

doi:10.12301/spxb202200462

文章编号:2095-6002(2022)06-0026-11

引用格式:梁森,房子林,李培,等.噻唑类食品香料的研究进展[J].食品科学技术学报,2022,40(6):26-36.



LIANG Sen, FANG Zilin, LI Pei, et al. Research progress of thiazole flavor compounds[J]. Journal of Food Science and Technology, 2022,40(6):26-36.

噻唑类食品香料的研究进展

梁森,房子林,李培,田红玉*,孙宝国

(北京工商大学轻工科学技术学院/北京市食品风味化学重点实验室,北京100048)

摘要:噻唑类香料是一类重要的含硫杂环类香料,由于其香气浓郁、特征性强,一直备受调香师的喜爱。随着分析技术的不断发展,越来越多的噻唑类化合物在食品中被鉴定出来。目前,经美国食用香料与萃取物制造者协会(FEMA)安全评价的噻唑类香料有39种(噻唑类29种、噻唑啉类10种),我国GB 2760—2014中允许使用的噻唑类香料有29种。重点对经过FEMA安全评价的39种噻唑类香料的研究现状进行了汇总,介绍了其允许使用情况、香气特征和天然存在情况等。总结了食品加工过程中噻唑类风味化合物可能的形成途径,包括含硫化合物热降解和美拉德反应两类。在食品加工过程中,含硫氨基酸在较高温度下会经过脱氨、脱羧等发生热降解反应形成噻唑及其衍生物。此外,硫胺素加热时也可以降解成多种含硫和含氮挥发性风味物质,其中噻唑类降解产物主要有4-甲基-5-(β -羟基乙基)噻唑、4-甲基噻唑、4,5-二甲基噻唑、4-甲基-5-乙基噻唑等。从传统化学合成、光化学合成和电化学合成3个方面介绍了噻唑类化合物典型的化学合成方法及其反应机理。最后,指出突破合成香料行业中存在的香料新品种开发与创新不足、传统生产工艺落后及环境污染严重等瓶颈问题,是未来促进我国合成香料产业快速稳定发展的研究重点。

关键词:噻唑类香料;食品香料;含硫香料;香气特征;合成方法**中图分类号:**TS201.2;TS202.3**文献标志码:**A

食品香料作为一类非常重要的食品添加剂,对食品风味起着举足轻重的作用。在食品香料中,含硫香料占有非常重要的地位,由于其香气阈值低、特征性强,被广泛用于食用香精尤其是肉味香精的调配,对提高香精的质量和档次具有重要作用。近些年,含硫香料的发展速度非常快,在已经通过美国食用香料与萃取物制造者协会(Flavor and Extract Manufacturers Association, FEMA)安全评价的2980种食品香料中就有400多种含硫香料^[1]。

含硫香料根据结构的不同主要分为:硫醇类、硫醚类、硫酯类、缩硫醛(酮)类、噻唑类等杂环类。其

中,噻唑类香料是一类重要的含硫杂环类香料,由于其香气浓郁、特征性强,一直备受调香师的喜爱。噻唑类香料通常具有青香、坚果香、烤肉香、蔬菜香、爆米花等香气特征,可广泛用于食品香精、烟用香精及调味品中^[2]。

由于噻唑类化合物具有独特的香气特性,有关其天然存在、香气特性、合成、应用等方面的研究非常活跃。因此,本研究重点对经过FEMA安全评价的39种噻唑类香料的允许使用情况、香气特征、天然存在情况,食品中噻唑类化合物的可能形成途径以及人工合成方法进行介绍,以期对噻

收稿日期:2022-05-02

基金项目:国家自然科学基金资助项目(31901619)。

第一作者:梁森,男,副教授,博士,主要从事香料化学方面的研究。

*通信作者:田红玉,女,教授,博士,主要从事有机合成方法及香料化学方面的研究。

噻唑类香料化合物的分析、合成、应用等研究提供参考。

1 噻唑类食用香料的允许使用情况、香气特征及天然存在情况

噻唑又称1,3-硫氮杂茂,是一类含有硫、氮原子的具有芳香性的五元杂环化合物。噻唑啉又称二氢噻唑,有4,5-二氢噻唑(2-噻唑啉)、2,5-二氢噻唑(3-噻唑啉)和2,3-二氢噻唑(4-噻唑啉)3种异构体,香料中常见的是2-噻唑啉和3-噻唑啉(图1)。

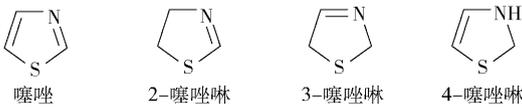
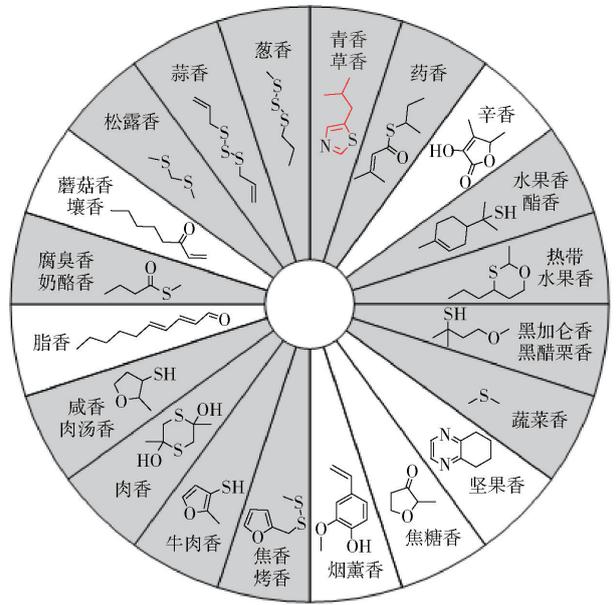


图1 噻唑类化合物的结构特点

Fig.1 Structural characteristics of thiazoles compounds

1967年,Stoll等^[3]在可可提取物中分离出具有强烈坚果样气味的4-甲基-5-乙基噻唑,自此以后人们才意识到该类化合物在食品中的存在及作为香料的重要性,有关其香气特性的研究也受到了越来越多的重视^[4]。例如,在高影响力香料风味轮^[5](图2)的20种关键风味中,作为青香型最具代表性的化合物——2-异丁基噻唑具有典型的新鲜青香、番茄叶香气,其对番茄的风味具有重要影响^[6]。



