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右旋糖酐在食品中的应用研究进展

常国炜 黎志德 刘桂云 梁达奉 黄曾慰

(广东省科学院生物与医学工程研究所, 广东 广州 510316)

摘要: 右旋糖酐是一类微生物多糖, 主链是由 α -1,6-糖苷键链接的葡萄糖链, 其应用研究已在多个食品领域开展。文章综述了近年来新来源右旋糖酐的结构、功能分析及其生产菌的研究趋势, 对右旋糖酐在蛋白质精深加工、面包烘焙、益生元等食品领域中的创新应用研究现状进行了阐述, 指出了当前相关研究和政策中存在的问题和未来研究方向。

关键词: 右旋糖酐; 蛋白精深加工; 面包烘焙; 益生元

Research progress on application of dextran in food

CHANG Guowei LI Zhide LIU Guiyun LIANG Dafeng HUANG Zengwei

(Institute of Biological and Medical Engineering, Guangdong Academy of Sciences,
Guangzhou, Guangdong 510316, China)

Abstract: Dextran is a kind of microbial polysaccharide consisting of a glucose chain linked by α -1, 6-glucoside bond. Its application research has been carried out in many food fields. In this review, the structure and function analysis of new sources of dextran and the research trend of producing bacteria in recent years were summarized, and the research status of innovative applications of dextran in the field of protein deep processing, bread baking, prebiotics, etc., were described. The existing problems in current research and policy and future research directions were also discussed.

Keywords: dextran; protein deep processing; bread baking; prebiotics

右旋糖酐(dextran)是一类由右旋糖酐蔗糖酶(EC 2.4.1.5)转化蔗糖生成的多糖,其糖链只有葡萄糖残基,并主要以 α -1,6-糖苷键连接成主链,支链由葡萄糖残基或葡萄糖链(简单或复杂的)以 α -1,2-、 α -1,3-或 α -1,4-糖苷键的一种或多种连接在主链上,其中 α -1,6-糖苷键一般占总糖苷键65%以上。不同微生物或酶在不同条件下产生的右旋糖酐结构均有差异,从而导致性质差异^[1]。右旋糖酐及其衍生物已作为药物在世界范围内被广泛使用,包括右旋糖酐、右旋糖酐铁^[2]、硫酸葡聚糖钠^[3]、右旋糖酐-(1-氯-2,3-环氧丙烷)聚合物(dextranomer)^[4]等。在生物医学研究领域,右旋糖酐硫酸钠常用于结肠炎相关研究^[5],异硫氰酸荧光素葡聚糖则用于体内通透性研究^[6]。右旋糖酐的共同特征是拥有半缩醛基和大量可改性或修饰羟基,具有较好生物相容性和较强抗消化性,其作为水凝胶^[7]、药物载体^[8]、生物活性创面敷料^[9]等研究已广泛开展并取得一定成果。

在食品领域,早年已有文献表明右旋糖酐会抑制糖生产带来不良影响^[10],研究重点为如何利用右旋糖酐酶(EC 3.2.1.11)等方法消除其影响^[11]。近年来,由于右旋糖酐中性多糖的性质,其在蛋白糖基化的应用受到重视。另一方面,由于主粮结构变革,其水胶体效应在面包烘焙领域又有进一步应用。此外,随着肠道菌群研究火热,右旋糖酐典型的益生元效应应拓展出多种创新应用思路。文章将对右旋糖酐结构和功能研究现状进行简要综述,并重点总结右旋糖酐在食品领域中的应用研究现状,以期帮助人们了解其在食品领域应用中的潜力,拓展其在食品工业中的实际应用

1 右旋糖酐研究进展

1.1 新型右旋糖酐的结构和功能分析

近3年新发现的右旋糖酐进一步扩大家族组成,这得益于研究人员对乳酸菌胞外多糖的兴趣(由于乳酸菌胞外多糖可能具有抗氧化、免疫调节、抗癌等活性功能^[12])。

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通信作者: 黄曾慰(1984—),男,广东省科学院生物与医学工程研究所高级工程师,硕士。E-mail: zengwei.huang@qq.com

