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大蒜药理作用和除臭方法及机制研究进展

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摘要: 大蒜因其特有的辛辣风味以及具有抗菌、抗寄生虫、抗肿瘤、抗氧化和预防心脑血管疾病等药理作用被广泛应用于食品、保健和医药领域。大蒜素是大蒜中主要的生物活性物质,其性质不稳定,可分解为多种带有刺激性气味的硫化物,具有强烈刺激性臭味,并导致食用后残留口臭,大大限制了大蒜的应用。因此,如何有效去除大蒜臭味,并保留大蒜独特风味和生物活性是大蒜除臭研究热点,也是大蒜制品生产应用的前提。该文总结大蒜素理化性质、药理作用以及大蒜刺激性臭味的来源,并阐述水果、蔬菜、高脂及高蛋白食物或食物提取物对大蒜素臭味的消除效果及机制,以期为大蒜素的应用提供理论参考。

关键词: 大蒜;大蒜素;理化性质;药理作用;食物;除臭

Advances in Pharmacological Effects and Deodorization Methods and Mechanisms of Garlic

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Abstract: Garlic is widely used in the fields of food, healthcare, and medicine due to its unique spicy flavor and pharmacological effects such as antibacterial, antiparasitic, antitumor functions, and antioxidant and the ability to prevent cardiovascular and cerebrovascular diseases. Allicin is the main bioactive substance in garlic. Its properties are unstable, and it can be decomposed into various sulfides with pungent odors. It has a strong pungent odor and thus leads to residual halitosis after consumption, which greatly limits the application of garlic. Therefore, how to effectively remove the odor of garlic and retain its unique flavor and biological activity is a research hotspot in the field of garlic deodorization, and obtaining solutions to this is the prerequisite for the production and application of garlic products. This paper summarized the physical and chemical properties and pharmacological effects of allicin as well as the source of the pungent odor of garlic. It also elaborated on the elimination effect and mechanism of fruits, vegetables, high-fat and high-protein foods or food extracts on the odor of allicin, so as to provide a theoretical reference for the application of allicin.

Key words: garlic; allicin; physical and chemical properties; pharmacological effects; food; deodorization

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大蒜(*Allium sativum* L.)是百合科葱属植物蒜的地下鳞茎^[1],起源于中国西部,具有独特辛辣风味,富含多种营养物质,广泛用作餐桌食材,已有数千年历史。大蒜素是从大蒜中提取出来的一种具有挥发性且带有刺激性臭味的有机硫化合物,是大蒜中主要的生物活

性物质,具有抗病原微生物、抗肿瘤、抗氧化和预防心脑血管疾病等多种药理作用^[2]。大蒜素易分解形成挥发性物质,包括二烯丙基硫化物、二烯丙基二硫化物、二烯丙基三硫化物、烯丙基甲基二硫化物等,是刺激性臭味的主要来源,会引发口腔异味,存留较久且不易去

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除,大大限制了大蒜素的应用^[3]。目前有多种大蒜素除臭方法,其效果、机制和对活性成分的破坏程度也存在差异,随着社会对食品安全健康的重视,选用天然、无毒副作用的除臭方法是未来发展趋势。苹果^[4]、柿子、李子、欧芹、菠菜^[5]、薄荷^[6]、蘑菇^[7-8]等果蔬类可降低硫化物挥发,减弱大蒜臭味;高脂及高蛋白质食物如牛奶^[9]、酸奶^[10]也可显著降低大蒜挥发物浓度;甘草^[11]、迷迭香^[12]等也有一定除臭效果。本文主要对大蒜素理化性质、药理作用以及大蒜素刺激性气味去除方法及机

制的研究进展进行综述,以期为大蒜素的开发利用提供参考。

1 大蒜素理化性质

大蒜素并非大蒜中的天然成分,新鲜大蒜只含有蒜氨酸,当新鲜大蒜细胞受外力破损后,细胞质中的蒜氨酸在液泡中蒜氨酸酶的催化下代谢成一种油性物质,即大蒜素 (allicin),学名二烯丙基硫代亚磺酸酯,分子式为 $C_6H_{10}S_2O$ ^[13]。蒜氨酸转化为大蒜素的转化过程见图1。