灰色底纹物质是含硫香料化合物。

图2 高影响力香料风味轮

Fig.2 Flavor wheel for high impact aroma chemicals

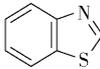
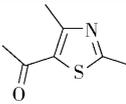
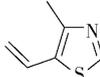
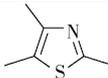
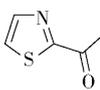
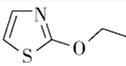
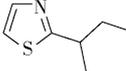
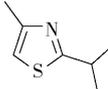
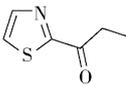
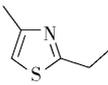
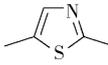
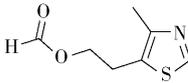
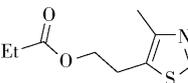
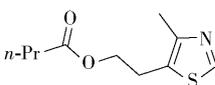
随着分析技术的不断发展进步,在食品及 Mailard 反应产物中检测到了越来越多的噻唑类化合物。目前经过美国食用香料与萃取物制造者协会批准允许使用的噻唑类香料有39种,GB 2760—2014《食品安全国家标准 食品添加剂使用标准》中允许使用的食品用合成香料名单中有29种噻唑类香料,这些香料的香气特征与天然存在情况见表1^[7-40]。

表1 FEMA 允许使用的噻唑类香料香气特征和天然存在情况

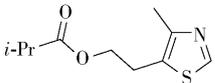
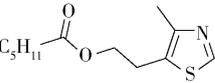
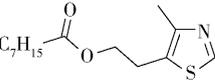
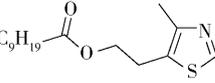
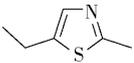
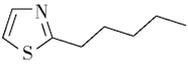
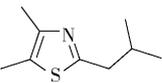
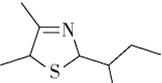
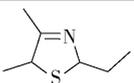
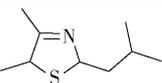
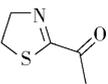
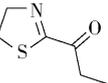
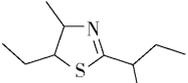
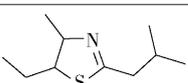
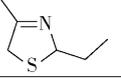
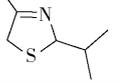
Tab.1 Aroma characteristics and natural existence of thiazole flavors permitted by FEMA

噻唑名称	结构式	FEMA 号	GB 2760 编码	香气特征	天然存在
2-异丁基噻唑		3134	S0733	番茄叶香气、青香	番茄、酵母抽提物、烤牛肉、番茄汁、圣女果、香菇等
2,4-二甲基-5-乙基噻唑		3145	—	肉香	熟牛肉
2-甲基-5-甲氧基噻唑		3192	—	硫化物味、蔬菜香	—
4-甲基-5-噻唑乙醇		3204	S0727	肉香、硫化物味、坚果香	烤牛肉、烤可可、贝类、酒、猪肉、芝麻油、火腿、酵母抽提物、亚麻籽、圆白菜等
4-甲基-5-噻唑乙醇乙酸酯		3205	S1260	肉香	—

续表 1

噻唑名称	结构式	FEMA 号	GB 2760 编码	香气特征	天然存在
苯并噻唑		3256	S0734	肉香、坚果香、咖啡香	酵母抽提物、酸菜、雪蟹、醋、烤羊肉串、糟鱼、苦芥、圆白菜、桃、白酒、馒头、六安茶、刺梨果等
2,4-二甲基-5-乙酰基噻唑		3267	S1223	烤香、坚果香、肉香	海葵
4,5-二甲基噻唑		3274	S0785	烤香、坚果香、青香	芝麻油、桃、炒牛肉、鱿鱼、烤牛肉、山羊肉、白菜、熟香椿等
4-甲基-5-乙烯基噻唑		3313	S0730	坚果香、可可香	大蒜、龙舌兰酒、番荔枝、芒果酒、比利时无酒精啤酒等
2,4,5-三甲基噻唑		3325	S0728	可可香、坚果香、壤香	烤牛肉、熟香椿、蓝蟹、花蟹、鸡汤、靖远羊肉、西蓝花等
2-乙酰基噻唑		3328	S0731	坚果香、谷物香、爆米花样香气、烤香	圆白菜、烤羊肉串、糟鱼、咖啡豆、猪肉、大蒜提取物、油条、牛油火锅调料、牛奶巧克力、可可、烤鹅、羊脂等
2-乙氧基噻唑		3340	S1222	焦香、坚果香	酱油、味噌、牛肉、黄酒等
2-仲丁基噻唑		3372	—	青香、药草香	芥菜
2-异丙基-4-甲基噻唑		3555	S0732	坚果香、硫化物味	酵母抽提物、熟香椿、啤酒、榴莲、菜籽油、扁桃汁、桃等
2-丙酰基噻唑		3611	S0950	烤香	熟鲑鱼、菜籽油等
噻唑		3615	S0903	青香、甜香、坚果香、番茄香气	醋、菜籽油、威士忌、绿茶、咖啡等
2-乙基-4-甲基噻唑		3680	S0729	烤香、坚果香	烤牛肉、芝麻油、鸡汤、酸菜等
4-甲基噻唑		3716	S0725	坚果香、青香、烤肉香	烤羊肉串、菜籽油、绿茶、咖啡、鸡汤、卷心菜、芥菜油、乳饮料等
2,5-二甲基噻唑		4035	S1459	—	酵母抽提物、芝麻油、咖啡等
2-(4-甲基-5-噻唑基)乙醇甲酸酯		4275	S1394	坚果香、烤香	—
2-(4-甲基-5-噻唑基)乙醇丙酸酯		4276	—	坚果香、烤香	—
2-(4-甲基-5-噻唑基)乙醇丁酸酯		4277	S1155	坚果香、烤香	—

