半乳甘露聚糖的性质、改性及应用

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摘要　半乳甘露聚糖是一种中性多糖，具有优异的增稠、胶凝特性。此外，它还具有多种生理功能，例如促进肠道双歧杆菌的增殖，降低血压和血糖，预防便秘、结肠癌、心血管疾病。其性质受到分子质量大小，甘露糖/半乳糖比例及半乳糖基沿主链的分布等因素影响。随着亲水胶体工业的发展，半乳甘露聚糖的改性(物理、化学、酶法)已成为其在食品、制药、生物医学等领域应用的重要研究课题。近年来，国外对半乳甘露聚糖的研究较多，本文概述半乳甘露聚糖的物理性质、生理活性、改性及应用，以期为我国半乳甘露聚糖的发展提供参考。

关键词　半乳甘露聚糖；性质；改性；应用
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半乳甘露聚糖是中性半纤维素生物聚合物，主要从植物种子胚乳中提取，位于种子胚乳细胞壁中。如槐种子发育中，半乳甘露聚糖最先在邻近胚的胚乳细胞的粗面内质网的囊泡腔内形成，并通过细胞质膜分泌至细胞壁周围。此后，半乳甘露聚糖的积累逐渐向种皮方向扩展，及至种子成熟时，除糊粉层外，所有胚乳细胞几乎全由多糖所填充[1]。半乳甘露聚糖因其功能(粘结剂、乳化剂、稳定剂、增稠剂、脂肪替代品)和生物活性(降血糖，预防便秘，调节胰岛素水平，改善肠道细菌，降低胆固醇，预防癌症)而广泛应用于化妆品、药物、生物医学、食品、纸张等行业。近年来，国内外对半乳甘露聚糖的研究较多。本文从半乳甘露聚糖的提取方法、性质(物理性质、生理活性)、改性及应用4个方面进行概述，以期为我国半乳甘露聚糖的发展提供参考。

1　半乳甘露聚糖的提取方法

在工业上，半乳甘露聚糖主要是从瓜尔豆、长角豆、胡芦巴和塔拉等植物种子的胚乳中提取得到。20世纪初美国将长角豆胶用于工业上。到20世纪40年代，长角豆胶的供应无法满足在食品和其它行业上的需求，瓜尔胶开始得到重视[2]。其提取通常采用水提醇沉法，将去除胚芽的瓜尔豆胚乳干燥粉碎后加水，经乙醇沉淀，离心分离后干燥粉碎得到瓜尔胶[3]。田菁[4]、皂荚[5]、决明子[6]等也可通过水提醇沉法提取得到半乳甘露聚糖。稀酸或稀碱也被用于提取，如将葫芦巴种子干燥后粉碎得到原料粗粉，分散于水中，离心得上清液，加入磷酸三钾或磷酸氢二钠，再加入乙醇，搅拌均匀，静置分相，取下相溶液离心，得到半乳甘露聚糖[7]。目前，也有大量研究采用物理方法辅助提取。Niknam 等[8]采用超声或微波辅助提取皂荚中的半乳甘露聚糖，半乳甘露聚糖的乳化能力、乳化稳定性和发泡稳定性均有显著提高。Rashid 等[9]利用高压冷等离子体协助提取葫芦巴中半乳甘露聚糖，提取率可提高1倍，且其具有更高的水结合能力、溶胀指数、黏度和更低的熔融焓。

2　半乳甘露聚糖的性质

2.1　物理性质

半乳甘露聚糖是一种中性杂多糖。其主链由 d-甘露糖通过 β-1,4 糖苷键连接，侧链由 d-半乳糖通过 α-1,6 糖苷键连接，如图1所示[10]。半乳甘露聚糖通常被认为是无规线圈聚合物，在碱性条件下可形成少量螺旋结构[11]。半乳甘露聚糖主要提取自长角豆、瓜尔豆、塔拉和葫芦巴等植物。其性质受到分子质量大小，甘露糖/半乳糖比例(M/G)及半乳糖基沿主链的分布等因素影响。半乳甘

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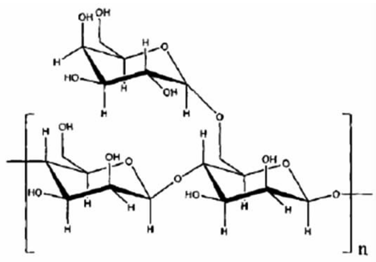

