坚果的主要生物活性成分及其保健作用

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摘 要: 坚果作为高档零食, 其营养价值和保健功能也越来越受到人们的关注。本论文综述了常见坚果(如澳洲坚果、核桃、榛子、杏仁、松子、板栗、山核桃、开心果, 日本核桃、巴西坚果、花生等)中的酚类(原花青素、酚酸、黄酮、单宁、烷基酚、维生素 E 等)、酸类、甾醇类、色素(类胡萝卜素、叶绿素等)、硒、糖苷、功能性脂肪酸等营养物质和生物活性成分,并阐述了食用坚果与预防心血管疾病、延年益寿、预防糖尿病、控制体重等保健作用的关系。这对于进一步研究坚果与健康的关系、正确挑选与消费坚果均具有较好的指导意义。

关键词: 坚果; 生物活性成分; 功能性; 保健作用

Bioactive components of nuts and their health effects

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ABSTRACT: Nuts are not only high-end snacks, and their nutritional values and health care functions also give rise to more and more people's attention. This paper summarized the bioactive components such as the phenols (phenol, procyanidins acid, flavonoids, tannin, alkylphenol, vitamin E, *etc*.), acids, sterols, pigments (carotenoids and chlorophyll), selenium, glycosides, functional fatty acids and so on in common nuts (such as macadamia nuts, walnuts, hazelnuts, almonds, pine nuts, chestnut, hickory, pistachios, walnuts, Brazil nuts, Japanese peanut, *etc*.). It also described the relationships between eating nuts and health care function, such as prevention of cardiovascular disease, prolonging life-span, prevention of diabetes, and weight control. This has a good guiding significance for the further study of the relationship between nuts and health, and the correct selection and consumption of nuts.

KEY WORDS: nuts; bioactive components; functionality; health care

1 引 言

坚果含有许多生物活性成分和营养素[1,2], 其所含宏量营养素主要是脂肪、蛋白质和碳水化合物, 微量营养素主要是矿物质和维生素[3,4], 脂溶性活性成分如单不饱和脂肪酸(monounsaturated fatty acids, MUFA)、多不饱和脂肪酸(polyunsaturated fatty acid, PUFA)、甘油一脂、甘油二酯、三酰甘油酯(tri-acylglycerol, TAG)、甾醇酯、生育酚、生育三烯酚、植物甾醇与烷甾醇、角鲨烯、萜类、鞘脂类、类胡萝卜素、叶绿素、烷基酚类、精油等[1,2,4] 。此外, 坚果还含有植物活性物质(水杨酸、羟基苯甲酸、羟基肉桂酸等酚酸, 黄酮醇、黄酮、黄烷醇、儿茶素、黄烷酮、花青素和异黄酮等黄酮类化合物, 二苯乙烯类, 木质素, 萘醌, 鞣花单宁和鞣花鞣质等水解单宁, 缩合单宁或原花青素, 鞣花酸, 酚醛,

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生物碱, 香料成分, 肌醇六磷酸酯, 萜烯, 植物雌激素等[4-24])。尤为重要的是, 坚果含有许多类型的抗氧化成分[11,25]。

坚果是被公认的健康食品, 尤其是其具有较好的预防心血管疾病的作用[26,27]。研究表明: 食用坚果可以增强心血管疾病模型的抗氧化能力和减少炎症风险[28,29] 。最新实验与临床研究表明: 坚果具有抗肿瘤[30] 、提高认知能力[31]、减少哮喘[32,33]和肠炎[34]症状等功效。但也有观点认为: 坚果脂肪酸含量高, 易于氧化或导致肥胖等不利于健康的作用。