续表 1

噻唑名称	结构式	FEMA 号	GB 2760 编码	香气特征	天然存在
2-(4-甲基-5-噻唑基)乙醇异丁酸酯		4278	S1393	坚果香、烤香	—
2-(4-甲基-5-噻唑基)乙醇己酸酯		4279	S1154	坚果香、烤香	—
2-(4-甲基-5-噻唑基)乙醇辛酸酯		4280	S1143	坚果香、烤香	—
2-(4-甲基-5-噻唑基)乙醇癸酸酯		4281	S1392	坚果香、烤香	—
5-乙基-2-甲基噻唑		4388	—	坚果香	酵母抽提物、咖啡、炸鸡、猪肉、红鳍东方鲀肉等
2-戊基噻唑		4641	—	脂香、青香、甜香	可可脂
4,5-二甲基-2-异丁基噻唑		4647	—	—	土豆、羊肝、芫荽精油、熟牛肉、麦芽汁、秋葵种子等
2-仲丁基-4,5-二甲基-3-噻唑啉		3619	S1324	肉香、辛香、蔬菜香	比利时无酒精啤酒
2-乙基-4,5-二甲基-3-噻唑啉		3620	S1323	肉香、蔬菜香	洋葱芽、比利时无酒精啤酒等
2-异丁基-4,5-二甲基-3-噻唑啉		3621	S0519	肉香、辛香、药草香	比利时无酒精啤酒
2-乙酰基-2-噻唑啉		3817	S0901	烤香、爆米花香气、硫化物味	高达奶酪
2-丙酰基-2-噻唑啉		4064	S1422	爆米花香气、玉米香气	高达奶酪
5-乙基-4-甲基-2-(1-甲基丙基)-噻唑啉		4318	S1450	—	—
5-乙基-4-甲基-2-(2-甲基丙基)-噻唑啉		4319	S1436	—	—
4-甲基-3-噻唑啉		4644	—	蒜香、壤香、焦香	洋葱、白芝麻等
2-乙基-4-甲基-3-噻唑啉		4695	—	桃子、杏干、硫磺味	洋葱、芝麻油等
2-异丙基-4-甲基-3-噻唑啉		4767	—	巧克力香、咖啡香、烤香	芝麻油

统计的 FEMA 批准允许使用的噻唑类香料时间截至 2022 年 5 月,“—”表示未被 GB 2760—2014 批准或无文献报道其香气、天然存在情况。

2 食品中噻唑类化合物的可能形成途径

2.1 含硫化合物热降解产生

在食品加工过程中,氨基酸在较高温度下会经过脱氨、脱羧等发生热降解反应,特别是含硫氨基酸(如胱氨酸、半胱氨酸、谷胱甘肽等)加热反应会形成噻唑及其衍生物^[41-43](图3)。

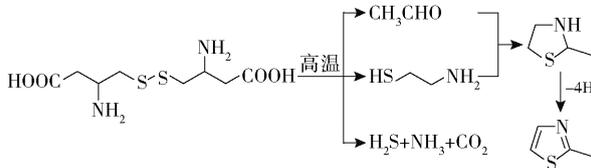


图3 胱氨酸受热降解产生噻唑类衍生物的可能途径

Fig. 3 Possible pathway for formation of thiazole derivatives by thermal degradation of cystine

此外,研究表明硫胺素加热时也可以分解成多种含硫和含氮挥发性香味物质,已经鉴定的硫胺素分解产物有68种,其噻唑类降解产物主要有4-甲基-5-(β -羟基乙基)噻唑、4-甲基噻唑、4,5-二甲基噻唑、4-甲基-5-乙基噻唑等^[44-45](图4)。

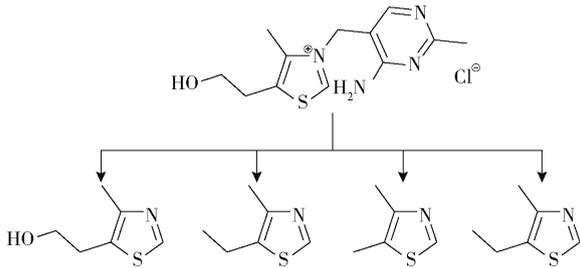


图4 硫胺素受热降解产生的噻唑类化合物

Fig. 4 Thiazole derivatives produced by thermal degradation of thiamine

2.2 美拉德反应产生

美拉德反应广泛存在于食品贮藏和加工过程中,指羰基化合物(醛、酮、还原糖以及具有类似结构的化合物)和氨基化合物(胺、氨基酸、肽、蛋白质等含氨基的化合物)在特定的温度下发生的一系列复杂反应,是食品风味形成的重要途径之一。含硫氨基酸参与 Maillard 反应,会产生噻唑等许多含硫化合物,对于食品风味起到非常重要的作用。

2.2.1 L-半胱氨酸与还原性糖降解产物的美拉德反应

L-半胱氨酸与还原性糖的降解产物(乙二醛、

丙酮醛、丁二酮等)发生美拉德反应,可以产生噻唑类化合物。1973年,Milders等^[46]利用L-半胱氨酸和核糖模型体系反应,证实了噻唑类化合物的产生,并提出了2-位酰基噻唑的可能的生成途径(图5)。首先,L-半胱氨酸中的氨基与核糖降解产生的 α -酮羧基的醛基发生亲核加成、脱水生成亚胺,再经脱羧、异构化、环化、氧化脱氢生成2-位酰基噻唑。

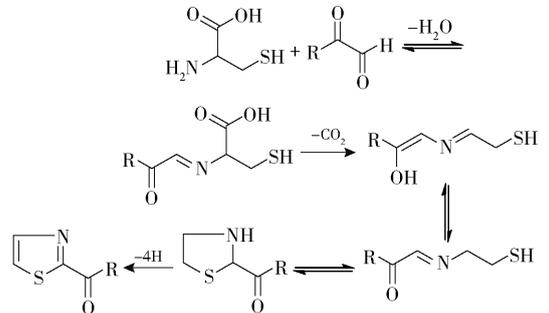


图5 L-半胱氨酸与核糖模型体系反应生成噻唑类化合物

Fig. 5 Formation of thiazole compounds from reaction of L-cysteine-ribose system

2.2.2 L-半胱氨酸降解产物半胱胺与还原性糖降解产物的美拉德反应

L-半胱氨酸受热脱羧产生的半胱胺也可以与还原性糖的降解产物发生美拉德反应,产生噻唑类化合物。1978年,Sakaguchi等^[47]报道了利用半胱胺和葡萄糖降解产物(甲醛、乙醛、丙醛、乙二醛、丙酮醛等)经醛氨缩合、环化、氧化脱氢制备噻唑类化合物,实验结果表明噻唑类化合物C-4、C-5来源于半胱胺,C-2来源于葡萄糖降解产物(图6)。2003年,Cerny等^[48]利用半胱胺和核糖模型体系实验发现,噻唑类化合物仅有C-2来源于核糖,C-4、C-5来源于半胱胺。