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新型右旋糖酐结构表征见表1,性能表征见表2。

新型右旋糖酐的获取主要有两种途径:①从环境中筛选生产菌后发酵获取;②通过右旋糖酐蔗糖酶并催化获取。右旋糖酐蔗糖酶可通过生产菌培养分离,或通过基因工程手段外源表达而得。通过调整酶催化条件(pH或受体等)改变右旋糖酐结构和产率^[21],是开发新型右旋糖酐的高效途径。

右旋糖酐乃至多糖的结构分析已有一套较完整的研究方法,能较全面表征其一级结构和聚集态。如酸水解后利用高效液相色谱(HPLC)或气相色谱(GC)(衍生化后)测定单糖组成;气质联用(GC-MS)(配合甲基化反应)或核磁共振(NMR)测定连接方式和比例;多角度激光散射检测器(MALLS)测定相对分子质量;红外光谱(IR)测定糖苷键构型;扫描电镜(SEM)和原子力显微镜(AFM)测定其表面及溶解后形态;X射线衍射(XRD)测定其结晶情况;刚果红试验(CgRT)分析其聚集态等。

新型右旋糖酐中不乏无支链结构的,或糖苷键构成

复杂的,相对分子质量低至万级,高至亿级,且空间结构各异。在热力学分析中,新型右旋糖酐热解温度介于280~326℃,远高于一般食品加工处理温度,具有食品应用所需热稳定性。在抗氧化能力分析中,右旋糖酐在1~8 mg/mL 显示出显著抗氧化性能。在体外模拟试验中,右旋糖酐显示出对胃液、淀粉酶的抗消化性和刺激益生菌生长的益生元活性。此外,多种流变学、高分子物理与化学特性被表征,这为其后续开发应用提供数据支持。总体而言,新发现右旋糖酐来源和结构各异,一定程度影响其功能水平,但影响机理并未深入阐明,这也是今后研究方向之一。

1.2 右旋糖酐及其生产菌研究趋势

右旋糖酐在医药和食品方面的良好应用特性促进了从不同生长环境中分离和研究新的生产菌的科学兴趣,右旋糖酐蔗糖酶的编码基因、调控元件、蛋白结构等方面的研究逐步成为主流。杜仁鹏^[14]^[15-120]利用全基因组测序,筛选出生产菌右旋糖酐蔗糖酶调控基因,利用实时定量

表1 新型右旋糖酐结构表征
Table 1 Structural characterization of novel dextran

微生物名称	微生物来源	键型比例				相对分子质量	聚集态	表面微观结构	三维表面结构	参考文献
		α -1,6	α -1,4	α -1,3	α -1,2					
肠膜明串珠菌(<i>Leuconostoc mesenteroides</i>)BI-20	蜂花粉	80.00	—	20.00	—	1×10^8	无定形	高度分支纤维状	—	[13]
肠膜明串珠菌DRP105 (酶法合成)	酸菜	100.00	—	—	—	9.85×10^7	—	光滑、有光泽,呈多分枝片状、紧凑结构	不均匀圆形或球状隆起,多糖链网状构型	[14] ¹⁰⁵⁻¹¹⁷
假肠膜明串珠菌DRP-5 (<i>Leuconostoc pseudomesenteroides</i>)(酶法合成)	自酿葡萄酒	97.30	—	2.70	—	3.083×10^6	无定形	致密、光滑、不规则片状,有大量管状分支	表面致密,有峰状隆起	[15]
乳明串珠菌(<i>Leuconostoc lactis</i>) AV1n	牛油果	89.80	—	9.00	1.20	2.61×10^8	—	—	—	[16]
昆氏乳杆菌(<i>Lactobacillus kunkeei</i>) AP-27	蜂花粉	99.50	0.50	—	—	2.5×10^4	无定形	致密、规则、球状	—	[17]
昆氏乳杆菌AK1	蜂花粉	95.22	4.78	—	—	4.5×10^4	晶体	致密、规则、球状	不均匀颗粒状,多糖链间无明显交联(溶液状态)	[18]
茵氏乳杆菌(<i>Lactobacillus ingluviei</i>)DSM 14792(酶法合成)	鸡粪	69.00	6.00	24.00	1.00	5.46×10^5	主要是非晶态,少量晶态	无规则、多空隙和裂缝	球形颗粒、不规则块状颗粒(溶液状态)	[19] ¹⁷⁻⁵⁶
融合魏斯氏菌(<i>Weissella confusa</i>)XG-3	香瓜	100.00	—	—	—	3.19×10^6	无定形	光滑、多孔和分支结构	不规则、粗糙,圆形块状和链状	[20]
甘草醇溶乳酸杆菌(<i>Liquorilactobacillus hordei</i>) TMW 1.1822 (酶法合成)	水开菲尔	95.70	—	4.30	—	pH 4.0: 1.09×10^8 ; pH 5.5: 1.86×10^8	—	—	—	[21]