本文所综述的坚果是指带有较坚硬外壳、内含有可食用核的一类干果, 如: 澳洲坚果、核桃、榛子、杏仁、松子、板栗、山核桃(pecan, 又名碧根果)、开心果, 日本核桃(Japanese walnut, *Juglans ailantifolia* var. *cordiformis*)、巴西坚果(Brazil nut, *Bertholletia excels* H.B.K)等; 根据国外的坚果分类方法, 这里也把花生视为坚果一并综述。本文综述常见坚果食物的主要生物活性物质, 主要从酚类、酸类、功能性油脂类和其他生物活性物质 4 个方面介绍, 并分析这些营养和生物活性成分与坚果保健作用的关系。

2　坚果主要生物活性成分

坚果富含酚类植物化学成分, 是摄入常见膳食多酚的重要来源之一[29]。Bolling 等[11]详细综述了杏仁、腰果、榛子、澳洲坚果、山核桃、松子、开心果、核桃、花生等坚果化学成分。这些主要的生物活性成分有: 酚类、酸类、油脂类以及一些其他活性成分。图 1 显示了坚果中一些活性成分的分子结构。

2.1　酚类

Folin-酚法(一种非特异性测定总酚的方法)测定数据表明: 坚果中的酚类物质含量丰富。坚果中含有游离型多酚与无法用溶剂法萃取的结合型多酚。结合型多酚常与膳食纤维、木质素或其他细胞壁成分以共价键的形式结合。结合型多酚的体内抗氧化能力占总酚 10%~60%[35]。值得注意的是, 澳洲坚果含有最多的结合型多酚[36] 。杏仁中含有 1~2 mg 结合型原花青素, 约 8 mg/100 g 结合型酚酸[37,38] 。结合型多酚亦很少表征, 其含量一般是由强酸或强碱水解其提取物后测得的。板栗、山核桃、开心果多酚含量大于 1 g 没食子酸当量/100 g(即以没食子酸为参考标准而计算出的多酚含量), 而大多数坚果仅大于 0.1 g 没食子酸当量/100 g(表 1)。因此, 有些坚果是最高的食物多酚来源之一[39]。应该注意的是, Folin-酚法测定结果可能难以解释不同黄酮与总酚的比值[40]。

2.1.1　原花青素

原花青素是杏仁、榛子、核桃、开心果中的最丰富的多酚(表 1)。虽然在杏仁、花生、榛子中也发现过 A 型原花青素, 但坚果主要含 B 型原花青素[41]。坚果中原花青素是高度聚合的, 其平均聚合度一般为 2.6~10.8[42]。

2.1.2　水解单宁

水解单宁包括与葡萄糖链接的没食子酸(鞣花鞣质)或六羟基二苯酸(鞣花单宁), 六羟基二苯酸又经酸水解可分解成没食子酸和鞣花酸。这些水解单宁一般是先经水解、再提取后, 经定量没食子酸或鞣花酸而测到的。因此, 坚果的单宁结构多未精确表征。目前仅表征了核桃水解物中存在 A 型和 B 型 glansreginins(见图 1)和 A-D 型 glansrins[43]。多数坚果(如杏仁、核桃和山核桃)含有高丰富的水解单宁。在榛子提取物中鉴定出了没食子酸。 脱脂腰果仁中的没食子酸含量为 22 mg/100 g[44,45]。

表 1　坚果中已报导的植物化学物质(mg/100 g)

Table 1　Nutrient substances that have been reported in nuts (mg/100 g)