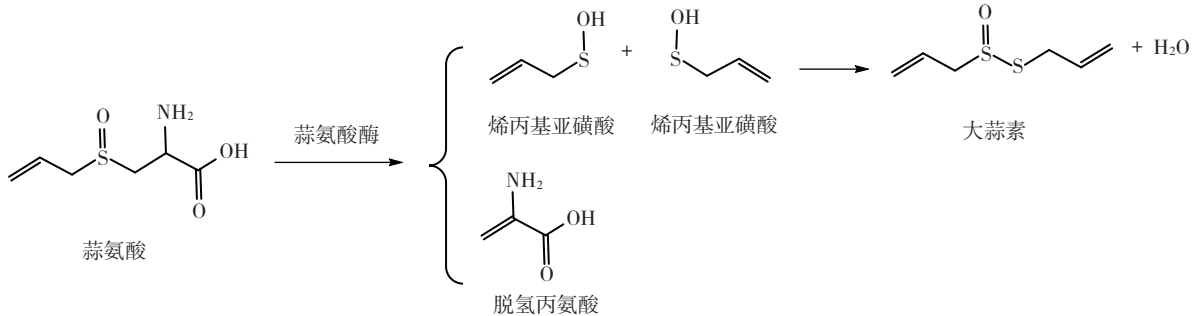


图1 蒜氨酸经酶催化转化为大蒜素的过程

Fig.1 Conversion of alliin to allicin by enzymatic catalysis

大蒜素在0.2 kPa压力下沸点为80~85℃,相对密度为1.112 g/cm³,折光率1.572,与乙醇、乙醚及苯等有机溶剂可互溶,难溶于水,对热碱不稳定,对酸稳定,在pH6.0、温度5℃时较为稳定^[14-15]。通常情况下大蒜素不稳定,挥发性极强,会迅速降解生成二烯丙基硫化

物、二烯丙基二硫化物、二烯丙基三硫化物和烯丙基甲基二硫化物等多种含硫有机化合物,进一步分解或聚合生成链式或杂环类化合物,如二噻烯和阿藿烯等,而具有刺激性气味^[2,16]。大蒜素及其形成的硫化物结构式见图2。