表 2 新型右旋糖酐性能表征
Table 2 Performance characterization of novel dextran

微生物名称	热解温度/℃	其他特性	参考文献
肠膜明串珠菌 BI-20	315.60	抗氧化性:剂量依赖型,ABTS ⁺ ·、铜离子还原法(CUPRAC)清除率 36.1%,35.0%(1 mg/mL);抗消化性:模拟胃液或 α-淀粉酶处理 6 h 均无降解	[13]
肠膜明串珠菌 DRP105 (酶法合成)	317.72	溶解度 88.23%;持水率 387.34%	[14] ¹⁰⁵⁻¹²⁰
假肠膜明串珠菌 DRP-5 (酶法合成)	325.62	溶解度 94.08%;持水率 402.71%;乳化活性 83.81%(大豆油);抗氧化性:DPPH·、·OH、O ₂ ⁻ ·、ABTS ⁺ ·清除率分别为 29.56%,18.13%,23.85%,40.46%(6 mg/mL);ABTS ⁺ ·清除率 38.65%(4 mg/mL)	[15]
乳明串珠菌 AV1n	—	回旋半径 100.30 nm;黏附性:细菌分泌右旋糖酐可使其黏附在 Caco-2 细胞上,或在聚苯乙烯板形成生物被膜	[16]
昆氏乳杆菌 AP-27	308.00	—	[17]
昆氏乳杆菌 AK1	280.00	抗氧化性:剂量依赖型,DPPH·、CUPRAC 清除率 46.23%,28.00%(4 mg/mL);ABTS ⁺ ·清除率 91.6%(8 mg/mL);抗消化性:模拟胃液和 α-淀粉酶处理 6 h 消化率 3.1%	[18]
茵氏乳杆菌 DSM 14792 (酶法合成)	320.00	平均粒径 162.4 nm;零剪切黏度 2 868 Pa·s(12%);流体性质:牛顿型流体(3%)、假塑性流体(6%~12%)	[19] ¹⁷⁻⁵⁶
融合魏斯氏菌 XG-3	306.80	Zeta 电位 8.6 mV(2 mg/mL);粒径 353.2 nm(2 mg/mL);抗氧化性:剂量依赖型,DPPH·、ABTS ⁺ ·、O ₂ ⁻ ·、·OH、H ₂ O ₂ 清除率分别为 45.26%,45.76%,28.13%,48.65%,67.22%(5 mg/mL);益生元活性:刺激多种益生菌生长	[20]
甘草醇溶乳酸杆菌 TMW 1.1822(酶法合成)	—	pH 4.0:粒径 73.5 nm;流变学:黏弹性(10%) pH 5.5:粒径 94.3 nm;流变学:凝胶(7.5%)	[21]

荧光 PCR 验证表达情况,初步筛选关键基因;利用同源双交换技术构建基因缺失突变菌株,确认关键基因,进行过表达获得重组酶蛋白,表征其结构与天然菌株无显著差异,最终合成出高相对分子质量无分支结构右旋糖酐。陈自卫^{[19]57-89}研究了一种可合成含有 4 种糖苷键 α-葡萄糖的右旋糖酐蔗糖酶,发现部分氨基酸残基影响键型特异性、转糖基酶活及转糖基酶活/水解酶活(T/H),推测 V 结构域可能参与绑定并且拖动正在合成的多糖链远离或靠近催化中心,而 IV 结构域可能充当控制 V 结构域摆动的“铰链”,参与决定键型特异性。上述两项研究进一步阐明右旋糖酐合成机理,为下一步控制右旋糖酐结构打下基础。