坚果种类	总酚[95]	原花青素	没食子酸+没食子单宁	鞣花酸+鞣花单宁	黄酮类化合物[97]	酚酸	芪类	植酸盐[3]
杏仁	47~418	176[95]	14~41[50]	49~63[50]	11	0.2~0.7[11]	0.008~0.01 [45]	350
巴西坚果	112~310	*	8.3[42]	ND	ND	11[11]	ND	190
腰果	137~274	2[95]	22[41]	ND	2	ND	ND	290
板栗	1580~3673	*	276~907[95]	149~1052[87,95]	0.02	4~142[97]	ND	ND
榛子	291~835	491[95]	0.2~4.3[98]	ND	12	2[11]	ND	230
扁核桃	148~248[99]	ND	ND	9~24[99]	ND	34~62[99]	ND	ND
澳洲坚果	46~156	*	ND	ND	ND	4[11]	ND	150
花生	0.1~420	11[95]	ND	ND	1	3~6[11]	0.005~0.08[95]	170
美洲山核桃	1284~2016	477[95]	22[100]	301[87]	34	6~10[100]	ND	180
松子	32~68	*	ND	ND	0.5	ND	ND	200
开心果	867~1657	226[95]	1~2[101]	ND	16	1[11]	0.009~0.16[95]	290
山核桃	1558~1625	60[95]	0.1	6~823[95]	3~65[95,97]	36[95]	ND	200