图 1　半乳甘露聚糖结构图[10]

Fig.1　The structure of galactomannans[10]

露聚糖的分子质量范围很宽,提取的植物来源、产地、制备工艺以及贮藏过程中的生物降解均会影响其分子质量。Haddarah 等[12]在黎巴嫩不同海拔和不同地点随机采集了 9 个黎巴嫩长角豆品种提取半乳甘露聚糖，得率为 40%~60%，分子质量(Mw)为 535~826 ku。葫芦巴、瓜尔胶、塔拉和刺槐豆胶中提取的半乳甘露聚糖其 M/G 比例分别约为 1∶1,2∶1,3∶1 和 4∶1[13]。Sun 等[14]从皂荚中提取的半乳甘露聚糖,M/G 比例约为 2.54∶1~2.66∶1,Mw 为 1 913 ku。Zhou 等[15]从田菁中提取的半乳甘露聚糖 M/G 比例为 2.4∶1,Mw 为 1 420 ku。

半乳甘露聚糖具有良好的水溶性和交联性,溶于水后可形成半透明的黏性液体。半乳甘露聚糖溶液在低质量浓度(<0.5%,*m*/*V*)下表现为牛顿流体,在较高质量浓度(1%,*m*/*V*)下表现为非牛顿流体[16]。Haddarah 等[12]提取的 9 种黎巴嫩长角豆胶,通过流变学研究表明,当质量浓度小于或等于 0.1%(*m*/*V*)时,长角豆胶表现为牛顿流体;当质量浓度较高(0.5%~2%,*m*/*V*)时,长角豆胶表现出剪切稀化行为,流动行为特性指数(*n*)均小于 1,显示其为非牛顿流体。甘露糖和半乳糖之间的链内和链间氢键降低了它们的溶解度;然而,半乳糖侧基的空间位阻可以增加其溶解度[17]。因此,半乳糖侧基的比例越高,其溶解度越大。例如,半乳糖含量较高的葫芦巴胶、瓜尔豆胶,由于半乳糖基造成的空间位阻，较难凝胶化，在冷水中几乎全部溶解。塔拉胶在冷水中能溶 70%,45 ℃时则完全溶解[18]。槐豆胶在冷水溶液中仅部分溶解,溶液需加热到 80 ℃才能完全溶解[19]。Tao 等[20]通过乙醇分级沉淀法对瓜尔胶或刺槐豆胶酶解产物进行分级,在相同乙醇浓度下，未水解半乳甘露聚糖的半乳糖的比例越低,其降解产物的分子质量越大,这一现象亦能说明半乳糖侧基的比例越高溶解度越大。

事实上,M/G 比例是决定半乳甘露聚糖理化性质的主要因素,包括形成黏性溶液、稳定乳剂和成膜的能力[21]。半乳甘露聚糖在水溶液中,可与其它多糖(黄原胶、阿拉伯糖、透明质酸等)协同作用形成三维网状凝胶[22]。其中半乳甘露聚糖主链上未取代区可以通过氢键与多糖形成稳定的三维结构。半乳糖侧基在主链上的分布也影响协同作用[23]。半乳甘露聚糖也能与淀粉协同增稠。研究表明,4%玉米淀粉/0.352%半乳甘露聚糖混合物的表观黏度显著高于 4%玉米淀粉糊与 0.352%半乳甘露聚糖溶液的表观黏度之和。淀粉为分散的悬浮液,半乳甘露聚糖位于连续相,由于多糖的增稠特性，在连续相中半乳甘露聚糖浓度的增加引起连续介质黏度的显著增加[24]。半乳甘露聚糖-蛋白质混合凝胶的结构受混合体系离子强度、蛋白质和半乳甘露聚糖性质等多种因素的影响。半乳甘露聚糖和蛋白质则可能由于热力学不相容而发生相分离[25]。在 pH 值为 7 的条件下,在大豆蛋白热诱导凝胶中加入不同的半乳甘露聚糖，半乳甘露聚糖的 M/G 比也会影响相分离的速度[26]。

2.2　生理活性

一般来说，多糖在不同的溶液中会表现出不同的构象,包括单螺旋、三螺旋和随机螺旋;通常具有高免疫调节活性的为三螺旋构象多糖，而三螺旋结构并不是多糖发挥免疫活性的必要结构[27-28]。半乳甘露聚糖具有促进益生菌生长、抗癌、改善 2 型糖尿病、抗胆碱酯酶等生理活性[29]。

