

专家论坛专栏

编者按:麻辣是一种受人喜爱的刺激口味,在烹饪麻辣食品时,辣椒和花椒是不可或缺的两种香辛料。研究发现,辣椒和花椒不仅可以为美食增色添香,还含有对人体有益的生理活性成分,有助减肥、降脂、降糖。为此,本期栏目特邀专家对辣椒和花椒中含有的生物活性物质及其生理功效进行系统阐述,希望为我国天然香辛料的深入研究和开发提供有益借鉴和帮助。

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花椒麻味物质的生理作用研究进展

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摘 要:花椒(*Zanthoxylum bungeanum*)是芸香科(*Rutaceae*)花椒属(*Zanthoxylum* L.)植物的果实,其果皮名为“椒红”,是我国传统的“八大调味品”之一,也是我国传统的中药配料,具有温中散寒、除湿、杀虫、止痛等作用。花椒在我国种植面积和产量居世界第一,作为农业产业结构调整 and 退耕还林的优选经济树种,集生态效益、社会效益和经济效益于一身,近年来其种植面积以20%~30%的速度逐年增加。花椒的药用价值早已得到认可,现代医学研究认为花椒具有抗氧化、杀虫、麻醉、抗炎镇痛、降血脂、除皱、抗癌、祛风除湿等多种作用,而花椒麻素作为花椒中特有的生物活性成分,其生理功效的评价也已成为现代医学的研究热点,但目前大多研究还停留在花椒麻味物质生理作用效果的初步研究水平,没有对其生理作用机制进行深入的研究,导致目前对花椒的开发还多限于食用方面,在新药和日用化工等的开发和利用方面仍不足。因此,对花椒中麻味物质的主要种类、麻味物质的生理作用两个方面的国内外研究进展进行综述,旨在为麻味物质进一步系统深入的研究提供一定参考。

关键词:花椒;麻味物质;生理功能;种类

中图分类号:TS201.2

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花椒(*Zanthoxylum bungeanum*)是芸香科(*Rutaceae*)花椒属(*Zanthoxylum* L.)植物的果实,其果皮名为“椒红”,是我国传统的“八大调味品”之一,也

是我国传统的中药配料,具有温中散寒、除湿、杀虫、止痛等作用^[1]。目前,我国花椒已形成年产值约100亿元的巨大产业,每年以20%~30%的速度不

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断增加,并已形成了重庆的江津、酉阳,四川的金阳、汉源,山东的泰安、莱芜,甘肃的武都,陕西的韩城,山西的芮城等全国闻名的花椒产业基地,已成为当地农业的支柱产业和农民脱贫致富的一条好途径。花椒在全世界约有 250 个种,主要分布于非洲、亚洲、美洲及大洋洲的热带和亚热带地区,中国约有 45 个种,13 个变种。中国大面积人工栽培的花椒品种从果皮颜色分主要是青花椒 (*Z. schinifolium* Sieb. et Zucc, 又名青川椒、崖椒、野椒、香椒子) 和红花椒 (*Z. bungeanum* Maxim., 又名川椒、秦椒、蜀椒、大红袍等)。从品种上分主要有:1) 大型花椒,如大椒、狮子头、大红袍、正路椒、娃娃椒。2) 小型花椒,如小椒、小红椒、小黄金、茂椒、豆椒、火椒等。3) 其他花椒,如秋杂椒、白沙椒、高脚黄、枸椒、臭椒等。我国花椒以陕西韩城为代表的大红袍,以四川茂汶、汉源为代表的正路椒,以四川的金阳和重庆江津为代表的青椒,以及遍及各地的枸椒等品种为主,其中种植面积和产量大红袍占 45%,青花椒占 25%,正路椒占 10%,枸椒占 20%。