注: ND 为未检出; *已检出, 但通过定性方法或没有在所有坚果的基础上量化。数据来源 Venkatachalam 等[3]。

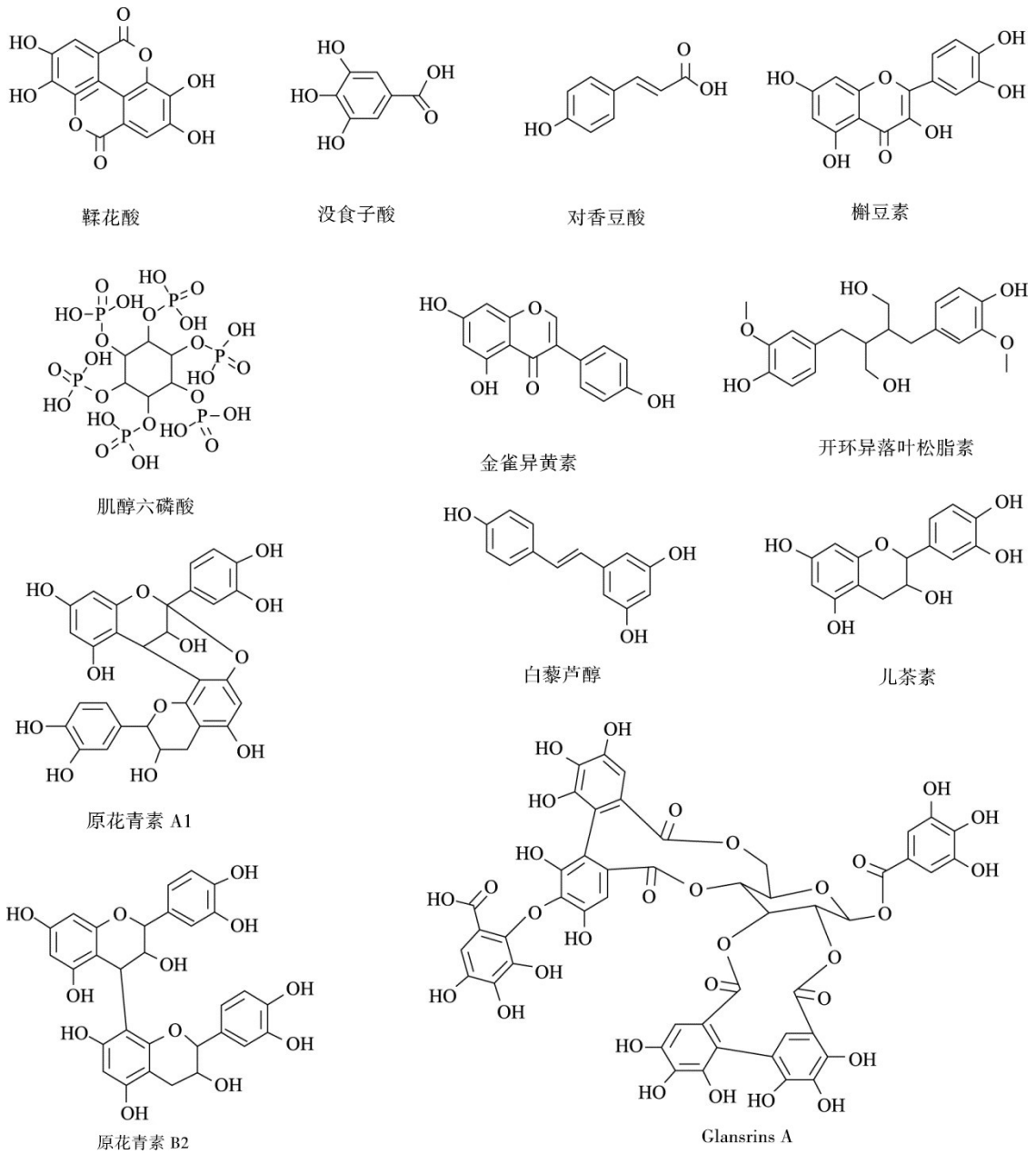

图 1 坚果中常见生物活性成分的分子结构

Fig. 1 Molecular structures of common biological active ingredients in nuts

巴西坚果中含有 5.2 mg/100 g 游离没食子酸, 其脱脂粕中含有 8.2 mg/100 g 结合型没食子酸[46]。相比之下, 花生中的没食子酸或水解单宁含量均较低[47]。

2.1.3 烷基酚

腰果油含有 146~242 mg/100 g 的腰果酸(anacardic acid)和腰果二酚(cardols)[48], 而开心果油含有 16 种不同的腰果酚(cardanols, 44 mg/100 g)[49] 。其他坚果中的烷基酚类未见表征和报道。腰果油中 12 种烷基酚(腰果酸、腰果酚、腰果二酚、2-甲基腰果二酚等)的报道见参考文献[50]。另外, 腰果壳、腰果提取液等腰果产品中也含有不同含量和种类的烷基酚类物质。

2.2 酸类

坚果中酸性的主要活性成分是酚酸与肌醇六磷酸。山核桃和巴西坚果富含酚酸(见表 1), 其含量为分别为 36 mg/100 g 和 11 mg/100 g, 但并未精确表征其多酚结构。花生含有对香豆酸和原儿茶酸, 而咖啡酸只存在于西班牙花生中[37,43] 。若将没食子酸(游离或结合型)归为酚酸, 则栗子、山核桃和杏仁富含酚酸, 其含量为 14~900 mg/100 g (见表 1)。

大多数坚果中均含肌醇六磷酸, 主要以肌醇磷酸盐形式存在; 杏仁和榛子中, 1 到 6-肌醇磷酸盐均有存在[51]。坚果中一般含有 150~290 mg/100 g 肌醇磷酸酯[3]。据报道: 核桃醌(juglone), 一种萘醌类物质, 在核桃中含量丰富, 为 7~19 mg/100 g(10 个品种平均值)[52]。

2.3　功能性油脂类

图 2 列出了坚果中的部分脂溶性活性成分的化学结构。表 2 总结了坚果中的脂溶性活性成分(脂质、生育酚、植物甾醇、鞘脂类、类胡萝卜素、叶绿素和烷基酚类等)。

2.3.1　脂　质

坚果油脂的含量从欧洲板栗的 2.26%到澳洲坚果的 75.77%[4], 含量差异极大, 坚果对人体健康的益处部分是因为其脂肪酸为人类饮食脂肪组分。MUFA 是大多数坚果油的主要脂溶性生物活性成分; 除了巴西坚果外, 欧洲板栗、日本核桃、松子、核桃均富含 PUFA[10]。

2.3.2　维生素 E

不同坚果的维生素 E 含量差异很大, 平均含量范围从 6.15 mg/100 g(澳洲坚果油)到 59.60 mg/100 g(板栗油)[10], 具体见表 2。大量研究报道了各种坚果油的维生素 E 含量和种类[1,4,53-61]。Alasalvar 等[23]综述了十二种坚果(杏仁、巴西坚果、腰果、板栗、日本核桃、榛子、澳洲坚果、花生、山核桃、松子、开心果、核桃等)维生素 E 的含量和种类。维生素 E(包括 *α*-、*β*-、*γ*-和 *δ*-4 种生育酚与相应的生育三烯酚)是一种脂溶性维生素, 其常通过中断油脂自由基氧