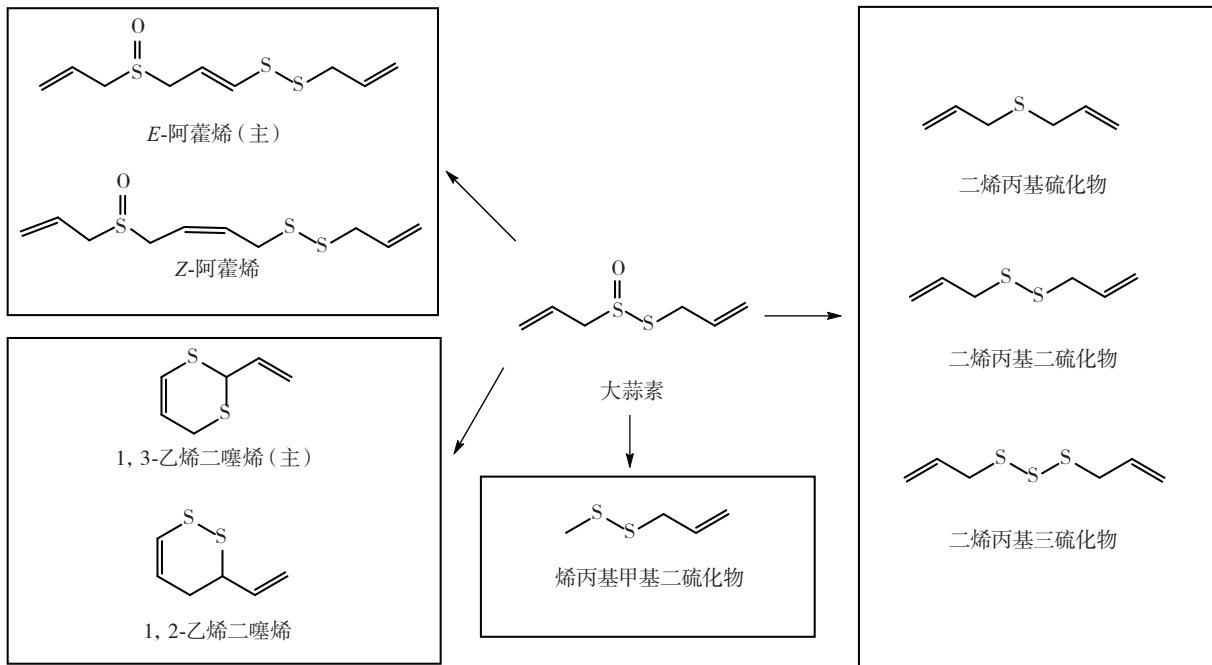


图2 大蒜素及其形成的硫化物结构式

Fig.2 Structural formulas of allicin and sulfides formed by allicin

2 大蒜素的药理作用

2.1 抗病原微生物作用

大蒜素是大蒜发挥生物活性的主要有效成分,具

有抗菌、杀菌作用,主要通过抑制细菌、真菌等微生物的物质代谢,破坏菌体细胞壁和细胞膜结构的完整性,使胞内营养物质外流,并穿透胞内线粒体、高尔基体等

细胞器膜,导致细胞器破坏从而造成细胞死亡^[17-18]。

细菌感染可能会引起败血症、支气管炎、肺炎等疾病,危害人体健康。大蒜素对多种细菌具有显著抑制作用,大蒜水提物对枯草芽孢杆菌和金黄色葡萄球菌等革兰氏阳性菌株以及大肠杆菌和肺炎克雷伯菌在内的多种革兰氏阴性菌株具有良好的抗菌活性^[19]。大蒜素在温度低于 50 °C、pH 值呈弱酸性(pH6)时对金黄色葡萄球菌和大肠杆菌抑菌效果最好^[20]。研究发现大蒜素分解产物二烯丙基三硫能够有效杀灭或抑制感染根管中的粪肠球菌^[21]。此外,有研究者证实大蒜素对变异链球菌和蜜蜂球囊菌的最低抑菌浓度(minimum inhibitory concentration, MIC)分别为 12.8 mg/L 和 12.0 mg/L,最低杀菌浓度(minimum bactericidal concentration, MBC)分别为 25.8 mg/L 和 24.0 mg/L^[22-23]。大蒜素具有广谱抗菌作用,能有效抑制和杀灭多种细菌,被认为是一种重要的天然抗菌剂。

真菌感染人体皮肤、黏膜、内脏和深部组织,造成局部或全身散播性感染,是威胁人类健康的重要病原体。与细菌相比,大蒜素对真菌具有更显著的抑制作用^[24]。研究发现,大蒜素和大蒜提取物对阿萨希毛孢子菌^[25]、烟曲霉^[26]、白色念珠菌^[27]、隐球菌^[28]等真菌均具有显著抑制、灭杀作用。Schier 等^[29]发现大蒜素蒸汽对毛霉目真菌的抑制效果与直接使用抗真菌剂两性霉素 B(amphotericin B, amp B)效果相当。大蒜素与其他抗真菌药物联用,可大大提高治疗效果。大蒜素注射液与伏立康唑药物联合使用提高了肺部真菌感染的治疗效果,增强临床患者生命体征的稳定性^[30]。大蒜素与抗真菌药物伊曲康唑、特比萘芬组合具有协同作用,可增强对犬小孢子菌活性的抑制效果,为治疗犬支原体引起的头皮癣提供参考^[31]。

大蒜素通过干扰寄生虫的生理过程,如破坏其细胞膜或扰乱其代谢活动,从而起到抗寄生虫的作用。传统医学中也有利用大蒜来治疗寄生虫感染的记载,《本草纲目》中提及大蒜能治疗“中蛊”,即大蒜能治疗因寄生虫感染所引起的疾病。30 μg/mL 的大蒜素对梨形鞭毛虫、利什曼原虫、痢疾阿米巴原虫等多种寄生虫具有明显抑制作用^[24,32]。对感染血吸虫病的 BALB/c 小鼠预防性使用大蒜或大蒜素,可显著降低蠕虫活性,说明大蒜素是治疗血吸虫病的新辅助药物^[33]。大蒜素对阴道毛滴虫、疟原虫、布氏锥虫等其他寄生虫导致的感染性疾病也具有较好的治疗作用^[34-35]。此外,大蒜素可联用其他药物,提高对寄生虫活性的抑制效果。Salama 等^[36]研究发现大蒜素与乙酰二氮脒联合使用能显著抑制体内外巴贝虫的生长。大蒜素和伊维菌素联合使用可提高对鸡螨虫的灭杀能力^[37]。

