

高静水压加工对果蔬酚类化合物的影响研究进展

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摘要: 高静水压是一种典型的非热加工技术, 因其能有效保留食物中的营养物质和热敏性活性成分(如维生素和植物多酚), 以及维护果蔬活性成分的多种功能活性, 在高品质果蔬类产品的生产加工中极具发展潜力。酚类化合物是果蔬中分布最为广泛的一类植物次生代谢产物, 并具有一定的生理学特性。大量研究证实, 增加酚类化合物的摄入量能有效降低多种慢性疾病的发病率, 因此, 酚类化合物愈来愈成为天然产物领域的研究热点。本文综述了高静水压加工对果蔬酚类化合物含量、结构以及抗氧化、抗炎活性的影响, 旨在为高静水压技术在高活性果蔬产品中的应用提供参考。

关键词: 高静水压; 果蔬; 酚类化合物; 生物活性

Effects of High Hydrostatic Pressure Processing on Phenolic Compounds in Fruits and Vegetables: A Review

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Abstract: High hydrostatic pressure (HHP), a typical non-thermal technology, has great potential in the processing of fruit and vegetable products with high quality, because it can maintain nutrients and thermo-sensitive bioactive compounds, such as vitamins and polyphenols in foods, as well as maintain the functional activities of bioactive ingredients in fruits and vegetables. Polyphenols are among the most ubiquitous groups of secondary metabolites in fruits and vegetables, which have many pharmacological characteristics. A large number of studies have confirmed that increasing intake of polyphenols can reduce the incidence of chronic diseases. Therefore, polyphenols are increasingly becoming a research hotspot in the field of natural ingredients. In this article, we review the effects of HHP on the contents, composition, and antioxidant and anti-inflammatory activities of polyphenols in fruits and vegetables in order to provide a basis for the application of HHP in the processing of fruits and vegetables.

Keywords: high hydrostatic pressure; fruits and vegetables; polyphenols; bioactive activity

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众所周知, 果蔬类食品除了提供必需的维生素、矿物质、类胡萝卜素和膳食纤维外, 还含有多种生物活性物质, 如酚类化合物。酚类化合物本身是一种植物激

素, 直接影响植物的色泽、风味、香气等^[1]。流行病学研究表明, 膳食中增加果蔬及其制品摄入量可有效降低代谢综合征、糖尿病、非酒精性脂肪肝和心血管疾病

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等慢性疾病的风险,这与果蔬中含有的酚类化合物密切相关^[2-3]。热处理是果蔬类产品加工中最为普遍的工艺技术,其对酚类化合物的稳定性及活性的发挥构成威胁。苹果汁中原花青素热敏性最差,受热水解为(+)儿茶素、(-)表儿茶素和原花青素B₂^[4]。高静水压作为一种典型的非热加工技术,在高品质、高营养果蔬制品的生产加工中具有广阔应用前景。高静水压处理能更好地保留果蔬酚类化合物,因此本文就高静水压对果蔬酚类化合物含量、结构以及抗氧化、抗炎活性的影响展开论述。

1 高静水压处理在果蔬加工中的应用

高静水压即超高压技术,是一种以水为介质,在室温或温和条件下以100~1000 MPa处理原料的非热加工技术^[5]。以这种方式处理的食物能最大程度地保留其原有的新鲜度、风味和颜色^[6]。高静水压能破坏细胞组织、灭活微生物,其在果蔬加工中主要用于灭菌、提高生物活性成分萃取率、钝化酶活力等方面,此外还具有保持食品形状^[7],改善果蔬颜色、质构及风味^[8],促进果酒理化和感官特性变化^[9]等作用(表1)。该技术作为一项食品保鲜技术,也被用于增强活性成分功能或开发新产品。

1.1 灭菌

与传统热处理相比,高静水压不改变共价键,只影响弱的静电相互作用和细胞微结构^[10],对低分子质量化合物如维生素、色素和其他营养成分影响有限,所以能更好地保持食品的色泽、风味和营养,用于食品微生物灭活,特别适用于热敏产品。高静水压通过影响蛋白质和酶结构,或者改变食品体系的pH值来提高杀菌效率^[11],降低微生物细胞的活力。用于食品的高压设备通常采用室温下600 MPa处理几分钟,杀菌效果接近“冷巴氏杀菌”,不能完全杀菌,因为细菌孢子对压力具有一定的抵抗性,所以高静水压不能完全取代热杀菌,但高压可结合70~130 °C的热处理灭活细菌孢子^[12]。