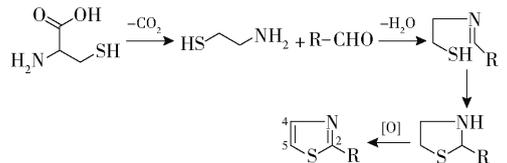


图6 半胱胺与醛反应生成噻唑类化合物

Fig. 6 Formation of thiazole compounds from reaction of cysteamine and aldehydes

2009年,笔者课题组^[49]发现在L-半胱氨酸与葡萄糖组成的Maillard反应体系中加入脂肪醛后,检测到了2-烷基噻唑烷烃。推测其形成的机理是

L-半胱氨酸在反应中脱羧生成半胱胺的氨基与脂肪醛的羰基发生亲核加成反应,得到的中间体脱水关环形成2-烷基噻唑烷类化合物。

2.2.3 L-半胱氨酸分解形成的醛、硫化氢和氨与 α -二羰基类化合物的美拉德反应

1976年, Takken等^[50]利用 α -二羰基类化合物、醛、硫化氢和氨为模型体系反应得到了不同取代基取代的噻唑啉和噻唑类化合物。首先, α -二羰基类化合物和硫化氢反应生成2-羟基-2-巯基羰基类化合物,与醛和氨反应生成的亚胺,依次经过亲核加成、环化、脱水等形成不同取代基取代的噻唑啉和噻唑类化合物,可能的反应路径见图7。

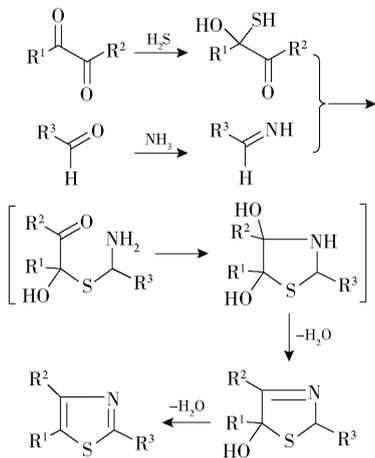


图7 α -二羰基类化合物与氨、硫化氢和醛反应生成噻唑类化合物

Fig. 7 Formation of thiazole compounds from reaction of α -dicarbonyls with ammonia, hydrogen sulfide and aldehydes

研究发现 α -二羰基类化合物可以由还原糖降解得到。1997年, Tai等^[51]以L-半胱氨酸和葡萄糖为模型体系反应得到了2-甲基噻唑、2,5-二甲基噻

唑和2,4,5-三甲基噻唑。推测该反应体系下噻唑类化合物的形成途径是由还原糖降解产生的 α -二羰基类化合物与L-半胱氨酸分解形成的醛、硫化氢和氨反应产生。2009年,笔者课题组^[52]利用L-半胱氨酸与葡萄糖反应,检测到噻唑、2-甲基噻唑、4-甲基噻唑、5-甲基噻唑、2,5-二甲基噻唑、2,4,5-三甲基噻唑和2-乙酰基噻唑共7种噻唑类化合物,其中2-乙酰基噻唑的含量最大。

3 噻唑类化合物典型的化学合成方法及其反应机理

3.1 传统化学合成方法

噻唑类化合物具有广泛的生物活性,在医药、农药、材料、香料等诸多领域具有广阔的应用前景,对其合成方法已有大量文献报道^[53-54],经典合成路线主要包括以下几种。

3.1.1 以 α -卤代羰基化合物和硫代酰胺为原料的方法

1887年, Hantzsch^[55-56]就提出利用 α -卤代醛酮与硫代酰胺、硫脲等反应合成噻唑类化合物(图8)。该方法作为合成2-取代噻唑类化合物的有效方法之一,被命名为Hantzsch法。该反应涉及亲核取代、亲核加成、环化脱水等步骤制备噻唑类化合物。

此外,文献还报道了一系列利用该方法制备噻唑类化合物的改进方法,这些研究多数在寻找合适的催化剂,文献报道的催化剂有 I_2 ^[57]、 Br_2 ^[58]、NBS^[59]、NIS^[60]、 $PhI(OH)OTs$ ^[61]、 HBr/H_2O_2 ^[62]、 $HBr/DMSO$ ^[63]、 $HI/DMSO$ ^[63]等(图8)。

3.1.2 以 α -酰胺基酮和五硫化二磷为原料的方法

α -酰胺基酮、酯等在五硫化二磷作用下,可生成

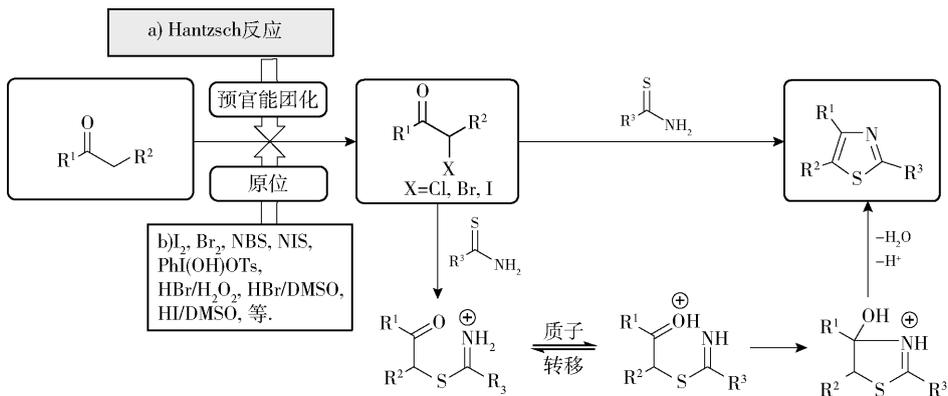


图8 Hantzsch 噻唑合成法

Fig. 8 Hantzsch thiazole synthesis method

噻唑类化合物,该方法叫作 Robinson-Gabriel 噻唑合成法。该反应涉及硫化、环化、脱水等步骤制备噻唑类化合物(图9)^[64]。

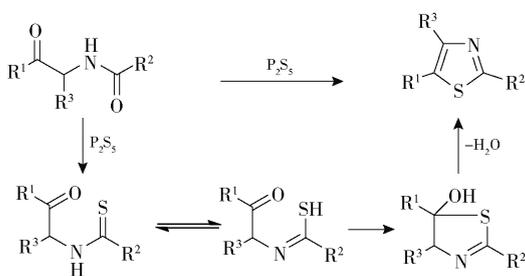


图9 Robinson-Gabriel 噻唑合成法

Fig. 9 Robinson-Gabriel thiazole synthesis method

3.1.3 以 α-氨基氰化合物和二硫化碳为原料的方法

α-氨基氰化合物与二硫化碳、氧硫化碳等反应可生成 5-氨基噻唑的,该方法叫作 Cook-Heilbron 噻唑合成法^[65]。该反应涉及加成、环化、异构化等历程,是一种合成噻唑及其衍生物的经典合成方法(图10)。