花椒果皮的化学成分主要有挥发油、生物碱、酰胺、香豆素、脂肪以及黄酮等。本课题组曾对全国 141 份花椒样品进行分析,发现花椒果皮中挥发油的含量为 1.19 ~ 7.54 mL/100 g,平均值为 3.69 mL/100 g,主要为烯烃类、醇类、酮类、环氧化合物类及酯类,构成了花椒特有的香气^[2],同时红花椒的挥发油含量普遍比青花椒的低^[3]。因此,曾有人作过这样的比喻:“红花椒像是大家闺秀,热情而奔放;青花椒像是小家碧玉,清丽而淡雅”。

1 花椒麻味物质概述

经过笔者研究团队及其他科研人员的研究发现,构成花椒麻味的化合物主要是一系列酰胺类物质,包括山椒素(sanshool)等 25 种化合物^[4-8],是链状不饱和脂肪酸酰胺,均具有强烈的刺激性^[9-10],因此,这类物质被称为“花椒麻味物质”或“花椒麻素”,他们的分子结构见图 1^[11]。随着现代分离及其检测技术的发展,花椒麻素的种类还在不断被发现。研究表明,花椒麻素在 -20 ℃ 石油醚中可结晶析出,为白色晶体,易溶于热石油醚、微溶于水。花椒麻素在常温下极不稳定,短暂暴露于空气中即可发生氧化或聚合反应而形成深色的黏稠膏状物质,但其反应机制尚不清楚。本课题组在对全国 141 份

花椒样品进行分析时发现,花椒果皮中酰胺类物质的含量为 1.27 ~ 20.11 mg/g,平均值为 11.96 mg/g^[12]。

2 花椒麻味物质的生理作用

据《本草纲目》中记载:“椒,纯阳之物,其味辛而麻,其气温以热。入肺散寒,治咳嗽,入脾除湿,治风寒湿痹,水肿泻痢;入右肾补火,治阳衰洩数,足弱,久痢诸证”。花椒的药用价值早已得到认可,而花椒麻素作为花椒中特有的生物活性成分,其生理功效的评价已成为现代医学的研究热点^[13-16]。

2.1 降血糖血脂作用

2014 年,陈朝军等^[17]发现灌胃质量比为 1:8、2:7 和 3:6 的花椒麻素与辣椒素均能延缓大鼠的体重增加,降低大鼠的血脂和肝脂水平,减轻大鼠的脂肪肝症状,对胆固醇代谢循环有较好效果;另外,灌胃花椒麻素和辣椒素后,可增加实验大鼠粪便中胆汁酸含量,下调回肠中 ASBT 和 BABP mRNA 表达量,上调 FXR mRNA 表达量^[18]。吕娇^[19]研究表明,分别以 4 mg/(kg·d)的花椒麻素组、去挥发油组、残渣组持续灌胃高脂血症大鼠 28 d 后,花椒麻素可升高高脂血症大鼠回肠 FXR mRNA 表达量和降低试验大鼠肝脏 CYP7A1 mRNA 表达量,调节胆固醇在体内的代谢循环。任文瑾^[20]研究表明,花椒精、花椒挥发油和花椒麻素均有调节血脂的作用,作用效果由大到小依次为花椒麻素(4 mg/(kg·bw))、花椒精(15 mg/(kg·bw))、花椒挥发油(9 mg/(kg·bw))、花椒麻素对肝脏胆固醇代谢的调节效果显著高于其他组。游玉明等^[21]以高脂膳食大鼠为模型,分别灌胃花椒油树脂(15 mg/(kg·bw))、花椒挥发油(9 mg/(kg·bw))、花椒麻素(4 mg/(kg·bw)) 28 d 后发现,花椒麻素可显著降低高脂膳食大鼠血清及肝脏中胆固醇(TC)和甘油三酯(TG)含量,增加粪便中胆汁酸及中性固醇含量,有效下调肝脏和回肠中 3-羟基-3-甲基-戊二酰 CoA 还原酶(HMG-CoAR)及回肠胆盐转运蛋白(ASBT)等基因 mRNA 表达,显著上调肝脏 7 α -羟化酶(CYP7A1)及回肠法尼酯受体(FXR)mRNA 表达。花椒麻素对高脂膳食大鼠脂质代谢紊乱有良好的改善作用。