2.2.1　促进益生菌生长　Miao 等[30]从决明子胶中制备的半乳甘露聚糖低聚糖，在体外发酵过程中可以促进潜在有益菌(双歧杆菌、乳杆菌、拟杆菌、细孔菌)的生长,该低聚糖可抑制潜在有害菌(梭杆菌、木霉、螺旋体等)的生长。在培养过程中,产生了乙酸和丙酸等短链脂肪酸，这种低聚糖是一种极具潜力的益生元。

2.2.2　抗癌　研究表明,Zhang 等[31]从草青霉中提取的半乳甘露聚糖能抑制半乳糖凝集素-8 (Gal-8)的活性,且其抑制能力随着半乳糖呋喃苷链的增加而增强。Gal-8 具有细胞黏附、生长、中性粒细胞调节、免疫调节、血小板功能调节等多种作

用;Gal-8 的表达水平不仅与肾癌、胃癌、肺癌、膀胱癌等多种肿瘤的转移、恶性程度、预后相关,且与哮喘等自身免疫病有关[32]。

2.2.3 抗炎 Tao 等[33]通过降解从田菁中提取出的半乳甘露聚糖得到 4 种不同分子质量的产物,均显示出调节免疫活性的能力，其免疫调节活性随着游离羟基数量的减少而减少，且其免疫调节活性依赖于 TLR4。TLR4 是介导内毒素/脂多糖应答的主要受体,而 TLR4/CD14 信号通路是介导内毒素诱导的炎性反应的重要通路。营养性肥胖、心肌梗死、动脉粥样硬化、哮喘等所引起的炎性反应与 TLR4 相关。大部分肿瘤组织均表达 TLR4;肿瘤细胞上 TLR4 激活后能以不同方式促进肿瘤的发生、发展、凋亡抵抗和侵袭、转移[34-35]。Souza 等[36]使用决明子半乳甘露聚糖凝胶治疗二度烧伤,显示半乳甘露聚糖可以促进皮肤愈合。研究表明由于半乳甘露聚糖显示出的调节免疫活性的能力,半乳甘露聚糖溶液可促进小鼠切除性皮肤创伤的愈合[37]。

2.2.4 改善 2 型糖尿病 Li 等[38]将田菁胚乳中提取的半乳甘露聚糖用于治疗 2 型糖尿病小鼠,小鼠的血糖和血脂明显降低。半乳甘露聚糖可以提高糖尿病小鼠的胰岛素敏感性，改善糖尿病小鼠肠道菌群组成，肠道菌群的改善对降低糖尿病小鼠的胰岛素抵抗和血糖具有重要作用。

2.2.5 抗胆碱酯酶 Tel-Çayan 等[39]从灵芝中提取的半乳甘露聚糖，其甘露糖/半乳糖约为 1∶14.4,分子质量为 5 090 u,对乙酰胆碱酯酶(AChE)和丁基胆碱酯酶(BChE)的抗胆碱酯酶活性具有较强的抑制作用。乙酰胆碱酯酶是生物神经传导中的酶,在胆碱能突触间降解乙酰胆碱,终止神经递质对突触后膜的兴奋作用，保证神经信号在生物体内的正常传递[40]。乙酰胆碱酯酶的抑制剂可以减少乙酰胆碱的消耗以治疗老年痴呆[41]。

3 半乳甘露聚糖的改性方法

目前,半乳甘露聚糖的改性可通过化学、物理和酶法改性。在化学改性中有机试剂和酸的使用较多,对环境不友好。此外,还需额外的分离和纯化,步骤更复杂。酶法和物理法相对清洁,而酶法耗时较长[42]。

3.1 化学改性

化学改性即利用化学反应改变半乳甘露聚糖的结构,产生新的生物活性或功能化合物[43]。半乳甘露聚糖吡喃甘露糖基和吡喃半乳甘露糖基上具有活性羟基,这些羟基可以被醚化、酯化、氧化。裂解通常发生在糖苷键[20]。

羧甲基半乳甘露聚糖是采用羧甲基取代半乳甘露聚糖部分羟基而得到的阴离子型衍生物。Verma 等[44]采用一氯乙酸对决明子半乳甘露聚糖改性后,其溶胀性增强。羧甲基化的半乳甘露聚糖与阳离子如 Ca^{2+}发生离子凝胶化，与氯化钙的反应制备了负载双氯芬酸的离子凝胶珠，可以进一步调节药物释放速度。