1.2 活性成分萃取

植物细胞壁中多糖(纤维素、半纤维素和果胶)组分阻碍细胞内生物活性成分(如植物酚类化合物)释放。高压破坏膜结构,有利于从植物组织中释放酚类化合物、 β -胡萝卜素等活性成分。如600 MPa显著增加了甘薯粉 β -胡萝卜素的萃取率^[13]。高静水压作为天然生物活性物质的冷萃取方法,压力水平是萃取过程中最重要的参数之一,其与生物活性成分溶解度直接相关。有研究表明,压力对细胞器和细胞有直接机械破坏作用^[14],随着压力的增加,可溶性成分溶解度增加,萃取物平衡浓度提高^[15];同时,高强度压力还会引起细胞形变、蛋白质变性等变化^[16],也有利于生物活性成分的萃取。高静水压在提高生物活性成分萃取率方面具有潜在优势。

1.3 调节酶活力

高强度的高静水压处理会导致蛋白质变性,许多酶如多酚氧化酶(polyphenol oxidase, PPO)、过氧化物酶(peroxidase, POD)因发生不可逆变化而丧失功能。而高静水压温和处理可以激活酶活力,因为压力条件下酶的可逆构型有利于酶释放第二个活性中心或与底物发生相互作用^[17]。食品体系中酶的失活程度可能与处理条件和原料有关。高静水压也可与其他技术联用,如与温和热处理结合或与二氧化碳联用促进酶的失活^[12,18]。

1.4 提高产品品质

高静水压可以提高果蔬硬度,这与压力条件下果胶甲酯酶活性增强有关。压力导致细胞分裂,花青素、色素等渗入细胞间隙,使得果蔬产品颜色加深。由于压力在果蔬表面均匀且瞬间传递,因此不会对果蔬组织造成过度损伤^[19]。此外,高压还可促进红葡萄酒在贮藏过程中美拉德反应的发生和酚类物质的聚合,利于葡萄酒色泽、风味的形成^[9]。因此,高静水压在果蔬加工中可用于提高产品品质。

表1 高静水压处理在果蔬加工中的应用
Table 1 Application of high hydrostatic pressure in processing of fruits and vegetables

应用	果蔬	高压条件	优势	劣势	参考文献
灭菌	蓝莓	100~700 MPa/ 40~121 °C	灭活微生物和孢子	压力下花青素热稳定性降低,加速花青素降解	[20]
	石榴	350~550 MPa/ 30~150 s	减少腐败菌,延长保质期,保持色泽和抗氧化活性	对感官和营养特性的影响有待进一步研究	[21]
	桑葚	500 MPa/5 min	灭活微生物,增加贮藏稳定性,较好地保留总花青素、总酚含量、抗氧化活性、颜色和流变特性	高压二氧化碳杀菌效果较差	[22]
成分萃取	草莓	30、50、70、 90 MPa/5 min	促进酚类化合物的释放,不同酚类压力敏感性不同,压力对理化性质影响不显著	不能提高所有酚类化合物的含量	[23]
	桑葚	200、400、 600 MPa/20 min	增加矢车菊素3-O-葡萄糖苷含量,200、400 MPa/20 min,形成新的花青素	—	[24]
	猕猴桃	500 MPa/20 min	显著提高总酚含量和抗氧化活性	—	[25]
	番茄	450~650 MPa/5~15 min	提高抗氧化能力	大多数酚酸含量下降	[26]
	桑葚	135~595 MPa/ 2.5~32.5 min	降低PPO、POD活性,较好地保留花青素	—	[27]
钝化酶活力	红树莓和草莓	400、600、 800 MPa/15 min	降低与花青素降解有关的酶活性	PPO和 β -葡萄糖苷酶不能完全失活	[28]
	胡萝卜和菠菜	100、300、 500 MPa/20 min	钝化PPO活力,较好地保留抗坏血酸和类胡萝卜素,增强抗氧化活性	菠菜POD活力随压力增加而增加,压力会破坏胡萝卜、菠菜微观结构	[29]
	果蔬沙拉	630 MPa/6 min	灭活微生物,降低果胶甲酯酶、POD、PPO活力,保持较高的抗氧化活性	—	[30]
提高产品品质	蓝莓	400、600 MPa/1~5 min	保持硬度、颜色及抗氧化活性	造成蓝莓组织损伤	[19]
	葡萄酒	500~600 MPa/5~20 min	降低苦味和涩味,增强持久性	果香味较弱,酚类化合物减少	[31]