此外,Besrou-Aouam 等^[16]通过透射电镜观察到右旋糖酐对乳明串珠菌和某些魏斯氏菌(*Weissella* sp.)在生物和非生物表面的黏附和聚集性能的影响。其中,对于乳明串珠菌,右旋糖酐会增强其黏附和聚集性能;而对部分魏斯氏菌,则会削弱其性能。进一步地,通过代谢通量分析,预测了几种微生物在产右旋糖酐过程中的糖运输和中间代谢途径,这将为益生菌和新功能食品的开发提供良好基础。

2 右旋糖酐在食品领域中的应用

2.1 蛋白质精深加工应用

右旋糖酐的还原端 C1 具有还原性,能与蛋白质的 ε-氨基发生美拉德反应,并通过缩合、重排形成糖基胺重排产物即蛋白质—糖接枝物,能够显著改善蛋白质的功能性质,促进蛋白质精深加工应用。赵城彬等^[22]利用右旋糖酐与玉米醇溶蛋白接枝,使玉米醇溶蛋白热稳定性降低,三级结构松散,乳化性能增加,且与低相对分子质量(6 000)右旋糖酐反应生成的接枝物乳化活性最好[(23.28±0.71) m²/g],而与高相对分子质量(7 万)反应的则乳化稳定性最好[(26.44±0.47) min];杜沁岭等^[23]利用右旋糖酐与大豆 11S 蛋白接枝,增加了溶解性、乳化稳定性和持水性,且低相对分子质量(4 000)右旋糖酐对表面活性改善效果更明显;右旋糖酐与牛血清白蛋白反应得到类似效果^[24];Zhang 等^[25]利用右旋糖酐与大豆分离蛋白接枝提高其凝胶性能。这样的糖基化修饰不足之处是对于结构非常紧密的蛋白效果有限,想要更好效果需要对蛋白进行预处理以暴露更多内部基团。

右旋糖酐与蛋白的接枝物除了改善蛋白性能外,还可以作营养物质传递载体。Li 等^[26]利用右旋糖酐和酪蛋

白酸钠接枝并包埋植物甾醇,形成松散的纳米颗粒聚集体,大大降低植物甾醇结晶度,并有更好抗胃酸能力(提高3.86%)和肠道条件释放率(提高19.52%),提高植物甾醇生物利用度;Fan等^[27]利用右旋糖酐与牛血清白蛋白接枝物再包埋姜黄素,与游离姜黄素相比,有更好pH(2~7)/温度(25,95℃)稳定性和细胞抗氧化活性。该类方法在传递非水溶性营养物质达到较好效果,为营养物质在酸奶、果汁等酸性饮料中作为营养补充剂等功能性食品应用打下基础。

综合乳化性能增强和负载营养物质的功能,Yi等^[28]将右旋糖酐与乳清蛋白接枝,不仅改善乳化效果,还负载上白藜芦醇,并作为 β -胡萝卜素的乳化剂,形成三元传递体系。此类研究均以提高疏水营养物质水溶性、理化稳定性和生物利用度等为目标进行体系构建,所用接枝反应条件和营养物质负载条件温和,能有效保持各种物质生理活性,具有大规模生产的潜力。

右旋糖酐除了与其他物质形成共价键,还可以通过较弱的反应条件,与其他蛋白形成氢键结合,展示出成纤性能。Luo等^[29]将右旋糖酐和玉米醇溶蛋白混合,通过静电纺丝技术得到纳米纤维,并将姜黄素包埋,得到具有抗氧化和抗菌活性的纤维材料,有望开发成具有生物活性且可食用的食品包装材料,减少对不可降解材料的依赖。