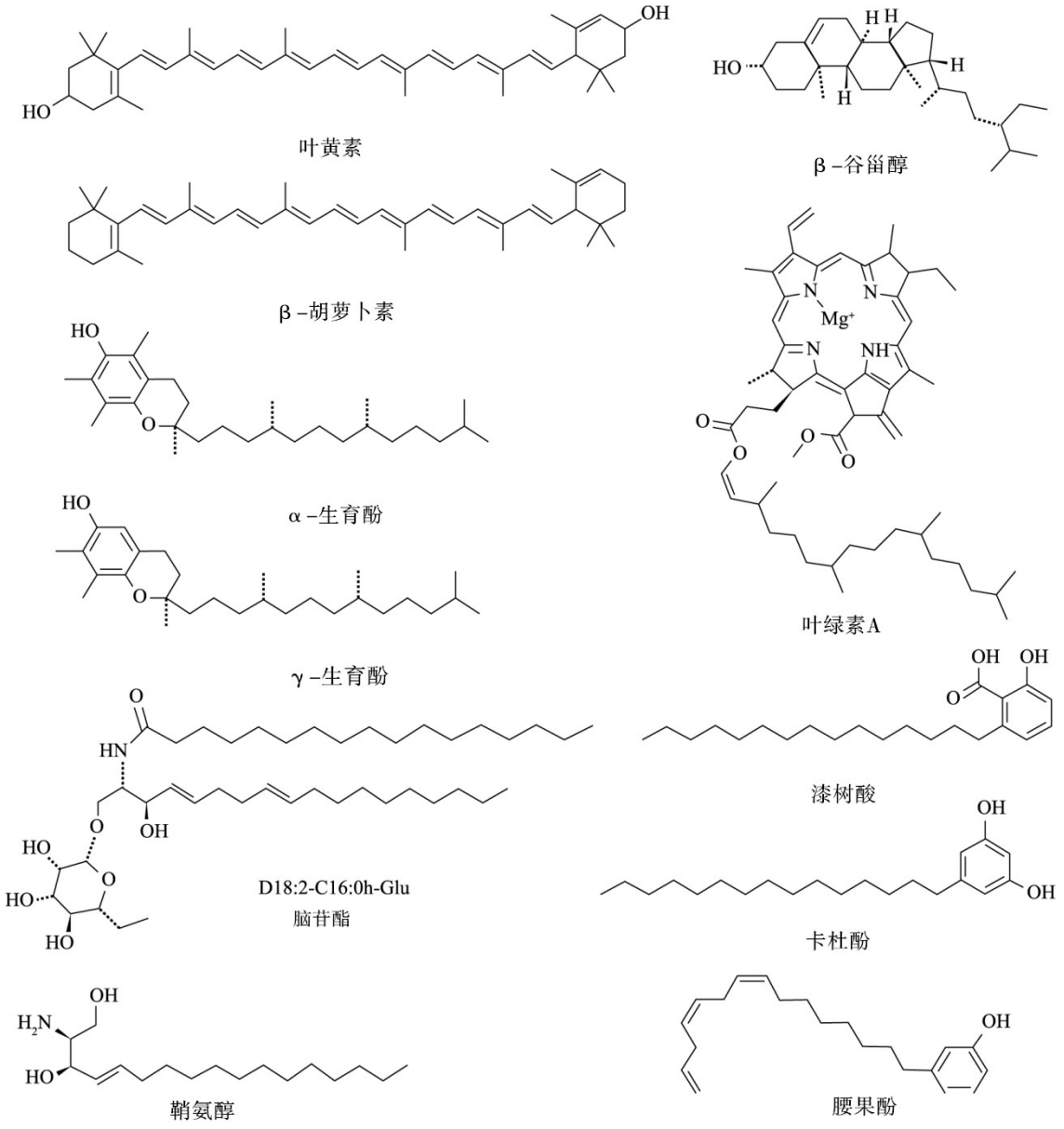

图 2　坚果中常见脂溶性成分的分子结构

Fig. 2　Molecular structures of common fat-soluble components in nuts

化链反应而起抗氧化作用[62]。一般认为其是坚果促进健康的重要成分[63]。相比之下, 榛子油是最好的维生素 E 的来源[53], 依次是开心果、杏仁、松子[1]和花生[56]。坚果油中维生素 E 的含量范围是 1.13~41.92 mg/100 g, 欧洲板栗最低、榛子含量最高[10]。

2.3.3 植物甾醇

植物甾醇类是坚果油中的重要脂溶性生物活性成分。坚果油的植物甾醇总含量见表 2。甜板栗油植物甾醇含量最高(800 mg/100 g), 依次是山核桃油(307 mg/100 g)、花生油(284 mg/100 g)、美洲山核桃油(283 mg/100 g)和杏仁油(271 mg/100 g)。相比之下, 澳洲坚果油总甾醇含量最低(128 mg/100 g)[47] 。日本核桃油中的植物甾醇含量未见报道。饱和甾醇为烷甾醇, 其与甾醇的差异是 B 环上 C_1 位置上烷基键; 板栗油中含 0.81%~2.26%烷甾醇。坚果油中的甾醇的主要 β-谷甾醇醇, 但也有少量的稀有甾醇、甾醇酯和烷甾醇[5] 。已有许多文献报道了杏仁、巴西坚果、腰果、栗色、日本核桃, 榛子、澳洲坚果、花生、山核桃、松子、开心果、核桃等坚果中植物甾醇含量和种类[64-71]。

2.3.4 鞘脂类

