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植物油角鲨烯含量及其影响因素

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摘　要: 植物油是一类经植物原料提取的富含多种微量营养成分的油脂。角鲨烯是植物油中营养伴随物之一, 对人体生理健康和疾病预防有着积极作用。通常, 不同种类植物油中角鲨烯含量差距明显, 甚至同种植物油中角鲨烯含量因地域、提取部位、加工工艺等因素也存在显著差异。因此, 了解植物油角鲨烯含量并探究影响其角鲨烯含量的因素, 可有效保留其角鲨烯成分, 提升植物油营养品质和健康价值。本文介绍了多种植物油角鲨烯含量, 并分析比较了植物油种类、原料品种、成熟度、产地、提取部位及油脂提取工艺、精炼工艺、储藏条件对其角鲨烯含量的影响, 以期为优化植物油选择及改进加工工艺提供参考, 并且为进一步提升植物油营养品质和健康价值提供理论基础。

关键词: 植物油; 角鲨烯; 营养伴随物; 影响因素

Content and influencing factors of squalene in vegetable oil

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ABSTRACT: Vegetable oil is a kind of oil extracted from plant raw materials, which is rich in a variety of micronutrients. Squalene is one of the nutritional concomitant in vegetable oil, which plays a positive role in human physiological health and disease prevention. Generally, the content of squalene in different kinds of vegetable oils varies significantly, while even the content of squalene in the same vegetable oil will vary significantly due to factors such as region, extraction site, and processing technology. Therefore, understanding the content of squalene in vegetable oil and exploring the factors affecting the content of squalene can effectively reserve its squalene and improve the nutritional quality and health value of vegetable oil. This paper introduced the content of squalene in various vegetable oils, analyzed and compared the effects of vegetable oil variety, raw material variety, maturity, origin, extraction site, oil extraction process, refining process and storage conditions on squalene content, in order to provide reference for optimizing the selection of vegetable oil and improving the processing technology, and provide a theoretical basis for further improving the nutritional quality and health value of vegetable oil.

KEY WORDS: vegetable oil; squalene; nutrient concomitant; influencing factors

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0 引　言

角鲨烯(squalene)是一种含 6 个异戊二烯双键的开链三萜烯类化合物, 结构如图 1 所示, 属于高不饱和的脂肪族烃类化合物。角鲨烯是类固醇生物合成前体, 是对人类健康最有用的生物活性化合物之一[1]。角鲨烯能够在人体皮肤和肝脏中合成, 通过低密度脂蛋白和极低密度脂蛋白在代谢系统中运输, 强化机体新陈代谢、更新细胞及促进组织生长[2]; 可以猝灭单线态氧来保护皮肤免受脂质过氧化, 保护细胞免受 DNA 氧化损伤[3]; 此外还具有预防心血管疾病、增强人体免疫力、抗肿瘤等多种生理功能[4–6]。角鲨烯在功能性食品、营养补充剂及医药等领域的应用[7–8]引起了极大关注。同时角鲨烯也是 LS/T 3249—2017《中国好粮油 食用植物油》营养伴随物的评价指标之一。

角鲨烯最开始是从鲨鱼肝油中获得。然而, 鉴于动物来源角鲨烯研究的种种限制及物种生态多样性的保护[9], 探索新的角鲨烯天然来源十分必要。自然界植物系种属繁多、品种多样、形态不一, 角鲨烯既存在于一些植物原料中, 如种子、果实、根、茎叶等[10–11], 也存在于植物油脂中, 如橄榄油、米糠油、油茶籽油等[12–14], 更在植物油加工后的残余物中也大量存在, 如橄榄油脱臭馏出物[15]。研究发现, 角鲨烯在不同植物油含量各不相同, 在同种植物油含量差异也较显著[16]。了解植物油角鲨烯含量并探究影响其角鲨烯含量的因素, 可有效保留其角鲨烯成分, 提升植物油营养品质和健康价值, 而以往报道对植物油角鲨烯含量影响因素的研究较为单一[14,17]。因此, 本文介绍了多种植物油角鲨烯含量, 从植物原料出发, 并结合地域、成熟度、提取部位及加工工艺等因素, 分析其对植物油角鲨烯含量变化的影响, 为优化植物油选择、加工和储存及植物油角鲨烯的进一步开发应用提供参考。