以 STZ 糖尿病大鼠模型,持续灌胃 9 mg/(kg·bw)、6 mg/(kg·bw) 和 3 mg/(kg·bw)的花椒麻素 28 d 后发现,花椒麻素可显著上调糖尿病大鼠肝脏中 GK 和 TRPV1 的表达,同时显著下调了大鼠肝脏中

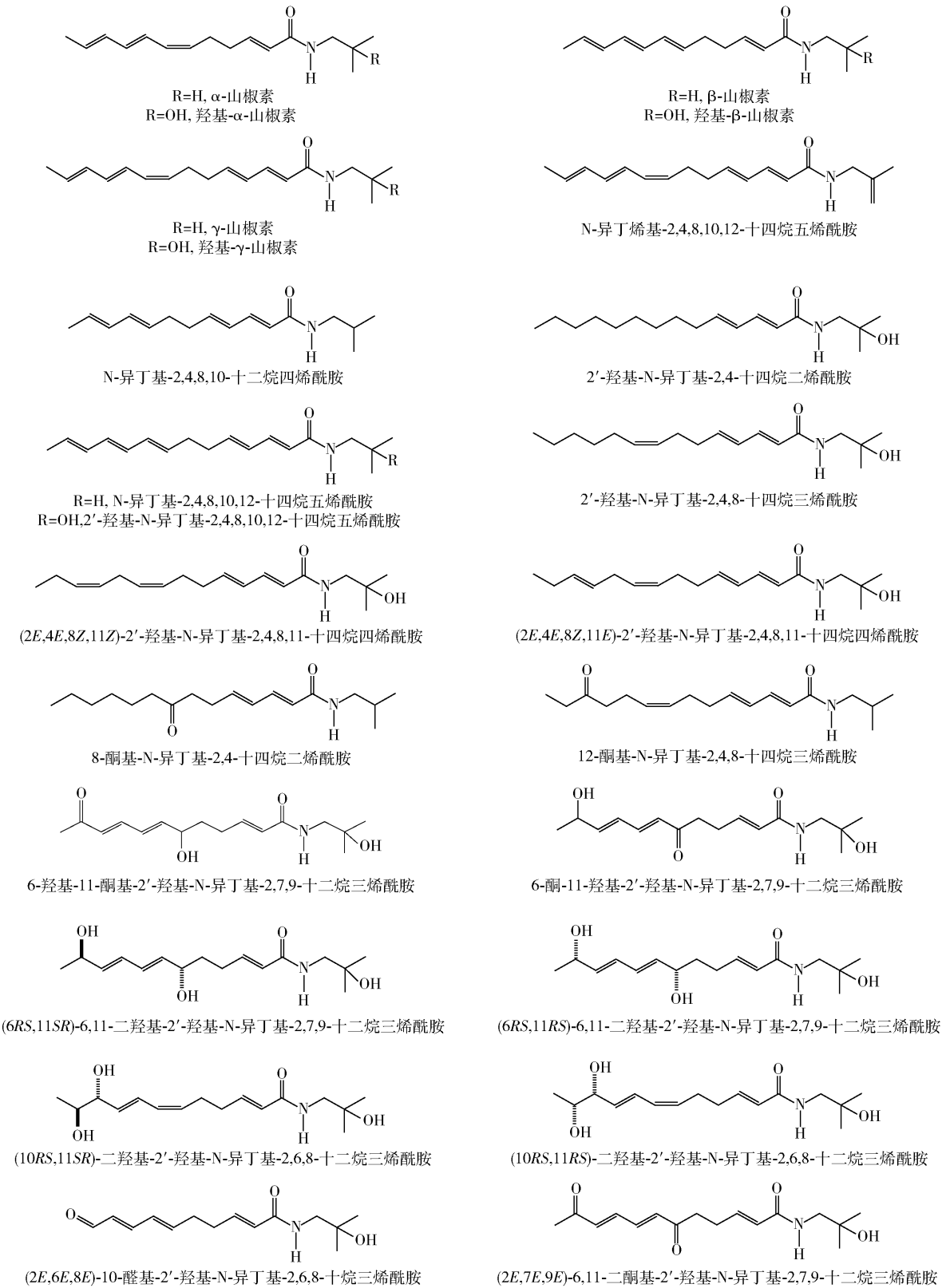


图 1 花椒麻素的主要分子结构

Fig. 1 Main alkylamides found in *Zanthoxylum bungeanum*

糖异生关键酶 PEPCK 和 G6Pase 的表达。此外,花椒麻素还可显著上调糖尿病大鼠胰腺中与胰岛素分泌相关的 PDX-1、GLUT2、GK 及其 TRPV1 的表达,并能下调大鼠肝脏及胰腺中 CB1 的表达^[22]。以上

结果表明,花椒麻素改善糖尿病大鼠糖脂代谢紊乱的可能机制是通过抑制糖异生作用,减少肝糖的输出,并能修复胰岛功能,促进胰岛素的分泌。另外,花椒麻素既是 TRPV1 受体的激活剂,也是 CB1 的拮抗剂,激活的 TRPV1 受体可通过上调 GLUT4 的表达,改善糖尿病大鼠糖脂代谢紊乱^[23]。

2.2 胃肠道保护作用

肠道微生物每天消耗约 60% ~ 80% 进入大肠的多糖、低聚糖、蛋白质、肽和糖蛋白等未消化残渣,肠道微生物可利用这些残渣合成必需氨基酸,如天冬氨酸、苯丙氨酸、缬氨酸和苏氨酸等,并参与机体蛋白质代谢^[24]。花椒麻素 (25 ~ 100 $\mu\text{g/mL}$) 在大鼠肠道的吸收过程属于一级动力学过程,属被动转运,吸收部位主要是空肠和回肠^[25],而肠道菌群种类繁多,数量是人体细胞的 10 倍,包含的宏基因组更是达到 100 多倍。