最近已有 2 篇论文综述了坚果中的鞘脂类的特征[47,72], 总的讲, 坚果鞘脂类的研究较少。Miraliakbari 等[71]测量了正己烷或氯仿萃取的杏仁、巴西螺母、榛子、山核桃、松子、开心果、核桃等 7 种坚果油的鞘脂类含量, 其值从 20 mg/100 g(榛子油)到 330 mg/100 g(开心果油)(见表 2)。他们利用非特异性方法测量了大多数坚果的鞘脂类成分[1,70,74] 。因此, 鞘脂类测定数据还有待精确测定方法证实。与牛奶、鸡蛋、大豆、肉(鸡肉、牛肉和猪肉)和谷物(小麦)等食物相比, 坚果鞘脂类的含量相对较低。

2.3.5 类胡萝卜素

与其他植物性食物相比, 某些坚果含有非常低的类胡萝卜素(如 α-胡萝卜素、β-胡萝卜素、β-隐黄素、叶黄素、番茄红素和玉米黄质[11,75-77]。开心果油含有 β-胡萝卜素和叶黄素(5 mg/100 g)[72]。在 12 种坚果油(表 2)中, 报道了腰果油(0.09 mg/100 g)、山核桃油(0.014 mg/100 g)、开心果油(6.70 mg/100 g)中的类胡萝卜素[73,74,78]。Trox 等[74]报道: 生腰果含痕量 β-胡萝卜素、叶黄素和玉米黄质。Bolling 等[11]认为大多数坚果都不是类胡萝卜素的良好来源, 因而难以从坚果中摄取足量的类胡萝卜素。

2.4 其他生物活性物质

坚果中还含有的其他活性成分, 例如叶绿素、类黄酮、二苯乙烯衍生物、硒(Se)等。叶绿素色素是坚果油的重要质量指标。在经常食用的坚果油中, 仅报道松子油(0.007 mg/100 g)和开心果油(24.09 mg/100 g)含有叶绿素[73,79]。在成熟的开心果样本中, 叶绿素 a 大约是叶绿素 b 的 3 倍[79]。除此之外, 未见其他坚果油叶绿素的报道。