注:—文献未提及。

2 果蔬酚类化合物

酚类化合物是植物在对抗病原体过程中产生的植物次生代谢物,以共轭形式存在,如糖苷^[32],或通过醚和/或

酯键与细胞壁结构组分(纤维素、半纤维素、木质素、果胶、蛋白质)结合,主要功能是提供抵抗紫外线辐射的保护^[33]。酚类化合物可以作为天然抗氧化剂、抗菌剂、抗辐射保护剂和细胞壁成分等^[34];然而酚类化合物不能在人或动物机体中合成,只能通过食物摄取,作为抵抗氧化应激的外源抗氧化剂。

2.1 种类和含量

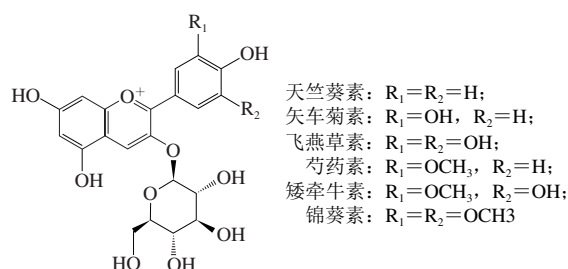


图1 不同花青素的化学结构

Fig. 1 Chemical structure of different anthocyanins

果蔬中酚类化合物有类黄酮、酚酸、香豆素、丹宁等,主要位于细胞液泡中,其中花青素(类黄酮)含量较为丰富,有天竺葵素、矢车菊素、飞燕草素、芍药素、矮牵牛素和锦葵色素等6种主要存在形式^[35](图1)。蔬菜中不含酰基和只有一两个单糖结构的简单花青素占总花青素的16%,水果中相应比例为74%;蔬菜中约70%的花青素含有一个或多个芳香酰基,而水果中只有11%^[36]。花青素B环中3,4-二羟基取代基是清除自由基的关键,易与羟自由基($\cdot OH$)、叠氮自由基($N_3\cdot$)和过氧自由基($ROO\cdot$)等反应^[37]。酚酸抗氧化活性主要归因于分子中的邻二羟基或3-OH取代基和烷基,能提高酚酸亲脂性和螯合能力^[38]。果蔬酚类化合物含量和组成差异可能取决于内在因素,如不同属、种或品种,以及外部因素如果实采收时间、位置、环境因素、加工条件和贮藏条件等^[39]。此外,提取方法或分析方法也会影响酚类化合物的种类及含量。

2.2 抗氧化、抗炎活性

果蔬之所以有利于人体健康,其中的酚类化合物发挥着非常重要的作用。一方面,酚类化合物可直接作为抗氧化剂,防止低密度脂蛋白氧化、血小板聚集和红细胞损伤^[40],或者通过减少细胞DNA氧化损伤间接抑制细胞癌变和肿瘤细胞增殖^[41]。还可以通过调节氧化应激敏感的核转录因子,如核因子 κB (nuclear factor kappa B, NF- κB),减少心脑血管疾病相关动脉粥样硬化的发生^[42];另一方面,酚类化合物具有抗炎作用,其重要机制是抑制类二十烷类生成酶——脂氧合酶(lipoxygenase, LOX)和环氧合酶(cyclooxygenase, COX)活性^[43],由这些酶催化的多不饱和脂肪酸,特别是花生四烯酸的转化产物可能增加许多疾病的风险。酚类化合物还可以通

过干扰NF- κB 、丝裂原活化蛋白激酶等炎症信号,或者抑制促炎细胞因子来抑制炎症反应^[44]。因此,果蔬酚类化合物通过有效抑制LOX、COX活力,调节相应信号通路或细胞因子起到抗炎作用。此外,酚类化合物还具有抑制癌症、心脑血管疾病和代谢紊乱等功能活性^[44-45]。