近年来的研究发现,肠道微生物组可参与机体蛋白质和糖类代谢,被认为是人体的“第二基因库”^[26]。Hashimoto 等^[27]探讨了山椒素对胃肠动力的影响,结果表明,花椒麻素可显著松弛胃体环形肌,可收缩结肠远端和回肠的纵行肌;可增加肠道缺血段的血流量,促进内源性肾上腺髓质素 (ADM) 的释放,改善肠道微血管循环障碍的作用。另外,花椒麻素能诱导迷走神经释放内在的乙酰胆碱和感觉神经元释放速激肽 (tachykinin),促进小肠蠕动。Tokita 等^[28]研究发现,羟基- α -山椒素及羟基- β -山椒素可能通过促进 P 物质、5-羟色胺和前列腺素 E2 等的分泌,从而促进肠道平滑肌细胞的收缩。此外,山椒素可通过调节 TRPV1 mRNA 表达量治疗术后肠粘连。Kono 等^[29]研究表明, α -山椒素具有改善克罗恩病 (Crohn's disease) 大鼠结肠微血管循环障碍的作用。

2.3 麻醉作用

花椒有较强的麻醉作用,临床上已将花椒麻素作为口腔科的安抚剂广泛使用。Tarus 等^[30]用花椒麻素涂抹于舌部 30 s 后,舌部麻木感显著,可持续 20 ~ 80 min,充分证明了花椒麻素是花椒产生麻醉作用的物质基础。Etsuko 等^[31]研究表明,服用 5% 花椒麻素的蔗糖溶液后,可产生强力的麻刺感和灼热感。花椒麻素的麻醉特性与其种类有关,其中羟基- α -山椒素局部麻醉作用比羟基- β -山椒素和羟基- γ -山椒素强,其半数有效量 (50% effective dose, ED_{50}) 低于利多卡因和丁卡因,接近于普鲁卡因^[32-33]。另外,一定浓度的花椒提取物可抑制蟾蜍