1 不同植物油角鲨烯含量

植物油种类丰富、来源广泛, 其含有多种饱和脂肪酸和不饱和脂肪酸, 如硬脂酸、油酸、亚油酸、亚麻酸、花生酸等, 多种维生素和钙、铁、磷、钾等矿物质, 以及多种微量营养成分[18–20]。食用植物油是日常生产生活必不可少的一类物质, 其含有的角鲨烯成分对人体健康有重要作用。表 1 列举了多种植物油中角鲨烯的含量。表 1 显示不同种类植物油角鲨烯含量不同, 其中橄榄油、苋菜籽油、南瓜籽油角鲨烯含量丰富, 是目前植物源角鲨烯重要来源之一; 菜籽油、大豆油、葵花籽油、亚麻籽油等常见食用植物油角鲨烯含量较低, 在 200 mg/kg 以内。此外, 部分植物油角鲨烯含量差距显著, 如油茶籽油、橄榄油、米糠油和南瓜籽油等。

不同植物油角鲨烯含量存在差异, 而植物油种类是由提取的植物原料决定。有研究表明, 植物原料中含有角鲨烯成分且含量不同[10], 因此, 不同原料经过制油工艺提取后, 所制得的植物油角鲨烯含量各异, 如表 1 所示。植物基因是植物内在属性, 控制着植物种类和植物生长发育全过程, 因此, 植物种类决定着植物油角鲨烯含量。有报道[45–46]称植物基因和酶对植物原料发育过程中角鲨烯含量起调控合成与转化作用, 通过转基因技术改变植物属性, 可以达到高产角鲨烯的目的。

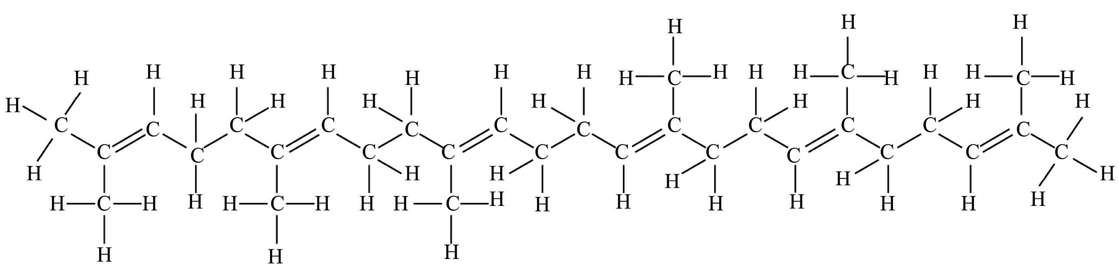

图 1　角鲨烯结构式

Fig.1　Structure of squalene

表 1　多种植物油角鲨烯含量

Table 1　Squalene content in various vegetable oils

植物油名称	角鲨烯含量/(mg/kg)	参考文献	植物油名称	角鲨烯含量/(mg/kg)	参考文献
菜籽油	9.8~124.5	[21–22]	玉米油	38.4~2568.4	[23–24]
大豆油	16.3~184.0	[13,22]	玉米胚芽油	68.0~90.7	[22]
葵花籽油	43.9~179.0	[21,23]	亚麻籽油	18.1~113.7	[25]
花生油	41.6~1343.0	[13,23]	米糠油	18.3~3189.0	[13,26]
芝麻油	14.7~607.0	[13,26]	南瓜籽油	310.0~4446.0	[27]
油茶籽油	29.2~2083.0	[21,28]	苹果籽油	10.0~340.0	[29]

表 1(续)

植物油名称	角鲨烯含量/(mg/kg)	参考文献	植物油名称	角鲨烯含量/(mg/kg)	参考文献
茶叶籽油	4.1~251.0	[30,27]	葡萄籽油	60.2~170.0	[31–32]
橄榄油	100.0~10200.0	[33–34]	牛油果油	190.0~258.0	[27]
苋菜籽油	42000.0	[35]	杏仁油	30.0~439.0	[36]
核桃油	6.4~320.0	[37–38]	榛子油	186.0~431.7	[37,39]
棕榈油	68.3~487.0	[22,40]	澳洲坚果油	80.0~304.0	[27]
胡椒油	65.4~172.0	[21]	香榧油	13.0~72.0	[41]
小麦胚芽油	69.2	[42]	清脉油	85.7	[42]
青刺果油	72.0	[42]	紫苏油	67.5	[42]
火麻籽油	97.0	[42]	沙棘油	20.4	[42]
月见草油	77.1	[42]	牡丹籽油	64.1	[43]
米糠胚芽油	131.4	[31]	芫荽籽油	451.0	[13]
红花籽油	54.6	[44]	豌豆油	40.9	[44]

2 同种植物油角鲨烯含量差异的影响因素

植物油角鲨烯含量差异较大，不同种类植物油角鲨烯含量不同，同种植物油角鲨烯含量也存在差异，其影响因素较多[47]。本文分析比较了原料种类、品种、成熟程度、产地、提取部位及植物油提取工艺、精炼工艺、储藏条件等因素对其角鲨烯含量的影响。