3 高静水压处理对果蔬酚类化合物的影响

3.1 对果蔬酚类化合物含量的影响

一定程度的高静水压能触发果蔬组织氧化应激反应,产生 H_2O_2 、诱导与丙二醛形成相关的脂质过氧化,从而影响酚类化合物代谢^[10,46]。具体的,100 MPa的压力可诱导植物组织中氧化应激,激活与次生代谢产物(如酚类化合物)生物合成相关代谢途径;150~200 MPa处理可引起细胞壁破坏和膜通透性改变,代谢活性逐渐降低^[10]。高静水压处理后番木瓜 H_2O_2 含量随压力增加而显著增加($P<0.001$);并且压力和时间对丙二醛水平都有显著影响^[47]。

高静水压处理通过破坏细胞组织,促进酚类化合物的释放。因为高压能引起带电基团的去质子化,破坏疏水键和盐桥,导致膜蛋白形态变化和变性,有利于酚类化合物渗透到细胞膜外,从而提高萃取率^[48]。如高压处理嘉宝果(jabuticaba),总酚含量增加38%^[49];一定压力处理草莓果酱后,天竺葵素-3-葡萄糖苷和天竺葵素-3-芦丁苷含量较传统热处理更为丰富^[50],除花青素外,还保留了9种酚类物质:儿茶素、鞣花酸、 β -羟基苯甲酸、对香豆酸、阿魏酸、咖啡酸、山萘酚、槲皮素及杨梅素^[6]。Hana等^[51]研究发现高静水压对龙眼中柯里拉京(corilagin)(一种水溶性鞣质)具有良好的选择性。500 MPa处理后,柯里拉京含量为9.6 mg/g m_d ,高于传统溶剂提取法得到的2.3 mg/g m_d (30 °C下用50%乙醇提取30 min)。

高静水压处理有利于提高果蔬中酚类化合物的贮藏稳定性,并促进酚类化合物释放。400~600 MPa高压处理杨梅,花青素保留量在98%以上。4 °C贮藏期间,花青素降解符合一级动力学变化,其降解速率随处理压力的增大而降低^[52]。高压处理后的橙汁也具有相似的特性^[53]。说明高静水压处理可以提高果汁花青素稳定性。

3.2 对果蔬酚类化合物结构的影响

压力可能改变酚类物质结构,形成新化合物。研究发现,600 MPa、70 °C处理葡萄酒模型溶液(葡萄酒陈化过程)30 min,矢车菊素3-O-葡萄糖苷(cyanidin 3-O-glucoside, Cy3gl)降解约25%,并且生成vitisin A衍生物(图2),有助于葡萄酒变红。热加压下葡萄酒中的锦葵色素-3-O-葡萄糖苷(malvidin-3-O-glucoside)含量减少,花青素单体降解,同时高分子质量产物含量增

加。花青素降解时首先去糖基化形成查耳酮,再生成各种苯甲酸衍生物,如原儿茶酸、2,4-二羟基苯甲酸等^[54-55]。高效液相色谱分析显示,200 MPa处理桑葚20 min,形成两种新花青素:飞燕草素-3-*O*-香豆酰葡萄糖苷和天竺葵素-3-*O*-香豆酰葡萄糖苷(图3);但在400 MPa/20 min处理条件下,仅生成飞燕草素-3-*O*-香豆酰葡萄糖苷^[24]。由于压力变化而导致花青素结构差异的主要原因是压力通过影响非共价键,导致羟基和氢氧化物离子在苷元氰化物上发生重排,从而形成新的花青素。

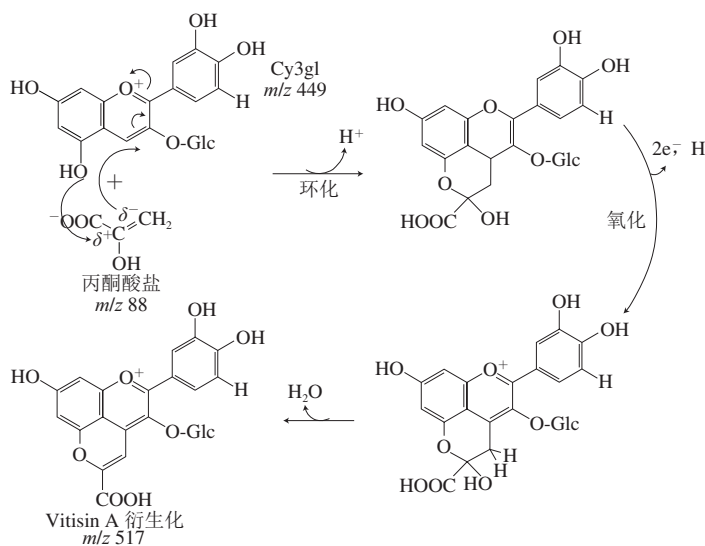


图2 受热/加压样品中Cy3gl与丙酮酸盐的缩合反应^[54]