酯化半乳甘露聚糖是半乳甘露聚糖中的羰基被无机酸或有机酸酯化而得的产物。辛烯基丁二酸酐(OSA)酯化葫芦巴半乳甘露聚糖,可用于提高半乳甘露聚糖水凝胶的机械强度，拓宽半乳甘露聚糖水凝胶的应用领域[45]。半乳甘露聚糖经酸酐酯化合成的膜具有良好的疏水性，优异的隔氧性能和较高的拉伸机械强度[46]。半乳甘露聚糖经辛酸酯化后与辛酸相似，均对结肠癌细胞系(HCT-116 细胞)具有抗增殖作用,对结肠炎具有潜在的治疗作用[47]。

Li 等[48]以瓜尔胶为原料,1,4-丁二醇二甘油酯醚为交联剂，制备了新型环氧交联半乳甘露聚糖水凝胶,可提高药物的累积释放率。Tao 等[49]通过 HNO_3-Na_2SeO_3 修饰得到 6 种硒代半乳甘露聚糖，其在体外对氧化损伤的保护作用强于未修饰的半乳甘露聚糖。Ono 等[50]通过氯磺酸硫化半乳甘露聚糖，产物在体内和体外均具有抗黄热病毒的活性。

在高温和强酸下,半乳甘露聚糖会发生水解,主要产生单糖和寡糖。常见的酸性催化剂有盐酸、硫酸和三氟乙酸,Liu 等[51]在最优条件下水解皂荚胶、瓜尔胶和胡芦巴胶，其单糖提取率分别为 95.18%,93.47%,93.50%。Xu 等[52]采用氯化亚铁(Fe^{2+})和乙酸(HAc)协同作用水解半乳甘露聚糖制备甘露寡糖,有效提高了甘露寡糖的产量,同时降低了单糖和 5-羟甲基糠醛(5-HMF)的生成。从甘露糖/半乳糖 M/G 比值的变化可以推断出 Fe^{2+}主要裂解主链,而 HAc 则辅助侧链的断裂,从而

高效水解半乳甘露聚糖制备甘露寡糖。瓜尔胶溶液在受热情况下，水解主要产生水溶性单糖和寡糖。水热温度 180~240 ℃,反应时间 3~60 min,瓜尔胶将水解为聚合度 20 的寡糖、单糖(甘露糖和半乳糖)、5-HMF;在 200 ℃水解 7 min 时,寡糖产量达到最大值 94.4%,此后随时间延长而降低;糖产量开始随时间延长而增加，半乳糖的产生在一定程度上先于甘露糖的产生，在 60 min 时达到 34.5%(甘露糖为 22.8%、半乳糖 11.7%);此后单糖继续分解为次级产物,如 5-HMF,其产率在 220 ℃,30 min 时达最大(26.3%)[53]。

3.2 酶法改性

酶解主要通过 β-甘露聚糖酶、α-半乳糖糖苷酶、多聚半乳糖醛酸酶等酶将半乳甘露聚糖水解。β-甘露聚糖酶在植物、动物以及微生物中均可见[54],如在半乳甘露聚糖酶解芽孢杆菌中发现 1,4-β-甘露聚糖酶[55]。β-甘露聚糖酶将甘露糖单元从半乳甘露聚糖的非还原端分离出来，以获得低聚合度的半乳甘露聚糖或半乳甘露寡糖[56]。α-半乳糖苷酶,是一种广泛存在于动物、植物和微生物中的糖苷水解酶,α-半乳糖苷酶可催化 α-1,6-连接的末端半乳糖残基的水解[57]。Yang 等[58]使用 β-甘露聚糖酶和 α-半乳糖苷酶共同酶解田菁种子中半乳甘露聚糖，半乳甘露聚糖不完全降解产物以及半乳甘露寡糖的产率分别为 78.84%和 30.94%,加入 α-半乳糖苷酶可以去除半乳甘露聚糖中甘露聚糖主链上的半乳糖取代基,减轻 β-甘露聚糖酶水解的位阻，且有利于提高不完全降解产物的生物活性。多聚半乳糖醛酸酶亦称果胶酶,多聚半乳糖醛酸酶水解果胶酸的 α-1,4-糖苷键生成寡聚半乳糖醛酸或半乳糖醛酸[59]。Shobha 等[60]使用多聚半乳糖醛酸酶酶解半乳甘露聚糖，该酶水解瓜尔胶后分子质量由 240 ku 水解至70 ku,甘露糖与半乳糖的比例由 1∶1.6 变为 1∶2.8。

