无疑为菌渣的利用提供了新途径。

表 2　拟除虫菊酯降解酶基本信息

酶	酶类型	来源	可降解拟除虫菊酯种类	降解环境		参考文献
				pH 值	温度(℃)	
氯菊酯酶	酯酶	*Bcillus cereus* SM3	A	7.5	37	[78]
拟除虫菊酯水解酶	—	*Aspergillus niger* ZD11	B,A,G,F	6.5	45	[79]
EstP	酯酶	*Klebsiella* sp. ZD112	A,B,G,F	7.0	40	[80]
B1	酯酶	*Culex pipiens*	F	7.5	30	[32]
Pye3	酯酶	蔬菜土壤宏基因组	B,A,G,F	7.0	40	[83]
PytH	酯酶	鞘脂菌属(*Sphingobium* sp.) JZ – 1	A,H,B,E,G	7.5	50	[84]
PytZ	酯酶	*Ochrobactrum anthropic* YZ – 1	B,E,I,A,F	7.5	35	[85]
Sys410	酯酶	吐鲁番盆地宏基因组	E,B,G,F	6.5	55	[86]
PytY	酯酶	*Ochrobactrum anthropic* YZ – 1	B,E,I,A,F	7.5	35	[87]
CMO	单氧酶	*Streptomyces* sp.	B	7.5	30	[88]
EstSt7	酯酶	*Sulfolobus tokodaii*	H,A,B,E,F,D	9.0	80	[89]
氨肽酶	氨肽酶	*Pseudomonas aeruginosa* GF31	B	7.0	60	[81]
EstPS	酯酶	产黄假单胞菌(*Pseudomonas synxantha*) PS1	B,H,G,D	8.0	60	[90]
Est684	酯酶	毛豆腐宏基因组	E,B,G	7.0	18	[91]
Est3385	酯酶	沼泽红假单胞菌(*Rhodopseudomonas palustris*) PSB – S	H	6.0	35	[92]
EstA	酯酶	*Bacillus cereus* BCC01	B,F,A,G,E	8.0	35	[46]

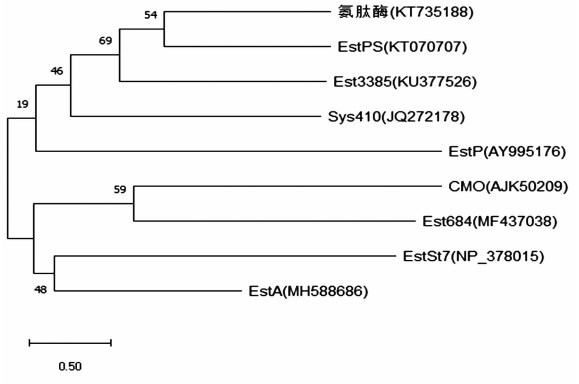

图1　拟除虫菊酯降解酶之间的进化关系

2.2　降解基因

随着基因工程技术的进步,对于拟除虫菊酯降解酶的研究已发展到基因层面。2006 年,Wu 等通过构建基因文库,从 *Klebsiella* sp. ZD112 中得到拟除虫菊酯水解酶基因 *EstP*,基因全长 1 924 bp,编码 637 个氨基酸,该酯酶不但可以降解拟除虫菊酯,还可以催化降解其他底物,如有机磷农药,这是关于拟除虫菊酯降解基因的首次报道[80]。Hu 等从拟除虫菊酯降解菌 *Bacillus cereus* BCC01 的基因组文库中筛选并鉴定了关键的拟除虫菊酯水解酶基因 *EstA*,该酶的 Ser^{94} 位于固定的五肽基序列 Gly – X – Ser – X – Gly 中,形成了一个凹形的活性中心,用于氯氰菊酯的生物降解,这是酯酶的典型特征[46]。丝氨酸在酶的催化位点参与酰化反应具有类似的情况,已在几种拟除虫菊酯水解酶中发现,如 *Sys410*[86]、*PytY*[87]、*Pye3*[83] 和 *Est684*[91]。

随着基因层面研究的深入,宏基因组技术作为一种辅助工具帮助研究者更具方向性地达到科研目的。Hong 等将甲基对硫磷降解基因 *mpd* 引入能够降解甲氰菊酯的菌株 *Sphingobium* sp. JQL4 – 5 的染色体中,成功构建出能够同时降解 2 种污染物的菌株[93]。目前此类研究成果相对有限,是未来期待发展的方向。