Fig. 2 Condensation reaction of cyanidin 3-*O*-glucoside and pyruvate in heated/pressurized samples^[54]

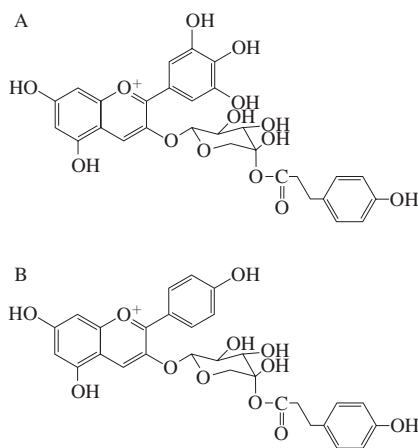


图3 天竺葵素-3-*O*-香豆酰葡萄糖苷(A)和飞燕草素-3-*O*-香豆酰葡萄糖苷(B)化学结构^[24]

Fig. 3 Structures of pelargonidin-3-*O*-coumaroylglucoside (A) and delphinidin-3-*O*-coumaroylglucoside (B)^[24]

3.3 对果蔬酚类化合物抗氧化和抗炎活性的影响

高静水压处理通过增加酚类化合物或其他抗氧化成分含量^[56],或者降低与酚类化合物相关酶的活性^[57],

抑制酚类化合物与其他成分非酶氧化和聚合反应,或通过改变果蔬微观结构而影响酚类物质与蛋白质、多糖相互作用^[7],最终利于保护果蔬酚类化合物的抗氧化和抗炎活性。

高静水压处理通过降低多种生物酶类的活性,如 β -葡萄糖苷酶、PPO、POD、果胶甲酯酶、多聚半乳糖醛酸酶来保持果蔬抗氧化活性^[58]。一般而言,400~900 MPa压力处理后苹果、葡萄、草莓等水果中的褐变相关酶的活性显著降低^[58]。然而不同果蔬中的酶对压力敏感性差异大^[59]。如红树莓和草莓经压力处理后, β -葡萄糖苷酶不能完全被灭活^[28],但这并不是一个坏结果,因为该酶参与从非挥发性葡萄糖苷中释放挥发性苷元过程,从而对水果风味释放发挥重要作用^[60]。杨梅中的PPO对矢车菊素3-葡萄糖苷没有直接作用,但加入没食子酸能刺激花色苷降解^[61]。600 MPa处理后仙人果薄壁组织和细胞结构被破坏,异鼠李糖苷含量增加近2倍,仙人果抗炎活性提高^[62]。说明高静水压处理能较好地保留果蔬食品的功能活性。

4 结语

与传统热加工相比,高静水压处理对果蔬酚类化合物含量和抗氧化、抗炎活性具有更好的保留作用,原因主要是高压破坏细胞膜结构,促进生物活性物质释放;降低PPO、POD等酶活性;抑制酚类化合物与其他物质非酶氧化和聚合反应;影响酚类物质与蛋白质、多糖相互作用。高压处理也会引起花青素、酚酸结构变化,形成新化合物。但高压条件如何影响酚类化合物与大分子物质相互作用,以及如何影响酚类化合物生物利用度等方面仍有许多科学问题需要揭示^[58]。此外,还应进一步探讨高压处理后新物质形成机制,这些物质可能是酚类化合物氧化、分解、缩合和异构化产物,具有一定的生物活性^[7]。

虽然高静水压非热加工技术在果蔬加工中优势明显,但目前仍受到两方面的限制:一是导致微生物和酶失活的压力动力学理论不够完善,不能保证高压处理过程可替代传统加热过程;二是开发食品连续压力加工机械仍是一项挑战,设备投资和维持成本高^[7]。因此,高静水压非热加工技术的发展及推广还需要大量的科学理论和装备技术作支撑。

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