综上所述,大蒜素是一种高效、安全、易得的广谱抗菌、抗寄生虫的生物活性物质,具有广泛应用前景。

同时,大蒜素与抗菌药物、抗寄生虫药物的联合应用具有显著协同效应,有望为细菌、真菌和寄生虫感染治疗开辟新策略。

2.2 抗肿瘤作用

我国人口多,基数大,并且随着人们生活习惯和环境的改变,罹患恶性肿瘤的人数不断上升,根据国家癌症中心定期报告的全国癌症发病率和死亡率的统计数据,我国 2022 年新发癌症病例 482.5 万例,死亡 257.4 万例,约占全球癌症发病和死亡病例数的 24.2% 和 26.4%。因此,如何预防、治疗肿瘤性疾病已成为各国研究者需要共同攻克的难题。临床研究显示大蒜素具备治疗癌症的功效及其降低患有某些癌症风险的能力^[38]。大蒜素通过 p53 介导的自噬可诱导人肝癌 Hep 3B 细胞凋亡,并增强肝癌细胞对 5-氟尿嘧啶的敏感性^[39-40]。季洪涛等^[41]研究发现,大蒜素通过降低细胞中线粒体膜电位,释放细胞色素 C、凋亡诱导因子等物质,可诱导人食管癌 EC-109 细胞凋亡。Li 等^[42]研究发现大蒜素通过降低信号转导及转录激活蛋白 3(signal transducer and activator of transcription 3, STAT3)活性可抑制小鼠结肠肿瘤的发生。李建波等^[43]发现,大蒜素通过 Wnt/β-catenin 信号通路抑制肺癌细胞生长、侵袭和迁移,并降低小鼠肺癌细胞增殖和淋巴结转移。综上所述,大蒜素可抑制多种肿瘤细胞增殖、转移,并促进肿瘤细胞凋亡,伴随大蒜素抗肿瘤功能和机制的深入研究,其有望为肿瘤预防和治疗提供新方法和新思路。

2.3 抗氧化作用

大蒜素中的二烯丙基硫化物、二烯丙基三硫化物等有机硫化物可与含硫蛋白质和谷胱甘肽发生氧化还原反应,从而抑制氧化应激,提高机体抗氧化能力^[44]。大蒜素通过激活沉默信息调节因子 1 (silent mating type information regulation 1, sirt 1) 保护人脐静脉内皮细胞(human umbilical vein endothelial cells, HUVEC)免受 H₂O₂ 诱导的氧化应激损伤,并延缓衰老^[45]。Nadeem 等^[46]研究发现,大蒜素与过氧化物酶直接作用,可下调还原型 β-烟酰胺腺嘌呤二核苷酸磷酸(reduced β-nicotinamide adenine dinucleotide phosphate, NADPH)氧化酶(NADPH oxidase, NOX)活性,降低细胞内活性氧(reactive oxygen species, ROS)的产生,抑制 Toll 样受体 4 (toll-like receptors, TLR)/接头蛋白髓细胞分化因子 88 (myeloid differentiation factor 88, MyD88)/核因子 κB (nuclear factor kappa B, NF-κB)、p38 丝裂原活化蛋白激酶(p38 mitogen-activated protein kinase, p38 MAPK)和 c-Jun 氨基末端激酶(c-Jun N-terminal kinase, JNK)的信号通路激活,从而改善神经炎症抗氧化能力。大蒜素可调控磷脂酰肌醇-3-激酶(phosphatidylinositol-3-kinase, PI3K)信号通路,减轻铅中毒鸡肝的氧化损伤