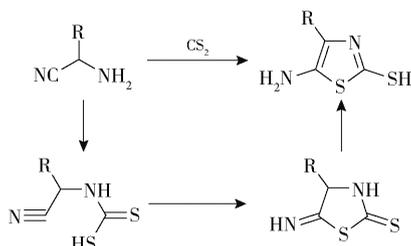


图10 Cook-Heilbron 噻唑合成法

Fig. 10 Cook-Heilbron thiazole synthesis method

3.1.4 以 α-卤代羰基化合物、硫代羧酸(盐)和乙酸铵为原料的方法

α-卤代羰基化合物和硫代羧酸反应生成 α-酰硫基酮,其与 NH₃ 反应经过烯胺中间体环化、脱水生成噻唑,是一种高效的“一锅法”制备二、三取代噻唑的方法(图11)^[66-67]。

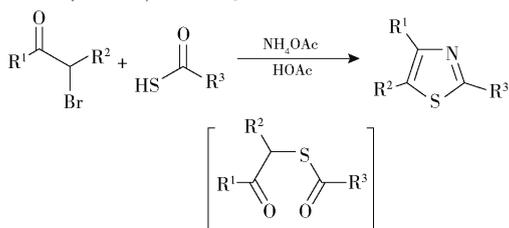


图11 α-卤代羰基化合物、硫代羧酸(盐)和氨生成噻唑类化合物

Fig. 11 Formation of thiazole compounds from reaction of α-halocarbonyl compounds, thiocarboxylic acids (salts) with ammonia

在这些噻唑类化合物的合成方法中,Hantzsch 法简单、有效,能引入众多基团,目前使用最广。但它们都或多或少存在一些不足,如使用有毒溶剂、需要昂贵催化剂、耗能大、产率低、反应条件苛刻、后处理困难等,限制了许多噻唑类香料化合物的生产及应用。因此,开发绿色环保节能减排新工艺,来突破合成香料行业中存在的传统生产工艺落后、环境污染严重等瓶颈问题是未来的工作重点。

3.2 光化学合成方法

光化学合成作为一种新的绿色合成方法,为有机合成化学提供了新途径、新方法和新技术,在天然产物、医药、香料等精细化学品的合成中具有特别重要的意义。2018年,Roslan 等^[68]利用光化学合成方法,使用四碘荧光素作为光催化剂,诱导硫脲原位产生硫自由基,与 1,3-二羰基化合物发生偶联反应来合成氨基噻唑衍生物(图12)。与传统合成方法相比,该光化学合成方法具有广阔的开发应用前景。

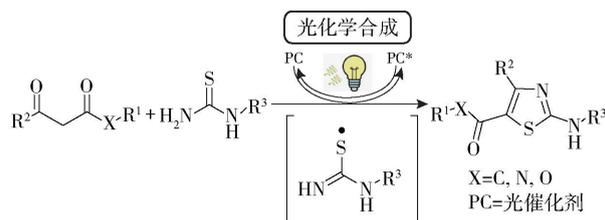


图12 光化学合成噻唑类化合物

Fig. 12 Photochemical synthesis of thiazole compounds

3.3 电化学合成方法

电化学合成以电子为试剂,通过电子的得失实现物质的氧化还原,从工艺本身消除了污染的形成,是名副其实的“绿色可持续化学”。近期,笔者课题组采用电化学合成方法,开发了碘负离子为电催化剂的电解体系,建立了一种噻唑类化合物的电化学合成方法(图13)^[69-70]。该方法为噻唑类化合物的合成提供了新的思路 and 方向。

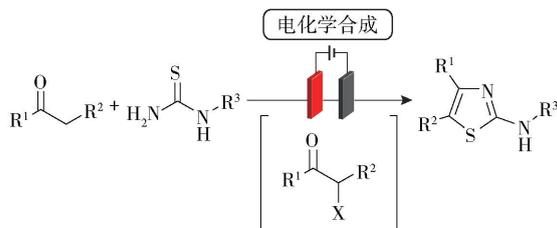


图13 电化学合成噻唑类化合物

Fig. 13 Electrochemical synthesis of thiazole compounds

4 展 望

随着现代分析技术的快速发展,越来越多天然存在的噻唑类化合物得以鉴定,其对食品特征香味的贡献也将进一步得到认识和发掘。尽管如此,噻唑类食品香料仍存在一些问题,新品种开发与创新不足,缺乏优势特色品种;传统生产工艺流程复杂、环境污染严重,限制了许多香料的生产及应用。因此,加快研究噻唑类香料分子结构与香气特性之间的关系,探索该类香料化合物的呈香规律,开展高品质噻唑类香料新品种的开发与应用研究,特别是高影响力、附加值高的香料新品种,是未来研究的重点。相较于噻唑类化合物传统的化学合成方法,光化学合成、电化学合成等绿色制备技术更符合绿色化学的原则,加快开展此类绿色制备技术的生产应用研究,突破实验室规模研究,开发出高质量、低能耗、环境友好的绿色工艺,是未来合成香料行业研究趋势。通过对噻唑类香料化合物的合成与应用进行深入研究,其在食品香精中的应用中也会发挥更加重要的作用,必将促进食品及相关行业的发展。

参考文献:

[1] COHEN S M, EISENBRAND G, FUKUSHIMA S, et al. GRAS 30 flavoring substances [J]. *Food Technology*, 2022, 76:58–70.

[2] 孙宝国, 何坚. 香料化学与工艺学: 第2版[M]. 北京: 北京化工出版社, 2004.

SUN B G, HE J. *Chemistry and technology of flavors and fragrances*: 2nd ed [M]. Beijing: Chemical Industry Press, 2004.

[3] STOLL M, DIETRICH P, SUNDT E, et al. Research on aromas: XV. cocoa aroma [J]. *Helvetica Chimica Acta*, 1967, 50(7):2065–2067.

[4] HO C T, JIN Q Z, LEE M H, et al. Positive identification of new alkyloxazoles, alkylthiazoles, and piperidine in roasted peanut flavor [J]. *Journal of Agricultural and Food Chemistry*, 1983, 31(6):1384–1386.

[5] BYRNE B, ROWE D. Natural aroma chemicals: nothing new under the sun [J]. *Perfumer & Flavorist*, 2009, 34(9):36–46.

[6] ROWE R. More fizz for your buck: high-impact aroma chemicals [J]. *Perfumer & Flavorist*, 2000, 25:1–19.