3.3 物理改性

物理改性技术是指采用热、力、光、电等手段来改变生物质原有的形态、结构、性质。关于通过物理方法改性多糖的研究常见报道,如 Kang 等[61]使用超声波处理黄原胶，其分子质量由 3.0×10^7 u 降至 1.4×10^6 u，在较低强度超声处理下主要破坏黄原胶分子骨架，随着强度的增加则主要破坏侧链，从而显著降低黄原胶的表观黏度和黏弹性；Yan 等[62]使用微波辐照低乙酰结冷胶,结果显示微波可以提高结冷胶链的持水能力，限制水的流动性,促进结冷胶凝胶化。物理方法通常是通过超声波、伽马射线、脉冲、电场等解聚高分子化合物,使由高分子化合物降解成低分子化合物。Niknam 等[63]使用超声处理含胡芦巴-胡皂素水包油乳液后,乳液具有弱凝胶行为。Gorji 等[64]在 0,5,10 kGy 下辐照瓜尔胶，溶液黏度 (质量分数 1%)在 0~10 kGy 范围内,随辐照剂量的增加而显著降低,辐照剂量(5,10 kGy)使瓜尔胶溶液(1%)由非牛顿流体转变为牛顿流体。Ravat 等[65]使用伽马射线处理半乳甘露甘露聚糖，半乳甘露甘露聚糖主链分子质量下降,黏度降低。Li 等[66]以瓜尔胶、壳聚糖和果胶为模型多糖,诱导电场(IEF)可辅助酸水解破坏多糖的紧密结构,并显著降低溶液黏度。

4 半乳甘露聚糖的应用

4.1 食品工业

半乳甘露聚糖在食品中常作为稳定剂与增稠剂使用。由于其黏度较高,半乳甘露聚糖很少在高于 1%(m/V)的质量浓度下使用。例如,瓜尔胶与长角豆胶被广泛地添加在冰淇淋中，以提升冰淇淋的外观质感,减少冰淇淋的溶化状况。冰淇淋或奶昔中的蛋白质-多糖混合物在一定浓度下是相分离不相容的[25],因此配方中的多糖通常控制在较低质量浓度(0.1%~0.6%,m/V)[67]。半乳甘露聚糖也可以用于淀粉类食品，以改善食品的质地。例如,将瓜尔胶代替面粉制备面包,可有效降低餐后血糖反应，显著提高烘焙产品的保质期和感官性能[68]。由于半乳甘露聚糖可以提高糖尿病小鼠的胰岛素敏感性,并改善肠道微生物群组成,半乳甘露聚糖也是一种潜在的益生元[69]。

半乳甘露聚糖是一种具有广泛应用前景的天然高分子材料，在食用涂层和食品包装方面也具有巨大的潜力。Souza 等[70]以 2.0%海藻酸盐、0.5%半乳甘露聚糖、0.5%腰果胶和 2.0%明胶配制葡萄的食用包衣,可减少葡萄水分流失、保持色泽和酚类化合物含量。Liu 等[71]以壳聚糖修饰的半乳甘露聚糖为原料,脱乙酰壳聚糖(DC)为改性剂制备的膜对大肠杆菌、枯草芽孢杆菌、金黄色葡萄球菌、

肺炎链球菌等不同类型的细菌均具有良好的抗菌性能,有望成为未来塑料包装的替代品。González 等[72]添加半乳甘露聚糖改善大豆蛋白膜,膜的含水量、总可溶性物质和溶胀率都显著降低。

4.2 生物医药

半乳甘露聚糖是一种天然、稳定、安全、无毒、亲水、可降解的生物高聚物,具有理想的物理和生物性能。例如,Pascoal 等[73]通过喷雾干燥将类胡萝卜素包裹在半乳甘露聚糖聚合物中, 可以提高类胡萝卜素的稳定性。