就同种植物油而言，制取植物油原料属于同一科属，其品种、成熟度及产地等因素对植物油角鲨烯含量有影响，其中，部分因素对其角鲨烯含量影响显著。

2.1 品种差异的影响

不同品种植物油角鲨烯含量存在差异。有报道意大利普利亚地区 5 个品种橄榄油角鲨烯含量[48]，其中 Peranzana 橄榄油角鲨烯含量最高，为 7050.0 mg/kg，而 Cima di Bitonto 橄榄油含量为 5050.0 mg/kg，角鲨烯含量相差 2000.0 mg/kg，其余品种橄榄油角鲨烯含量整体相差不大。其结果表明，油橄榄的品种对橄榄油角鲨烯含量有不可忽略的作用，受油橄榄品种影响，合成和转化角鲨烯的角鲨烯合成酶表达不同，以致橄榄油角鲨烯含量差距显著，如报道[33]“莱星”品种橄榄油角鲨烯含量仅 100 mg/kg。

2.2 原料成熟度的影响

原料成熟度不仅影响其含油率，更对其营养成分有较大影响[49]。有报道不同成熟期的橄榄油角鲨烯含量[50]，根据果实颜色，将油橄榄果成熟期分为成熟初期、成熟中期、完全成熟期 3 个阶段，其果实呈现绿色、樱桃色、黑色，角鲨烯含量分别为 6697.0、6318.3、4611.3 mg/kg，角鲨烯含量呈下降趋势。在油橄榄果成熟初期，角鲨烯在植物生长过程中不断积累，含量较高，后随着果实成熟度增加，在角鲨烯环氧化酶作用下转化为甾醇和三萜类化合物等植物分子，角鲨烯含量下降，而总甾醇和总三萜化合物含量增加[51]。

2.3 原料产地的影响

植物在不同地域生长，受栽种地域条件影响较大，包括土壤性质[52]如质地类型、酸碱度、有机质、微量元素等，气候条件[53–54]如降水量、日照、温湿度等。油茶籽在我国多个省份均有种植，不同产地的油茶籽油其角鲨烯含量存在差异，表 2 为不同产地油茶籽油的角鲨烯含量[55]。各产地角鲨烯含量差异显著，湖南邵阳油茶籽油角鲨烯含量最高，为 292.7 mg/kg，云南昆明油茶籽油角鲨烯含量最低，为 96.4 mg/kg，其余产地角鲨烯含量差别不大。我国油茶栽种范围广、产地较多，土壤砂质、质地松软、土壤 pH 中性或偏弱酸性、微量元素 Zn 含量丰富等地理条件有利于植物角鲨烯的积累[52]，因此，各地油茶籽油角鲨烯含量差异比较显著，如钟冬莲等[28]报道油茶籽油角鲨烯含量高达 2083.0 mg/kg。

2.4 提取部位的影响

苋属种类较多，不同部位营养分布不同，其植物油富含丰富的角鲨烯[56]，是目前植物性优质角鲨烯的重要来源之一，可用于开发具有促进健康功能的食品原料[57]。根据提取部位不同，可分为苋菜籽油和苋菜叶油。有报道不同提取部位的苋菜油角鲨烯含量[35]，中国产的 Ames 15330 品种苋菜籽油角鲨烯含量为 57500.0 mg/kg，苋菜叶油角鲨烯含量仅为 3700.0 mg/kg，两者相差 15.5 倍，因此，提取部位对其角鲨烯含量有显著影响。大多数植物油是种仁或果实提取，如橄榄油、芝麻油等，植物种子或果实是植物主

要营养成分富集区，因此，种子油或果实油富有营养价值。而叶片等部位利用较少，但部分植物叶片等部位也含有丰富的角鲨烯，如苋菜叶[35]、茶叶[11]，有待于进一步开发利用。

表 2　不同产地油茶籽油角鲨烯含量
Table 2　Squalene content of *Camellia oleifera* seed oil from different origins

产地	成熟度	部位	加工工艺	角鲨烯含量/(mg/kg)
湖南邵阳	成熟	种仁	索氏抽提-皂化提取	292.7
安徽-金寨	成熟	种仁	索氏抽提-皂化提取	199.3
浙江-衢州	成熟	种仁	索氏抽提-皂化提取	198.7
广西-河池	成熟	种仁	索氏抽提-皂化提取	171.7
贵州-黔东南苗族侗族自治州	成熟	种仁	索氏抽提-皂化提取	170.5
江西-九江	成熟	种仁	索氏抽提-皂化提取	166.3
湖北随州	成熟	种仁	索氏抽提-皂化提取	150.0
云南-昆明	成熟	种仁	索氏抽提-皂化提取	96.4