2.2 面包烘焙领域应用

面包是以小麦粉为主要原料的一类发酵焙烤食品,在存放过程中会逐渐老化,导致品质下降。添加抗老化剂是延缓面包老化的常用手段。其中,右旋糖酐作为面包抗老化剂是近年的研究热点。Zhang等^[30-31]发现高相对分子质量(200万)右旋糖酐能改善面团弹性性能和抑制面包老化,抑制支链淀粉回生,而低相对分子质量(1万)右旋糖酐却使面包结构松散,产生更多碎屑且碎屑硬度更大,不利于面包成型。进一步地,右旋糖酐和弱酸化对减缓面包老化、改善面包品质的协同作用也被发现^[32]。基于以上研究,Wang等^[33]在发酵面团原位生产右旋糖酐及弱酸,并利用双轴拉伸测试和动态机械热分析等手段,证明原位生产右旋糖酐也能改善面团黏弹特性、延展性和烘焙质量,为原位生产右旋糖酐作为面包改良手段奠定基础。

随着人们健康饮食意识和生活质量的提高,粮食多样化成为讨论和研究的热点。其中,在面包制作中使用杂粮或碾磨副产品作为小麦替代品成为热点。但其他谷物面筋含量较低,会使面团黏弹性和膨胀性变差^[34],而且部分杂粮还有异味,影响面包风味。而结合右旋糖酐结构特点,通过与水结合和模仿面筋黏弹特性,在面包制作中充当水凝胶,可改善面团流变学特性、烘焙性能和面包风味特性等^[35]。Wang等^[36]将珍珠小米磨粉,与小麦粉按质量比1:1混合并加入蔗糖,利用原位发酵生产右旋糖

酐,得到了含3.5%右旋糖酐的面团,拉伸性能提高,烘焙得到的面包体积增加13%、水分损失降低15%、老化速度降低10%、面包屑硬度降低43%,支链淀粉的重结晶明显减少,游离酚含量增加30%,预测升糖指数降低,体外蛋白质消化率上升。用类似方法研究添加高粱粉制作面包,还发现右旋糖酐对酸味、苦味有遮蔽作用^[37]。相比直接添加右旋糖酐,原位生成右旋糖酐减少了应用成本,但蔗糖转化的副产物果糖对面包风味的影响需要进一步评估。

2.3 益生元及其创新应用

益生元是指能选择性地刺激某些细菌生长与活性,且对寄主产生有益影响,改善寄主健康的不可被消化的食品成分^[38]。低聚异麦芽糖益生元作用的研究已被广泛报道^[39],而右旋糖酐有着与低聚异麦芽糖类似的结构,所以其益生元作用也被关注和研究。Kim等^[40]研究肠膜明串珠菌SPCL742生成的右旋糖酐对肠道微生物生态系统的益生元活性,发现该右旋糖酐能使解木聚糖拟杆菌(*Bacteroides xylanisolvens*)和双歧杆菌属(*Bifidobacterium* spp.)共生,提高短链脂肪酸、戊酸盐和泛酸盐浓度,抑制致病性大肠杆菌(pathogenic *Escherichia coli*)对人上皮细胞的黏附。Amaretti等^[41]和Tingirikari等^[42]发现食蜜魏斯氏菌(*Weissella cibaria*)(或其右旋糖酐蔗糖酶)生成的右旋糖酐可以提高肠道菌群中普雷沃氏菌属(*Prevotella* spp.)和拟杆菌属(*Bacteroides* spp.)的比例,并促进短链脂肪酸产生,这与菊粉(一种公认、成熟的益生元)的效应是一致的。

有报道利用酶在果汁中合成右旋糖酐后,直接研究果汁的益生元性能,旨在开发功能性果汁新产品。Leite等^[43-44]在鸡腰果汁和橙汁中添加右旋糖酐蔗糖酶原位合成右旋糖酐,再将果汁进行体外模拟消化和益生菌培养,发现右旋糖酐对模拟消化有抗性,并能刺激产酪乳杆菌(*Lactobacillus casei*) NRRL B-442、瘤胃乳酸杆菌(*Lactobacillus ruminis*)、短双歧杆菌(*Bifidobacterium breve*) NRRL B-41408、青春双歧杆菌(*Bifidobacterium adolescentis*)等益生菌的生长。在类似研究共同验证下,右旋糖酐的益生元效应已逐渐被业界认可。