[7] KOLTUN S J, MACINTOSH A J, GOODRICH-SCHNEIDER R M, et al. Sensory and chemical characteristics of tomato juice from fresh market cultivars with comparison to commercial tomato juice [J]. *Flavour and Fragrance Journal*, 2021, 36(1):121–136.

[8] WANG Z L, XIAO Q, ZHUANG J D, et al. Characterization of aroma-active compounds in four yeast extracts using instrumental and sensory techniques [J]. *Journal of Agricultural and Food Chemistry*, 2020, 68(1):267–278.

[9] YANG Y N, DENG Q C, JIA X, et al. Characterization of key odorants in peeled and unpeeled flaxseed powders using solvent-assisted flavor evaporation and odor activity value calculation [J]. *LWT – Food Science and Technology*, 2021, 138:110724.

[10] MARCINKOWSKA M, FRANK S, STEINHAUS M, et al. Key odorants of raw and cooked green kohlrabi (*Brassica oleracea* var. *gongylodes* L.) [J]. *Journal of Agricultural and Food Chemistry*, 2021, 69(41):12270–12277.

[11] GEORGE A B. *Fenaroli's handbook of flavor ingredients*: 6th ed [M]. Florida: The CRC Press, 2010.

[12] HE Z, CHEN H Y, WANG X Y, et al. Effects of different temperatures on bacterial diversity and volatile flavor compounds during the fermentation of Suancai, a traditional fermented vegetable food from northeastern China [J]. *LWT – Food Science and Technology*, 2020, 118:108773.

[13] TREMBLAY A, CORCUFF R, GOULET C, et al. Valorization of snow crab (*Chionoecetes opilio*) cooking effluents for food applications [J]. *Journal of the Science of Food and Agriculture*, 2020, 100(1):384–393.

[14] AL-DALALI S, ZHENG F P, SUN B G, CHEN F. Characterization and comparison of aroma profiles and aroma-active compounds between traditional and modern sichuan vinegars by molecular sensory science [J]. *Journal of Agricultural and Food Chemistry*, 2020, 68(18):5154–5167.

[15] DU W B, ZHEN D W, WANG Y T, et al. Characterization of the key odorants in grilled mutton shashlik with or without suet brushing during grilling [J]. *Flavour and Fragrance Journal*, 2021, 36(1):111–120.

[16] CHEN Z P, TANG H Q, OU C R, et al. A comparative study of volatile flavor components in four types of Zaoyu using comprehensive two-dimensional gas chromatography in combination with time-of-flight mass spectrometry

- [J]. Journal of Food Processing and Preservation, 2021, 45(3):e15230.
- [17] SHI J, TONG G Q, YANG Q, Characterization of key aroma compounds in tartary buckwheat (*Fagopyrum tataricum* Gaertn.) by means of sensory-directed flavor analysis[J]. Journal of Agricultural and Food Chemistry, 2021, 69(38):11361–11371.
- [18] NIU Y W, DENG J M, XIAO Z B, et al. Characterization of the major aroma-active compounds in peach (*Prunus persica* L. Batsch) by gas chromatography-olfactometry, flame photometric detection and molecular sensory science approaches[J]. Food Research International, 2021, 147:110457.
- [19] WANG Z, WANG Y, ZHU T T, et al. Characterization of the key odorants and their content variation in Niulanshan Baijiu with different storage years using flavor sensory omics analysis[J]. Food Chemistry, 2022, 376:131851.
- [20] HUANG Y L, WAN J W, WANG Z L, et al. Variation of volatile compounds and corresponding aroma profiles in Chinese steamed bread by various yeast species fermented at different times[J]. Journal of Agricultural and Food Chemistry, 2022, 70(12):3795–3806.
- [21] XIAO M J, ZHENG F L, XIAO M X, et al. Contribution of aroma-active compounds to the aroma of Lu'an Guapian tea[J]. Flavour and Fragrance Journal, 2022, 37(2):83–95.
- [22] HUANG M Z, LI T T, HARDIE W J, et al. Comparative characterization and sensory significance of volatile compounds in *Rosa roxburghii* Tratt fruit from five geographic locations in Guizhou, China[J]. Flavour and Fragrance Journal, 2022, 37(3):163–180.
- [23] DUSART A, MERTENS B, VAN HOECK E, et al. Occurrence of (suspected) genotoxic flavoring substances in Belgian alcohol-free beers[J]. Food Chemistry, 2022, 369:130917.
- [24] WANG F, GAO Y Q, WANG H B, et al. Analysis of volatile compounds and flavor fingerprint in Jingyuan lamb of different ages using gas chromatography-ion mobility spectrometry (GC-IMS)[J]. Meat Science, 2021, 175:108449.
- [25] HONG S J, JEONG H, YOON S, et al. A comprehensive study for taste and odor compounds using electronic tongue and nose in broccoli stem with different thermal processing[J]. Food Science and Biotechnology, 2022, 31(2):191–201.
- [26] POISSON L, PITTET J, SCHAERER A, et al. Quantitative validation of the in-bean approach in coffee roasting[J]. Journal of Agricultural and Food Chemistry, 2020, 68(17):4732–4742.
- [27] HAN D, ZHANG C H, FAUCONNIER M L, et al. Characterization and differentiation of boiled pork from Tibetan, Sanmenxia and Duroc × (Landrac × Yorkshire) pigs by volatiles profiling and chemometrics analysis[J]. Food Research International, 2020, 130:108910.
- [28] ABE K, HORI Y, MYODA T, et al. Characterization of key aroma compounds in aged garlic extract[J]. Food Chemistry, 2020, 312:126081.
- [29] DU W B, ZHAO M Y, ZHEN D W, et al. Key aroma compounds in Chinese fried food of Youtiao[J]. Flavour and Fragrance Journal, 2020, 35(1):88–98.
- [30] SUN J, MA M J, SUN B G, et al. Identification of characteristic aroma components of butter from Chinese butter hotpot seasoning[J]. Food Chemistry, 2021, 338:127838.
- [31] FRICKE K, SCHIEBERLE P. Characterization of the key aroma compounds in a commercial milk chocolate by application of the sensomics approach[J]. Journal of Agricultural and Food Chemistry, 2020, 68(43):12086–12095.
- [32] PORCELLI C, NEIENS S D, STEINHAUS M. Molecular background of a moldy-musty off-flavor in cocoa[J]. Journal of Agricultural and Food Chemistry, 2021, 69(15):4501–4508.
- [33] GASIOR R, WOJTYCZA K, MAJCHER M A, et al. Key aroma compounds in roasted white koluda goose[J]. Journal of Agricultural and Food Chemistry, 2021, 69(21):5986–5996.
- [34] LI J, YANG Y Y, TANG C H, et al. Changes in lipids and aroma compounds in intramuscular fat from Hu sheep[J]. Food Chemistry, 2022, 383:132611.
- [35] WANG P, TIAN H L, TAN F L, et al. Impact of commercial processing on volatile compounds and sensory profiles of flat peach juices by PLSR and BP network[J]. Journal of Food Processing and Preservation, 2020, 44(8):e14575.
- [36] YU P, YANG Y N, SUN J Y, et al. Identification of volatile sulfur-containing compounds and the precursor of dimethyl sulfide in cold-pressed rapeseed oil by GC-SCD and UPLC-MS/MS[J]. Food Chemistry, 2022, 367:130741.
- [37] PUA A, LAU H, LIU S Q, et al. Improved detection of