离体坐骨神经冲动的传导和兴奋性,降低神经干兴奋性^[34]。由此可见,花椒麻素具有潜在外用延长性交时间的作用。

2.4 消炎镇痛作用

Pereira 等^[35]研究表明,花椒麻素可显著减轻由福尔马林和辣椒素引起的疼痛。3 ~ 6 mL/kg 醚提物比 5 ~ 10 g/kg 水提物抑制小鼠因乙酸引起的扭体反应效果显著^[36]。Tsunozaki 等^[37]研究表明,花椒麻素可通过抑制 A δ 机械痛觉感受器上的电压门 Na⁺ 通道的兴奋达到镇痛效果。

2.5 抗肿瘤作用

You 等^[38]研究表明,花椒麻素对 HepG2 细胞的抑制作用具有明显的时间-剂量依赖效应,其不同浓度处理的 HepG2 细胞,可显著观察到 HepG2 细胞凋亡特征。Hashimoto 等^[27]研究表明,花椒麻素可减缓胃癌细胞周期循环,能有效调节胃癌细胞周期的失控。Chou 等^[39]研究表明,花椒麻素可有效引起试验鼠白血病细胞 WEHI-3 细胞和宫颈癌细胞 HL-60 DNA 损伤,诱导细胞凋亡,具有抑制白血球细胞的生物活性。花椒麻素具有抑制 NF1 缺陷型肿瘤细胞增殖的作用^[40]。Kyoung 等^[41]研究表明,花椒麻素对肺癌细胞 A549 仅有微弱的细胞毒性。

2.6 影响蛋白质代谢作用

糖尿病不仅引起体内血糖、血脂水平的升高,而且会引起机体内蛋白质代谢紊乱^[42]。花椒麻素具有促进胰岛素的分泌,而胰岛素则可通过激活 PI3K/Akt/mTOR 信号通路促进组织蛋白质合成,抑制蛋白质分解的作用^[22,43-44]。任廷远^[45]和 Ren 等^[16,46]运用大鼠动物在体实验,采用 qPCR 和 western-blot 等技术从核酸水平和蛋白水平研究了花椒麻素对不同体质 (健康、糖尿病-I 型) 大鼠个体的机体内蛋白质合成代谢的 mTOR 途径、AMPK 途径和分解代谢的 UPP 途径的影响,研究结果表明,花椒麻素对不同体质 (健康、糖尿病-I 型) 大鼠个体的机体内蛋白质合成的影响及机制存在差异。对健康大鼠的影响主要是增加相对骨骼肌重量、降低腹脂率;增加血清和组织 IGF-I 含量 ($p < 0.05$),而对 Ins 的影响不显著 ($p > 0.05$);促进机体内相应 α -酮酸的合成;并以 IGF-I $\rightarrow$ PI3K $\rightarrow$ PKB 信号途径激活 mTOR,而对氨基酸/氨基酸转运载体的信号途径和 AMPK 途径的影响不显著 ($p > 0.05$)。对糖尿病大鼠的影响主要是增加相对骨骼肌重量;不仅显著 ($p < 0.05$) 增加血清 Ins 含量,而且血清和组织中 IGF-I

含量同样显著($p < 0.05$)增加;可激活 AMPK 途径;糖尿病大鼠骨骼肌蛋白质合成增强是 mTOR 途径和 AMPK 途径的综合结果,而且 Ins/IGF-I $\rightarrow$ PI3K $\rightarrow$ PKB 途径占主导地位。虽然花椒麻素对不同体质(健康试验 SD 大鼠,糖尿病试验大鼠)蛋白质合成的信号途径均为 PI3K $\rightarrow$ PKB $\rightarrow$ mTOR。但两者又存在差异,在健康 SD 大鼠体内,花椒麻素激活 PI3K $\rightarrow$ PKB $\rightarrow$ mTOR 途径的信号因子为 IGF-I;而在糖尿病试验大鼠机体内,花椒麻素激活这一信号途径信号因子是 Ins 和 IGF-I 共同作用结果。结合相关文献可知,花椒麻素对健康 SD 试验大鼠主要体现为促进蛋白质合成;花椒麻素对糖尿病试验大鼠不仅促进蛋白质合成,而且对机制蛋白质分解具有抑制作用。