和细胞凋亡,提高鸡肝脏的抗氧化能力^[47]。此外,大蒜素抗氧化活性与浓度相关,当大蒜素浓度处于0.2~1.0 mg/mL时,随着大蒜素浓度的增加,其清除 DPPH 自由基、ABTS⁺自由基的能力呈现浓度依赖性^[48]。这些研究显示大蒜素可以通过多种途径保护细胞免受氧化损伤,提高机体抵抗力。

2.4 保护心脑血管作用

心血管病和脑血管病统称心脑血管病,具有“发病率高、复发率高、致残率高、死亡率高、并发症多”即“四高一多”的特点,是我国中老年人群的头号杀手。研究表明,大蒜素可有效预防、治疗心脑血管系统疾病。大蒜素通过增加心脏肥大(cardiac hypertrophy, CH)大鼠中血小板内皮细胞黏附分子的表达,改善 CH 大鼠心脏微血管内皮细胞的功能,从而为 CH 大鼠心脏提供保护^[49]。García-Trejo 等^[50]发现大蒜素下调 kelch 样 ECH 相关蛋白 1(kelch-like ECH-associating protein 1, Keap1)表达,增加核因子 NF-E2 相关因子 2 nuclearfactor erythroidderived 2-like 2, Nrf2)的表达,上调抗氧化酶活性,在高血压慢性肾病(chronic kidney disease, CKD)大鼠模型中具有降压、肾保护、心脏保护作用。此外,大蒜素通过抑制蛛网膜下腔出血后的细胞凋亡和氧化应激损伤,改善脑水肿和血脑屏障功能障碍^[51]。心血管疾病还与肠道菌群及其代谢产物密切相关,生大蒜汁和大蒜素能改善肠道微生物群的多样性,下调三甲胺-N-氧化物(trimethylamine N-oxide, TMAO)的产生,改善动脉粥样硬化,进而预防心血管疾病的发生^[52]。同时,大蒜素在扩张血管、改善血流灌注方面也具有一定促进作用,研究发现大蒜素上调烧伤创面组织一氧化氮合酶(nitric oxide synthase, NOS)的表达并降低病理状态下血管紧张素Ⅱ(angiotensinⅡ, AngⅡ)水平,提示大蒜素具有促进血管扩张的作用^[53]。上述研究结果表明,大蒜素通过不同机制保护心脏、扩张血管以及预防心脑血管疾病。

3 大蒜臭味来源及除臭研究进展

大蒜素在室温下不稳定,易分解为多种硫化物,是刺激性臭味的主要来源,其味道通常被描述为“刺鼻的”、“恶臭的”,严重限制了大蒜素的应用,并给日常食用者带来口气困扰^[13]。研究表明,水果、蔬菜、高脂及高蛋白食物等对大蒜具有一定的除臭效果。

3.1 水果在大蒜除臭中的研究应用进展

水果中含有丰富的多酚物质,并具有浓郁的芳香气味,其中多酚物质可中和硫化物,芳香气味在一定程度上掩盖大蒜臭味,从而减轻或消除大蒜的臭味。多种水果可用来去除大蒜气味,其中李子、柿子、桃子、枇杷、橘子、梨、葡萄、樱桃、猕猴桃、香蕉、蓝莓、柠檬已被证明可降低大蒜中挥发性物质的水平^[5]。其中柑橘类

虽具有良好的芳香气味,但其去臭效果并不理想^[5,54]。另外,有研究报道苹果具备高效除臭作用,且生苹果和苹果汁效果明显优于熟苹果,其机制可能是苹果中的多酚物质在氧化酶催化下与大蒜中硫化物反应,进而降低或消除大蒜臭味^[4]。有研究称柠檬中的绿原酸具有去除大蒜挥发性硫化物的活性,可降低大蒜臭味^[55]。综上,水果可一定程度上降低口腔中大蒜引起的硫化物挥发,进而减轻大蒜带来的臭味。