此外,多种更为创新的益生元应用思路正被实现。Kim等^[45]将右旋糖酐与邻苯二甲酸酐偶联制备纳米颗粒(PDNs),发现乳酸片球菌(*Pediococcus acidilactici*)可以将PDNs内化,通过调节代谢而提高抗菌肽产生和分泌,增强对革兰氏阳性和阴性病原体抗菌活性,提高肠道内益生菌比例和种类。这种新型作用机理有别于传统的降低pH和底物选择性机理,通过微生物内化作用直接调节代谢,是一条有望替代抗生素,成为解决细菌耐药性难题的新途径。Zheng等^[46]将右旋糖酐通过主客体相互作用包裹丁酸梭菌(*Clostridium butyricum*)孢子,经口服到肠

道,孢子在肠道厌氧环境中复苏,分解右旋糖酐,并在肿瘤组织富集(右旋糖酐的存在能改善黏附能力),丁酸梭菌分泌具有抗癌作用的短链脂肪酸,同时,右旋糖酐继续发挥益生元作用,系统地调节肠道菌群,将肠道菌群从促肿瘤型转化为抗肿瘤型。下一步,可考虑将卡培他滨和双氯芬酸等抗癌药物负载到右旋糖酐包裹物上联合应用,有望成为高度安全且功能丰富的益生菌/益生元联合抗癌药物治疗胃肠道肿瘤疾病的新型治疗设计途径。

2.4 其他应用

右旋糖酐的衍生物仍是重要的研究方向,以期在食品领域应用。例如,将右旋糖酐和没食子酸结合,显示出抗氧化性^[47]和 α -葡萄糖苷酶(EC 3.2.1.20)抑制活性,有望应用于降糖食品^[48];与酪蛋白磷酸肽、 Ca^{2+} 结合成钙传递系统,能抑制在胃肠道中磷酸钙沉淀生成,提高钙生物利用度^[49];与姜黄素接枝,提高抗氧化、抗菌和抗癌细胞增殖活性^[50];作为稳定剂与 Ag^+ 制备纳米银颗粒,提高对食源性致病菌抑制作用^[51]等。此类研究仍处于探索阶段,开发难度大,针对每种物质均需要考虑结合方式、合成反应途径和条件。

此外,有研究认为,对于澄清饮料,右旋糖酐会导致絮凝产生^[52],但对于苹果或葡萄汁等混浊果汁,为了保持混浊体系稳定性,加入霍尔迪乳酸杆菌(*Lactobacillus hordei*)原位生产右旋糖酐作为稳定剂,可使果汁保存数月混浊度不变^[53]。除了成纤性,右旋糖酐还有成膜性,辅以山梨醇增塑,可以制成低蒸汽渗透性和具有一定抗拉强度和弹性的食用薄膜^[54];右旋糖酐还应用于新型静电喷涂技术,与普鲁兰多糖混合制备用于静电喷涂乳剂,经喷涂后形成具有较好氧渗透性的微胶囊保护目标物质^[55]。

3 结论与展望

在医药领域,随着更高效安全的代血浆药物出现,右旋糖酐在该方面应用逐步减少,转向利润更高的医美行业,而在食品领域则往高值化进行。右旋糖酐有着多羟基、长链条的结构特征,是很好的改性平台物质和载体,具有较高研究价值和经济价值。应用各种现代生物技术、分离分析技术和创新思路,将有更多右旋糖酐被研究及低成本制备,并进一步推动其应用进程。

在法规方面,右旋糖酐早已收录于多国药典,并被FDA列入食品添加剂清单(通过GRAS认证)^[56],但未收录在中国GB 2760—2024《食品安全国家标准 食品添加剂使用标准》、GB 14880—2012《食品安全国家标准 食品营养强化剂使用标准》等食品标准中。国家卫健委公布的《可用于食品的菌种名单》已收明串珠菌属(*Leuconostoc* spp.)的3个亚种^[57-59],因此在乳制品、腌制食品等的生产工艺流程中添加相关菌种符合相关法律法规。综合国内外相关研究进展和政策导向,右旋糖酐在

食品中应用预期整体向好。

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(下转第 180 页)

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