半乳甘露聚糖也被广泛设计为各种药物运输的载体,如基质片、颗粒、纳米/纳米复合材料、聚合物胶束、水凝胶和药用材料,用于口服疫苗、口服胰岛素递送、控制药物递送、靶向癌细胞和巨噬细胞、伤口敷料等。例如,Dangi 等[74]将决明子半乳甘露聚糖和三甲基磷酸钠用于制备给药系统的水凝胶, 作为治疗结肠癌和其它结肠疾病的持续药物递送剂。Sindhu 等[75]研究发现制备的姜黄素–半乳甘露聚糖复合物可以提高姜黄素在减轻农药呋喃毒性方面的作用。Siqueira 等[76]制备了含有不同浓度半乳甘露聚糖的明胶薄膜, 大鼠间充质干细胞均能黏附在膜上,且没有表现出细胞毒性,显示含半乳甘露聚糖的明胶薄膜有望用于伤口愈合敷料。闫磊等[77]向水中加入谷氨酰胺接枝半乳甘露聚糖和增黏处理后的海藻酸钠, 加热至 60~70 ℃保温搅拌,再加入辅料,继续于 60~70 ℃保温搅拌,自然冷却,制备得到一种具有优良保湿性能、保湿效果且保湿时间长, 适用于作为皮肤止痒抑菌贴剂用水凝胶材料。透明质酸和半乳甘露聚糖也可以制备成薄膜或水凝胶, 其黏性和黏弹性有所改善[78]。

半乳甘露聚糖是曲霉细胞壁的成分。曲霉是已知的、最常见的、传播最广的霉菌之一,是一种条件致病菌。在免疫力低下的个体中容易发生肺部感染。当曲霉感染时,血液和体液(尿液、脑脊液、腹水、胸水等)中的半乳甘露聚糖会显著升高,故检测半乳甘露聚糖可用于曲霉感染的早期诊断[79]。

4.3 其它

半乳甘露聚糖在造纸、纺织、石油、化妆品等行业也有广泛应用。半乳甘露聚糖在造纸中主要被用来作为增强剂、絮凝剂、助留助滤剂等,在浆内起黏合作用。可单独使用,也可以与淀粉配合使用,一般仅添加 0.10%~0.35%即可[80]。半乳甘露聚糖可经过 H_2O_2 氧化、季铵盐改性、柠檬酸酯化制成各种衍生物,以改善纸张的性能[81-82]。

半乳甘露聚糖在纺织、化妆品中作为增稠剂和稳定剂。羧甲基半乳甘露聚糖可以改善印花性能[83]。半乳甘露聚糖在石油工业中主要利用其黏稠性配成凝胶制成水基压裂液[84],以提高后期油井的产量。

半乳甘露聚糖也可作为一种通过物理吸附和化学吸附作用于金属表面的混合型缓蚀剂应用于金属防腐方面[85]。Abbout 等[86]在环氧涂层中加入半乳甘露聚糖可以提高碳钢在酸性环境中长时间浸泡的耐腐蚀性。

5 结语

半乳甘露聚糖是一种有优异的增稠、胶凝能力的中性多糖, 其性质受到分子质量大小、甘露糖/半乳糖比例等因素影响。此外,它还具有多种生理功能,例如:抗癌、降血压、降血糖、促进小肠双歧杆菌的增殖, 半乳甘露聚糖的结构与生理活性之间的关系仍值得探索,以指导改性方向。半乳甘露聚糖广泛应用于食品、生物医药、造纸、纺织、石油、化妆品等领域,化学、物理和酶法相结合的改性或双重物理改性仍值得探索, 以拓宽半乳甘露聚糖的应用。

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The Property, Modification and Application of Galactomannan

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Abstract Galactomannan is a kind of neutral heteropolysaccharide, which has excellent abilities in thickening, stabilizing and gelling. Moreover, it has a variety of physiological functions, like promoting the proliferation of bifidobacterium in intestine, lowering blood pressure and blood sugar, and preventing constipation, colon cancer, cardiovascular disease. The properties differ in the ratio of mannose/ galactose units, molecular weight, and distribution of individual galactose branches along the main chain. With the development in the hydrocolloid industry, the modification of galactomannan has been an important research topic to ensure its use in food, pharmaceutical, biomedical and other fields. In recent years, there were many researches on galactomannan. The physical properties, physiological activity, modification and application of galactomannan were comprehensively introduced in this paper, in order to provide reference for the research of galactomannan in China.

Keywords galactomannan; property; modification; application