2.7 其他作用

近年来的研究表明,花椒麻素还具有抗氧化和除皱等功能。花椒麻素具有较强清除自由基的能力,一定剂量的花椒麻素可提高 HepG2 细胞内 SOD 酶活性,降低 MDA 的含量^[47]。Artaria 等^[48]研究结果表明,花椒麻素具有长期除皱效果,可作为一种新的化妆品成分开发。Chen 等^[49]人研究发现花椒麻素具有凝血功能,花椒麻素 5 位上的碳链中双键数量越多,抗血小板凝集活性效果越差。另外,花椒麻素对赤拟谷盗成虫有较好的驱避效果,且表现出剂量效应关系^[50-51]。

3 结 语

花椒麻味物质具有多种生理活性作用,如抗氧化、杀虫、麻醉、抗炎镇痛、降血脂、除皱、抗癌、祛风除湿等多种作用,但目前大多研究还停留在花椒麻味物质生理作用效果的初步研究水平,没有对其生理作用机制进行深入的研究,导致目前对花椒的开发还多限于食用方面,在新药的开发和利用方面仍不足。如对花椒麻味物质的生理作用进行更深入、全面的研究,必将推动花椒在医药、日用化工、农药方面开发利用,大大提高花椒的附加值。

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Study on Key Flavor Compounds in Fermented Milk Production of *Streptococcus thermophilus* Isolated from Different Areas

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Abstract: The key flavor compounds of fermented milk produced by six strains of *S. thermophilus* isolated from different regions were analyzed by solid phase microextraction-gas chromatography-mass spectrometry (SPME - GC - MS) technology, combined with aroma threshold and relative odor activity value (ROAV). The results showed that the total of 63 volatile compounds were finally detected in these fermented milk, including aldehydes, ketones, acids, esters, alcohols, aromatics, and hydrocarbon compounds. Among them, 12 kinds of volatile compounds, such as diacetyl, acetoin, acetaldehyde, and 2-nonanone had higher ROAV ($\text{ROAV} \geq 1$), which contributed greatly to the overall flavor of fermented milk. Principal component analysis and comparative analysis of similarity demonstrated that there was a high similarity among the flavor compounds of *S. thermophilus* fermented milk from the same area while that from different regions was lower. The results indicated that the pressure of growth environment can exert an influence on the aroma-producing characteristics of the fermented milk of the strain.

Keywords: volatile flavor compounds; *S. thermophilus*; relative odor activity value; chromatographic fingerprinting; principal component analysis

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Review on Physiological Function of Alkylamide Compounds from *Zanthoxylum bungeanum*

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Abstract: *Zanthoxylum bungeanum*, belonging to *Rutaceae* family and *Zanthoxylum* L. genus, is one of the traditional “eight major condiments” in China, which is an important ingredient in many kinds of traditional Chinese medicines due to the functional activities of cold-dispelling, dehumidification, anaesthesia, and acesodyne. China has the highest planting area and yield of *Zanthoxylum bungeanum*. As the economic tree plants, *Zanthoxylum bungeanum* has the ecological, social, and economical benefits. Recently, the planting area of *Zanthoxylum bungeanum* has been increasing at the speed of 20% ~ 30%. It has been widely accepted that *Zanthoxylum bungeanum* has diversely medical functions, such as antioxidant activities, insecticidal activities, anaesthesia, anti-inflammatory and analgesic, hypolipidemic, removing wrinkles, anticancer, and so on. As the special functional ingredients, alkylamide compounds (or hemp flavor substance) possess many biological properties. However, the mechanism of these biological properties were not fully understood. Therefore, *Zanthoxylum bungeanum* has not been fully applied in medicines and daily chemical products. This review summarizes updated researches on the main species of alkylamide compounds in *Zanthoxylum bungeanum* and their respective physiological functions in order to provide necessary reference for the further systematic study.

Keywords: *Zanthoxylum bungeanum*; alkylamide compounds; physiological function; types

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