3　降解途径

在不同报道中,拟除虫菊酯降解途径有相似性,但在中间过程及产物方面存在差异,这些差异可能是由于微生物的种类、拟除虫菊酯的结构及培养条件差异造成的。

3.1　酯键的断裂

拟除虫菊酯微生物降解机制的核心部分是酯键的断裂,将原农药分解为羧酸和醇[44]。此步骤通常为降解过程的的第 1 步,以 *Ochrobactrum tritici*

pyd－1 降解甲氰菊酯为例，酯键断裂后甲氰菊酯分解为间苯氧基氰基苄醇（3－phenoxybenzyl alcohol，PBAlc）和 2,2,3,3－四甲基环丙烷甲酸（图 2）[54]。类似过程中，多数情况下含环丙烷基团的降解产物为酸，含间苯氧基基团的产物为醇。也存在特殊情况，如在 *Brevibacterium aureum* 降解三氟氯氰菊酯过程中，原农药首先被分解为 2,2,3,3－四甲基环丙烷甲醇和 4－氟代－3－苯氧基苯甲酸（图 3）[48]。

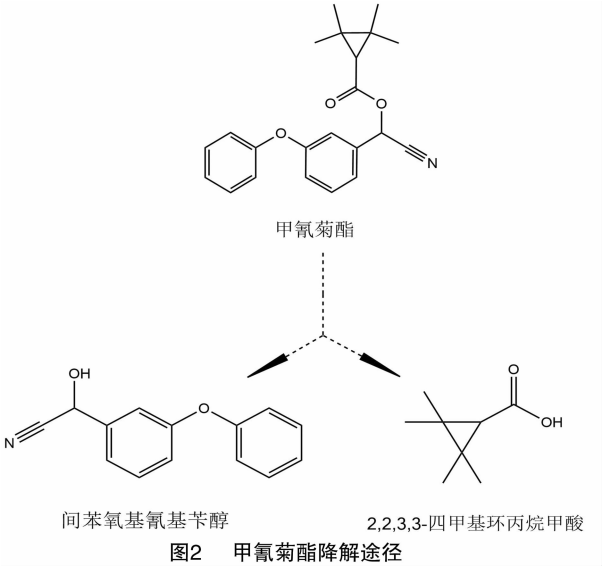

图2　甲氰菊酯降解途径

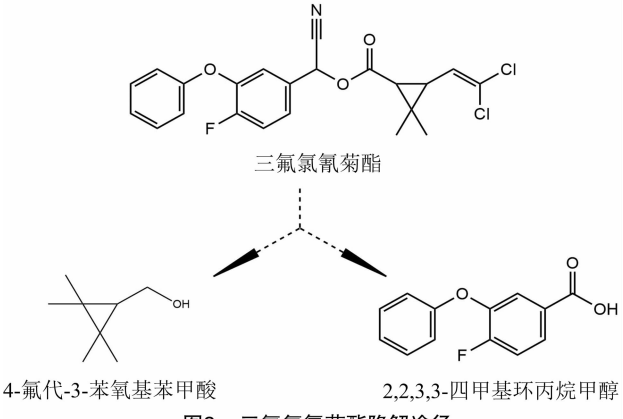

图3　三氟氯氰菊酯降解途径

大多数微生物对拟除虫菊酯的降解遵循上述规律，也存在特例，如 *Lysinibacillus sphaericus* FLQ－11－1 降解氟氯氰菊酯过程中，第 1 步并非打开酯键[52]。

3.2　常见代谢产物及其转化关系

“3.1”节相关降解案例中出现的 PBAlc，以及间苯氧基苄醛（3－Phenoxybenzaldehyde，PBAld）和 PBA 是拟除虫菊酯降解过程中最常见的代谢物，相比母体它们具有更强的毒性[94－95]。如 PBA 半衰期长达 180 d[96]，具有雌性激素特性，是一种内分泌米干扰物，对人体具有一定毒性[97－98]。

大多数拟除虫菊酯降解过程中都会出现这些常见的中间产物，特别是结构中包括间苯氧基基团的拟除虫菊酯，而氟氯氰菊酯、联苯菊酯、丙烯菊酯等不包括典型间苯氧基基团的拟除虫菊酯在降解过程中生成其他产物，但依然遵循酯键断裂生成醇和酸的规律。如 *Acidomonas* sp. 降解烯丙菊酯过程中生成一个烯丙酮醇[33]，联苯菊酯的微生物降解过程中，检测到 2－甲基－3－联苯甲醇[69]。