山核桃、核桃、榛子、开心果含有丰富的黄酮类物质(表 1)。杏仁含有儿茶素, 以及柚苷元、槲皮素和山柰酚等, 其黄酮苷主要为葡萄糖苷或芸香糖苷[80] 。榛子、开心果、核桃含有儿茶素、棓儿茶酸等黄酮类物质。腰果含有黄酮和黄烷醇类多酚。

表 2 已报导坚果油中脂溶性生物活性物质(mg/100 g)

Table 2 Fat-soluble bioactive substances that have been reported in the nuts oil (mg/100 g)

坚果种类	脂质[71](%)	母育酚[10]	植物甾醇[10,72]	鞘脂*[73]	类胡萝卜素	叶绿素	烷基酚
杏仁	49.93	28.60	271	240	ND	ND	ND
巴西坚果	66.43	20.15	208	290	ND	ND	ND
腰果	43.85	7.10	199	ND	0.09**[74]	ND	146~242[80]
板栗	2.26	59.60	800	ND	ND	ND	ND
榛子	60.75	51.31	165	20	ND	ND	ND
扁核桃	51.00	22.50	ND	ND	ND	ND	ND
澳洲坚果	75.77	6.15	128	ND	ND	ND	ND
花生	49.24	29.72	284	ND	ND	ND	ND
美洲山核桃	71.97	49.11	283	320	0.014[78]	ND	ND
松子	68.37	45.80	164	280	ND	0.007[79]	ND
开心果	45.39	39.77	184	330	6.70[76]	24.09[76]	44[74]
山核桃	65.21	43.72	307	290	ND	ND	ND

注: ND: 未检出; *代表计算坚果油使用氯仿/甲醇溶剂萃取; **代表数据是 β-胡萝卜素、叶黄素和玉米黄质的平均值, 来自 Trox 等[74]。腰果油中类胡萝卜素含量是在腰果油含量(43.85 g/100 g)基础上计算得的;

早就报道杏仁、花生、开心果中存在二苯乙烯类物质, 含量在 μg/100 g 级。杏仁含有白藜芦醇-3-*o*-葡糖糖苷(resveratrol-3-*o*-glucoside), 集中在种皮部分[81], 其白藜芦醇含量为 109 US; 2 年贮存期的花生, 其含量为 0.003~0.026 mg/100 g 花生[82] 。坚果中的硒(Se)是营养型抗氧化成分重要来源[4,18,83] 。巴西坚果是 Se 的极好来源, 约 5g 该果果仁可提供 RDA 的 174%的 Se[18]。

3　坚果的保健作用

消费坚果有利健康的文献很多。传统上, 坚果用于提高免疫力、助消化、促进伤口愈合、改善血液循环和止痛等[84], 并把这些保健作用主要归于在脂质和脂蛋白。但也常有人习惯上认为: 坚果含油量高, 其脂肪易于氧化败坏, 不属于健康食品，这些观点仍有待研究证实。根据已有的研究结果, 可以将坚果的主要保健作用归类为如下几种。

3.1　降低患心血管疾病风险

2003 年和 2004 年美国 FDA 已认定: 合乎要求的健康声称要摄食约 42.5 g/d 不同类型的坚果, 尤其是核桃, 可以减少患心脏病的风险, 可作为低饱和脂肪和低胆甾醇饮食的一部分[82-86]。2011 年, 欧洲食品安全局(EFSA)颁布法规 13 声称: 在均衡膳食中摄食 30 g 核桃以改善 endothelium-dependent 血管舒张[82] 。还声称基于坚果中的 MUFA/PUFA 和亚麻油酸/亚油酸而降低低密度脂蛋白[87]。