2.5　提取工艺的影响

不同加工工艺的油脂其品质不同，植物油提取工艺多样[38]，如浸出法、压榨法、水酶法、亚临界萃取和超临界 CO_2 萃取法等，不同的提取方法，植物油角鲨烯含量存在差异。有报道提取工艺对澳洲坚果油角鲨烯含量的影响[58]，压榨法、浸出法、水提法 3 种提油方法中，压榨法制备的澳洲坚果油角鲨烯含量最高，为 261.88 mg/kg；水提法次之，为 252.59 mg/kg；浸出法相对偏低，为 230.44 mg/kg。压榨法利用螺旋压榨机对油料进行挤压和剪切，油料被充分压榨，油脂品质较高，营养物质损失低，角鲨烯含量相对较高；水提法用水进行提取，因水与油脂不互溶，而角鲨烯不溶于水，能较好地保存于油脂中；浸出法以有机溶剂作为提取溶剂，角鲨烯易溶于有机溶剂，在提取、旋蒸、加热汽提等步骤中溶剂损失或挥发，可能造成油脂角鲨烯的损失，因此浸出法制取的植物油角鲨烯含量偏低[17,59]，且利用不同有机溶剂提取的植物油[43]，其角鲨烯含量有差别。因此选取合适的提取工艺对其角鲨烯的保留具有一定作用。

2.6　精炼工艺的影响

油脂精炼可以去除或减少有害物质，延长油脂保质期，但同时也会造成营养成分的损失，如脂肪酸、甾醇、角鲨烯、多酚[60]。植物油经粗提取后，得到毛油，进一步精炼，得到精炼植物油。有报道精炼工艺对葵花籽油角鲨烯含量变化的影响[60]，原油角鲨烯含量最高，为 176.8 mg/kg，经过脱酸、干燥和预冬化、脱色冬化、精制等工艺，角鲨烯含量逐步降低，分别为 136.8、130.8、118.3、97.2 mg/kg，其中脱酸工艺损失率为 22.60%，脱色冬化工艺总损失率达到 33.10%，精制工艺总损失率达到 45.02%。脱酸是利用碱液将油脂中的游离脂肪酸中和为脂肪酸钠盐并形成皂体，皂体中夹带着活性物质角鲨烯，随着皂体流失，导致角鲨烯含量下降。脱色是使用吸附剂(如活性白土)在真空状态下加热脱色，其吸附剂种类、用量和吸附效果直接影响脱色工段，在吸附剂吸附过程中，一定量的角鲨烯被混合吸附，使其含量降低。精制是油脂在高温(200~260℃)和低压(0.2 kPa~0.1 MPa)下进行的，低级醛酮和游离脂肪酸等异物在水蒸气汽提下夹带着角鲨烯一起被馏出，形成脱臭馏出物，此工段角鲨烯损失最严重，因此，植物油的脱臭馏出物是回收角鲨烯等活性物质的重要原料，而精炼工艺有待进一步优化改进，以避免营养物质流失，提升植物油营养品质。

2.7　储藏条件的影响

储藏条件的变化对油脂营养成分和氧化稳定性有极大程度的影响。在报道[61]中密封冷藏的橄榄油持续保存 36 个月，可以保持角鲨烯含量大致恒定；而在密封冷藏 18 个月后，随即在开盖冷藏和开盖室温两种条件下继续储藏，其角鲨烯含量均会出现较大幅度的下降，损失率约 90%。因此，空气或者氧气是影响植物油角鲨烯含量变化的重要因素，与空气或氧气接触，易使角鲨烯被氧化，引起角鲨烯大幅损失；而低温与密封条件相结合，能够达到植物油的长时间储藏，并能保持其角鲨烯含量的大致恒定。

3　结束语

随着人们生活品质和营养健康意识的提升，植物油的营养价值和健康功能备受关注。角鲨烯作为评价食用植物油品质的一项重要指标，对人体健康和疾病预防具有积极作用。通过对植物油角鲨烯含量影响因素的分析比较，植物种类和品种对植物油角鲨烯含量的影响是由植物基因决定的；原料成熟度、产地、提取部位及油脂储藏条件等因素的影响可人为干预调控以提升植物油角鲨烯含量；油脂提取工艺和精炼工艺易造成植物油角鲨烯较大损失，有待开发并采用更加高效合理的新型加工工艺，以降低其角鲨烯损失。当前对植物油角鲨烯含量的影响因素研究较为单一，以致即使是同种类同品种植物油其角鲨烯含量都存在较大差异。因此，在今后的研究中可将多种因素相结合，充分研究多变量因素对植物油角鲨烯含量的影响，同时深入研究植物基因对其角鲨烯的作用，以期得到更高角鲨烯含量的植物油，从而提升植物油的营养品质和健康功能，带动植物油产业升级发展，促进植物油行业更好地满足人民群众营养健康品质生活的需求。

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