- key odourants in Arabica coffee using gas chromatography-olfactometry in combination with low energy electron ionisation gas chromatography-quadrupole time-of-flight mass spectrometry [J]. Food Chemistry, 2020, 302: 125370.
- [38] WEI S H, XIAO X M, WEI L J, et al. Development and comprehensive HS-SPME/GC-MS analysis optimization, comparison, and evaluation of different cabbage cultivars (*Brassica oleracea* L. var. capitata L.) volatile components [J]. Food Chemistry, 2021, 340: 128166.
- [39] JIA X, WANG L F, ZHENG C, et al. Odorant differences in fragrant *Brassica napus* and *Brassica juncea* oils revealed by gas chromatography-olfactometry, odor activity values, and aroma recombination [J]. Journal of Agricultural and Food Chemistry, 2020, 68(50):14950 – 14960.
- [40] MAHMUD M M C, KEAST R, MOHEBBI M, et al. Identifying aroma-active compounds in coffee-flavored dairy beverages [J]. Journal of Food Science, 2022, 87(3):982 – 997.
- [41] SHU C K, HAGEDORN M L, MOOKHERIEE B D, et al. Volatile components of the thermal degradation of cystine in water [J]. Journal of Agricultural and Food Chemistry, 1985, 33(3):438 – 442.
- [42] SHU C K, HAGEDORN M L, MOOKHERIEE B D, et al. pH effect on the volatile components in the thermal degradation of cysteine [J]. Journal of Agricultural and Food Chemistry, 1985, 33(3):442 – 446.
- [43] ZHANG Y G, CHIEN M J, HO C T. Comparison of the volatile compounds obtained from thermal degradation of cysteine and glutathione in water [J]. Journal of Agricultural and Food Chemistry, 1988, 36(5):992 – 996.
- [44] DWIVEDI B K, ARNOLD R G, LIBBEY L M. Chemistry of thiamine degradation. 4-methyl-5-(β -hydroxyethyl) thiazole from thermally degraded thiamine [J]. Journal of Food Science, 1972, 37(5):689 – 692.
- [45] HARTMAN G J, CARLIN J T, SCHEIDE J D. Volatile products formed from the thermal degradation of thiamin at high and low moisture levels [J]. Journal of Agricultural and Food Chemistry, 1984, 32(5):1015 – 1018.
- [46] MILDERS E J. Volatile components from the non-enzymic browning reaction of the cysteine/cystine-ribose system [J]. Zeitschrift Fuer Lebensmittel Untersuchung Und Forschung, 1973, 152(4):193 – 201.
- [47] SAKAGUCHI M, SHIBAMOTO T. Formation of heterocyclic compounds from the reaction of cysteamine and D-glucose, acetaldehyde, or glyoxal [J]. Journal of Agricultural and Food Chemistry, 1978, 26(5): 1179 – 1183.
- [48] CERNY C, DAVIDEK T. Formation of aroma compounds from ribose and cysteine during the Maillard reaction [J]. Journal of Agricultural and Food Chemistry, 2003, 51(9):2714 – 2721.
- [49] 张浩, 田红玉, 孙宝国, 等. 脂肪醛 Maillard 模型体系含硫挥发性产物的影响 [J]. 食品科学, 2009, 30(11):33 – 36.
- ZHANG H, TIAN H Y, SUN B G, et al. Effects of aliphatic aldehydes on volatile sulfur-containing compounds in Maillard model systems [J]. Food Science, 2009, 30(11):33 – 36.
- [50] TAKKEN H J, VAN DER LINDE L M, DE VALOIS P J, et al. Reaction products of α -dicarbonyl compounds, aldehydes, hydrogen sulfide and ammonia [M] // CHARALAMBOUS G, KATZ I. Phenolic, sulfur and nitrogen compounds in food flavors. Washington DC: American Chemical Society, 1976: 114 – 121.
- [51] TAI C Y, HO C T. Influence of cysteine oxidation on thermal formation of Maillard aromas [J]. Journal of Agricultural and Food Chemistry, 1997, 45(9):3586 – 3589.
- [52] TIAN H Y, ZHANG J, SUN B G, et al. Preparation of natural isovaleraldehyde by the Maillard reaction [J]. Chinese Chemical Letters, 2007, 18(9):1049 – 1052.
- [53] 崔胜峰, 王艳, 吕敬松, 等. 噻唑类化合物应用研究新进展 [J]. 中国科学:化学, 2012, 42(8):1105 – 1131.
- CUI S F, WANG Y, LÜ J S, et al. Recent advances in application of thiazole compounds [J]. Scientia Sinica (Chimica), 2012, 42(8):1105 – 1131.
- [54] NARASIMHAMURTHY K H, SAJITH A M, JOY M N, et al. An overview of recent developments in the synthesis of substituted thiazoles [J]. ChemistrySelect, 2020, 5(19):5629 – 5656.
- [55] HANTZSCH A, WEBER J H. Thiazole compounds [J]. Berichte Der Deutschen Chemischen Gesellschaft, 1887, 20:3118 – 3132.
- [56] HANTZSCH A. Thiazoles from thiamides [J]. Justus Liebigs Annalen der Chemie, 1889, 250:257 – 273.
- [57] ZHANG Q, WU J F, PAN Z X, et al. A one-pot synthesis of 2-aminothiazoles via the coupling of ketones and thiourea using I_2 /dimethyl sulfoxide as a catalytic oxida-