其他最近的研究表明, 坚果成分有益于心脏保护。Apo E-鼠饲喂高脂肪坚果膳食降低了 55%动脉粥样硬化斑块的发展, 而饲喂核桃油鼠则无此效果[88]。

3.2　抗衰老

最近的研究进一步支持增加摄食坚果可降低死亡率。护理健康研究和健康专家随访研究(the nurses' health study and the health professionals follow-up study)报道了 24 和 30 年、以 118962 成人为研究对象的 2 项长期“摄食坚果和死亡率间关系”随访研究结果[89]：每周消费 7 次以上坚果可以降低死亡率(P<0.001)[90]。癌症、心血管、心脏和呼吸系统等疾病死亡率与摄食坚果频率呈负相关[90]。澳大利亚蓝山眼研究(Australian Blue Mountains Eye Study)的观测数据也支持这一发现。高频率摄食坚果与依赖于年龄、性别炎性疾病活动紧密相关(P=0.02), 且这一趋势并不明显依赖于多变量调整[91]。

干预研究也提供了消费坚果、有益健康的新证据。预防地中海干预研究显示: 参与者(7447 名成年人)坚持地中海式饮食并食用坚果和橄榄油代替其他脂肪, 其效果与低脂饮食相当[92]。摄食者每天食用 30 g 混合核桃、榛子、杏仁, 平均随访 4.8 年后, 饮食橄榄油和坚果的 2 组地中海饮食均降低了心血管疾病率。摄食坚果组较对照组的危险比率为 0.72(95%CI, 0.54, 0.96)[93]。摄食坚果组全因死亡率的风险也降低了。每周食用 3 次以上坚果组的总死亡率风险最低(HR 0.36 95%CI, 0.22, 0.66)[94]。此外, 在预防地中海的高血管风险组, 其认知能力得到改善(n=522)[25]。细微精神状态检查和时钟画测试评估表明: 6.5 d 干预实验后, 食用坚果和橄榄油 2 组受试者的认知能力高[25]。

3.3　减肥作用

虽然坚果属于高脂肪、高能量、有增加体重风险, 但食用 1~6 月坚果的临床试验显示: 没有发现体重增加[94-96]。药理研究认为: 该结果很大程度上是由于食用坚果形成的高饱腹感造成了 65%~75%的能源补偿反应。此外, 由于生物利用度差, 坚果能量吸收效率是有限的[97]。

短期摄食核桃皮(5.6 g)3 d 后, 与基线相比, 参试人员降低了餐后反应的充血指数, 该实验是在 15 名健康超重和中度肥胖成人中进行的[98] 。

3.4　预防糖尿病

坚果可减少胰岛素抵抗和 II 型糖尿病的风险。高脂血症成人(II 型糖尿病者)摄食杏仁 56 g/d(共 4 周)后, 较对照组减少了 C-反应蛋白(C-reactive protein)、IL-6 和 TNF-α 水平, 增加了抵抗 Cu 诱导低密度脂蛋白(low-density lipoprotein, LDL)氧化的能力[23] 。另外一个交叉研究是对 15 位女性 II 型糖尿病患者, 使其食用 42.5 g 花生酱并含有丰富碳水化合物的早餐后, 降低了餐后葡萄糖, 并增加了饱腹感的激素分泌[21] 。坚果茶多酚还可以通过抑制碳水化合物消化抑制高血糖症。杏仁和板栗单宁已被确定为有效的 α-淀粉酶抑制剂, 并证实其可以减少饲喂玉米淀粉鼠的血糖[99-101] 。

4　结　论

坚果含有丰富的抗氧化等生物活性成分和脂溶性营养素成分, 有益于心脏健康、提供必需脂肪酸、延年益寿、调节肥胖与糖尿病等代谢性疾病等。随着我国饮食结构、农业产业结构的调整, 我国坚果的产量和消费会逐年增加。有必要加强坚果的消费、宣传营养与保健作用研究。

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