3.2 蔬菜在大蒜除臭中的研究应用进展

蔬菜作为餐桌常客,不仅营养成分丰富多样,也常常与大蒜共食,是较为理想的大蒜除臭物质来源。研究发现,欧芹、菠菜、生菜、薄荷、莴苣和茄子等蔬菜可显著去除大蒜臭味,其中以薄荷叶的除臭效果最佳^[5-6]。通过电子传感器、感官评估和气相色谱(gas chromatography, GC)分析,发现蘑菇提取物中含有大量多酚类化合物,可降低大蒜溶液中甲硫醇含量,进而减弱大蒜中挥发性气味^[7-8]。海带汁和半胱氨酸可有效减弱大蒜气味,海带中的硫胺素与大蒜素结合形成无味的蒜硫胺素,半胱氨酸可作用于蒜酶的活性部位,与其结合后形成稳定化合物,减弱蒜酶活性从而消除大蒜气味^[56]。管萃等^[57]研究发现,将大蒜素包埋于淀粉的螺旋空腔内形成相应的络合物,可抑制硫化物的挥发,减弱其臭味,同时保护了大蒜的营养成分和活性成分。综上所述,蔬菜在大蒜除臭效果中表现突出,但其机制和工艺有待进一步开发,以期提升大蒜制品利用提供有利条件。

3.3 高脂及高蛋白食物在大蒜除臭中的研究应用进展

大蒜素为亲脂性物质,理论上高脂、高蛋白类食物如牛奶、酸奶、花生等对大蒜应具有一定的除臭效果。Hansanugrum 等^[9]发现牛奶有助于减少食用大蒜后产生的臭味,且牛奶与大蒜一并食用的消除效果最佳,此外,全脂牛奶因其脂肪含量较高,降低二烯丙基二硫化物和烯丙基甲基二硫化物等疏水挥发性物质的效果较脱脂牛奶更为突出。Kaur 等^[10]研究发现,酸奶及其组分对大蒜具有除臭作用,其中乳清蛋白、酪蛋白等通过二硫键、氢键和疏水相互作用等方式,可降低挥发性硫化物的浓度,达到除臭效果。

3.4 其它物质在大蒜除臭中的研究应用进展

中草药作为我国传统医学瑰宝,其在大蒜除臭中也多有研究和应用。甘草、当归、金银花等中草药对大蒜气味具有一定的减弱和消除作用,其中甘草效果最好,甘草黄烷酮是甘草中的主要活性物质,可与硫化物发生反应^[11]。薄荷中某些成分和迷迭香酸协同作用,可有效减弱大蒜气味^[12]。蜂蜜含有丰富的果糖、麦芽糖、糊精等黏性物质,能紧密包裹大蒜形成的挥发性硫化物,在减少大蒜营养成分流失的同时,达到除臭的作

用^[58]。近年来发现黑孜然籽精油可与大蒜中的有机硫化物发生共价反应,有效削弱大蒜精油臭味^[59]。使用以上中草药剂制成漱口水、饮品或将其提取物与大蒜混合,可减轻大蒜味道,但并不能完全消除,因此对大蒜机制和有效成分的深入研究将有助于开发更有效的大蒜除臭产品。

4 小结与展望

大蒜被广泛应用于日常饮食和各类疾病防治中,大蒜素作为其主要活性成分,具有显著的抗病原微生物、抗肿瘤、抗氧化和预防心脑血管疾病等生物活性,且无明显副作用,是一种极具研究价值与开发前景的传统食材和药物,但由于大蒜素易分解为多种具有刺激性臭味的硫化物,严重限制了大蒜素的应用。本文着重介绍大蒜素的理化性质、药理作用、臭味来源,并总结水果、蔬菜、高脂和高蛋白类食材以及中草药等物质对大蒜除臭效果的研究与应用,其除臭机制多归于多酚类物质与硫化物发生反应、多酚氧化酶氧化硫化物和分子间的物理或化学相互作用。目前去除大蒜素臭味的方法还未完善,利用食物或食物提取物对大蒜素除臭虽能保持大蒜的营养和生物活性,但除臭效果并不显著。日后,仍需对大蒜素及各类物质的除臭机制进行深入研究,从分子机制、剂型、剂量和联合应用等多个角度进一步优化除臭工艺,突破大蒜应用的瓶颈问题,为提升大蒜制品的应用提供有利支撑。

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