- tive system[J]. *Journal of Chemical Research*, 2021, 45 (1/2):89–94.
- [58] RAHATGAONKAR A, RATHOD A. Microwave-assisted synthesis of 2-amino-4-substituted phenyl-thiazole [J]. *Asian Journal of Chemistry*, 2006, 18(2):1039–1042.
- [59] GUNDALA T R, GODUGU K, NALLAGONDU C G R. Citric acid-catalyzed synthesis of 2,4-disubstituted thiazoles from ketones via C-Br, C-S, and C-N bond formations in one pot: a green approach[J]. *Journal of the Chinese Chemical Society*, 2017, 64 (12): 1408–1416.
- [60] ZARNEGAR Z, ALIZADEH R, AHMADZADEH M. C-N bond formation in alicyclic and heterocyclic compounds by amine-modified nanoclay [J]. *Journal of Molecular Structure*, 2017, 1144:58–65.
- [61] MORIARTY R M, VAID B K, DUNCAN M P, et al. A one-pot synthesis of 2-amino- and 2-(arylamino)-substituted thiazoles and selenazoles using [hydroxy (tosyloxy)iodo]benzene, carbonyl compounds and thioureas or selenoureas: a modification of the Hantzsch synthesis [J]. *Synthesis*, 1992, 845–846.
- [62] RAIENDIRAN C, NAGARAJAN P, CHARY M T. Eco-friendly water as a solvent for the one-pot synthesis of 2-aminothiazoles[J]. *Journal of Chemical and Pharmaceutical Research*, 2016, 8(2):813–820.
- [63] ZARNEGAR Z, SADEGHI M, ALIZADEH R, et al. HX-DMSO: a novel liquid halogenating system for synthesis of 2-aminothiazoles via Csp³-H bond functionalization[J]. *Journal of Molecular Liquids*, 2018, 255: 76–79.
- [64] GABRIEL S. Synthesis of oxazoles and of thiazoles. II [J]. *Berichte Der Deutschen Chemischen Gesellschaft*, 1910, 43:1283–1287.
- [65] COOK A H, HEILBRON S, LEVY A L. Studies in the azole series. II. the interaction of α -amino-nitriles and carbon disulphide[J]. *Journal of the Chemical Society*, 1947, 1:1598–1609.
- [66] DUBS P, STUESSI R. Simple new syntheses of 2,4-disubstituted and 2,4,5-trisubstituted 1,3-thiazoles [J]. *Synthesis*, 1976 (10):696–697.
- [67] VENKATESWARARAO E, JALANI H B, MANOJ M, et al. Exploration and optimization of an efficient one-pot sequential synthesis of di/tri-substituted thiazoles from α -bromoketones, thioacids salt, and ammonium acetate[J]. *Journal of Heterocyclic Chemistry*, 2016, 53(5):1449–1456.
- [68] ROSLAN I I, NG K H, GONDAL M A, et al. Visible light-mediated coupling of thioureas and 1,3-dicarbonyls: towards a leaving group-free synthesis of aminothiazoles [J]. *Advanced Synthesis & Catalysis*, 2018, 360(8):1584–1589.
- [69] LI P, YANG S F, FAGN Z L, et al. An efficient one-pot synthesis of 2-aminothiazoles via electrochemically oxidative α -C-H functionalization of ketones with thioureas[J]. *Journal of Environmental Chemical Engineering*, 2022, 10:107487.
- [70] YANG S F, LI P, FAGN Z L, et al. A one-pot electrochemical synthesis of 2-aminothiazoles from active methylene ketones and thioureas mediated by NH₄I [J]. *Beilstein Journal Organic Chemistry*, 2022, 18:1249–1255.

Research Progress of Thiazole Flavor Compounds

LIANG Sen, FANG Zilin, LI Pei, TIAN Hongyu*, SUN Baoguo

(School of Light Industry / Beijing Key Laboratory of Flavor Chemistry, Beijing Technology and Business University, Beijing 100048, China)

Abstract: Thiazoles are important flavor of sulfur-containing heterocyclic class, which have always been favored by flavorists due to their dense aroma and intensive characteristics. With the continuous development of analytical technology, more and more thiazole compounds had been identified in food. 39 thiazole flavors (29 thiazoles and 10 thiazolines) have been evaluated and recognized as safe by the Flavor and Extract Manufacturers Association of the United States, and 29 thiazole flavors are allowed to

(下转第 51 页)

binary and ternary conjugates were studied by UV-visible spectra and Fourier transform infrared spectroscopy. The effects of TA, MD and PD on the functional properties of SPI were studied by evaluating solubility, emulsification, foaming performance, antioxidant activity, thermal stability and surface hydrophobicity. The results showed that the covalent binding of TA, MD and PD with SPI changed the structure of SPI and reduced the content of β -sheet in the secondary structure of SPI. The grafting equivalent of TA was $(35.56 \pm 1.32) \mu\text{mol/g}$, the grafting degree of MD and PD was 46.54% and 32.26%, respectively. Ternary conjugates showed significantly higher solubility, emulsification, antioxidant activity, foaming performance, surface hydrophobicity and thermal stability compared with SPI ($P < 0.05$). The results could not only provide a theoretical basis for improving the functional properties and further understanding of the modification mechanism of SPI, but also provide a new food-grade raw material for the design of food functional ingredients delivery system, especially pine seed oil emulsion delivery system.

Keywords: soybean protein isolate; modification; ternary conjugates; functional properties; structure

(责任编辑:郝一铭)

(上接第36页)

be used in food according to flavor compound list in GB 2760—2014. Recent studies on permissible usage, aroma characteristics and natural occurrence of 39 thiazole flavors were introduced in this paper. The possible formation pathways of thiazole flavor compounds in food processing were reviewed, including thermal degradation of sulfur-containing compounds and Maillard reaction. During food processing, sulfur-containing amino acids underwent thermal degradation reactions such as deamination and decarboxylation at high temperatures to form thiazole and its derivatives. In addition, thiamine could also be degraded into a variety of volatile flavor substances containing sulfur and nitrogen when heated, and the thiazole degradation products mainly included 4-methyl-5-(β -hydroxyethyl) thiazole, 4-methylthiazole, 4,5-dimethylthiazole, 4-methyl-5-ethylthiazole, etc. The typical synthetic methods and reaction mechanisms of thiazole compounds were introduced from three aspects: traditional chemical synthesis, photochemical synthesis and electrochemical synthesis. Finally, it was pointed out that breaking through the bottleneck problems such as insufficient development and innovation of new flavors, backward traditional production technology and serious environmental pollution in the synthetic flavor industry would be the key points to promote the rapid and stable development of our country's synthetic flavor industry in the future.

Keywords: thiazole flavors; flavors; sulfur-containing flavors; odor characteristics; formation and synthesis methods

(责任编辑:李 宁)