在拟除虫菊酯代谢过程中，PBAlc、PBAld 及 PBA 三者之间常常相互转化，*Bacillus licheniformis* CY－012[99]、*Pseudomonas fluorescens* SM－1[16] 可氧化 PBAlc 为 PBA，*Acinetobacter baumannii* ZH－14[34] 转化 PBAlc 为 PBAld，进一步氧化为 PBA。而 *Microsphaeropsis* sp. CBMAI1675[22] 可将 PBAld 转化为 PBAlc，在 *Aspergillus oryzae* M－4[100] 降解目标物过程中，可观察到 PBAlc 与 PBA 的相互转换。

3.3　常见代谢产物的降解途径

相比拟除虫菊酯本身，针对其代谢产物如何降解的研究较少，但此类研究同样具有重要意义。其中，被讨论较多的代谢产物是 PBA[10]。

早期的相关研究仅限于细菌范畴，特别是 *Pseudomonas* sp. 菌株。1990 年 Engesser 等首次分离得到 1 株不能完全降解 PBA 的菌株类产碱假单胞菌（*Pseudomonas pseudoalcaligenes*）POB310[101]，并在后续研究中构建了基因工程菌 *Pseudomonas* sp. B13－D5 及 *Pseudomonas* sp. B13－ST1，新菌株同时具有降解氯酚的能力[96]。亦有研究者进行了 *Micrococcus* sp.[53]、*Sphingobium* sp.[64,84]、*Bacillus* sp.[27]、*Sphingobium* sp.[39,102] 及 *Stenotrophomonas* sp.[66] 等细菌菌属针对 PBA 降解的研究。

针对 PBA 降解的真菌领域研究起步较晚。首次报道是在 2012 年，袁怀瑜等筛选得到可在 22 h 内完全降解 100 mg/L PBA 的菌株 *Aspergillus niger* YAT1[103－104]。*Eurotium cristatum* ET1 亦为 PBA 的有效降解真菌菌株，其代谢产物包括苯酚和邻苯二酚[17]。*Aspergillus oryzae* M－4 降解 PBA 的产物食子酸为有毒代谢物[100]，该菌株无法单独代谢，加入 *Bacillus licheniformis* B－1 共培养可降解没食子酸，实现无毒化[19]，真菌中常有的木质素降解酶漆酶、LiP 和 MnP 也与 PBA 的降解相关[94]，它们在食用菌菌渣中被普遍检测到[82]。

综上所述，并非所有的拟除虫菊酯降解研究均

实现了完全矿化、无毒化。构建复合菌系可以帮助实现这一目标。

4　结论与展望

随着世界范围内人们环保意识的增强,研究者们就微生物修复农药污染开展了大量研究,其中关于拟除虫菊酯的降解也取得了较好的研究成果。笔者主要从降解菌株、降解基因及酶、降解机制几个方面对拟除虫菊酯类农药的微生物降解的现有研究进行了综述。首次对涉及 45 个菌属的拟除虫菊酯降解菌株信息进行了总结归纳;对拟除虫菊酯的降解基因及酶进行了信息总结,着重降解特性及分类;通过对微生物降解拟除虫菊酯的不同案例进行归纳整理,总结出了拟除虫菊酯降解途径的一般性规律,及可能存在的特殊情况;并着重分析了代谢产物 PBA 的降解,较为全面地对 1990 年至今的相关研究成果进行了总结。

现有研究成果为将来拟除虫菊酯类农药的降解及微生物环境修复相关研究提供了思路:(1)现有的大量研究成果,为利用基因工程技术,人为构建更为高效、广谱、抗逆的基因工程菌提供了良好基础;(2)构建多功能复合菌系,是以较低成本实现高效矿化有机污染物的途径,现有微生物降解拟除虫菊酯研究极少涉及这一领域;(3)土壤环境降解的研究有利于克服实际应用过程中的复杂环境因素,现有研究在土壤环境降解研究方面较为薄弱;(4)拟除虫菊酯的常见代谢产物 PBA 等,具有相比原农药更强的毒性及半衰期,但针对性的环境修复研究较少,此类研究具有重要意义;(5)随着萃取技术的优化,低抗性、易降解的天然除虫菊酯大量应用具有了可行性[105],推进此过程或开发更为高效、环保的新型菊酯,并进行相关微生物降解研究,亦有利于降低拟除虫菊酯造成的环境负担。

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