中药黄芩中寡糖的分离纯化与结构鉴定

张宇婷[1,2], 宋　娟[2], 刘　思[2], 王睿哲[1,2], 陈晓娟[2], 梁海珍[2], 马百平[1,2*]

(1. 广东药科大学, 广东 广州 510006;　2. 军事科学院军事医学研究院, 北京 100850)

摘要: 采用中压快速制备色谱、半制备高效液相色谱以及以电雾式检测器 (CAD) 触发自动馏分收集器的高效液相色谱等手段, 从黄芩醇提物的大孔吸附树脂水洗脱部位分离得到13个寡糖类单体化合物。采用质谱及核磁共振等波谱手段鉴定化合物结构, 分别为*α*-*D*-半乳糖-(1→6)-*α*-*D*-葡萄糖-(1→2)-*β*-*D*-果糖-(6→1)-*α*-*D*-半乳糖-(6→1)-*α*-*D*-半乳糖 (**1**)、*α*-*D*-半乳糖-(1→6)-*α*-*D*-半乳糖-(1→6)-*α*-*D*-葡萄糖-(1→2)-*β*-*D*-果糖-(4→1)-*α*-*D*-半乳糖 (**2**)、*α*-*D*-半乳糖-(1→2)-*α*-*D*-半乳糖-(1→6)-*α*-*D*-半乳糖-(1→6)-*α*-*D*-葡萄糖-(1→2)-*β*-*D*-果糖 (**3**)、棉子糖 (**4**)、水苏糖 (**5**)、毛蕊花糖 (**6**)、筋骨草糖 (**7**)、umbelliferose (**8**)、erlose (**9**)、loliose (**10**)、*α*-*D*-半乳糖-(1→6)-*α*-*D*-半乳糖-(1→6)-*α*-*D*-葡萄糖-(1→2)-*β*-*D*-果糖-(1→1)-*α*-*D*-半乳糖 (**11**)、rehmaglupentasaccharide E (**12**) 和 rehmaglupentasaccharide F (**13**)。所有寡糖单体均为首次从黄芩中分离得到, 聚合度为3～6。其中化合物**1**～**3**为新化合物, 属于非传统型棉子糖家族寡糖。化合物**4**～**7**为棉子糖家族系列寡糖; 化合物**11**～**13**亦为非传统型棉子糖家族寡糖。

关键词: 黄芩; 寡糖; 分离; 结构鉴定; 非传统型棉子糖家族寡糖

中图分类号: R284　　**文献标识码**: A　　**文章编号**: 0513-4870(2026)06-2230-11

Isolation and structural elucidation of oligosaccharides from *Scutellaria baicalensis* Georgi

ZHANG Yu-ting[1,2], SONG Juan[2], LIU Si[2], WANG Rui-zhe[1,2], CHEN Xiao-juan[2], LIANG Hai-zhen[2], MA Bai-ping[1,2*]

(*1. Guangdong Pharmaceutical University, Guangzhou 510006, China;　2. Academy of Military Medical Sciences, Academy of Military Sciences, Beijing 100850, China*)

Abstract: Thirteen oligosaccharides were isolated from the water-eluted fraction of *Scutellaria baicalensis* Georgi extract on macroporous adsorption resin, using techniques such as medium-pressure liquid chromatography, semi-preparative high performance liquid chromatography (HPLC), and a HPLC system equipped with a charged aerosol detector (CAD) as a trigger for fraction collector automatically. The structures of these compounds were identified by mass spectrometry (MS) and nuclear magnetic resonance spectroscopy (NMR) as *α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranosyl-(6→1)-*α*-*D*-galactopyranosyl-(6→1)-*α*-*D*-galactopyranoside (**1**), *α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranosyl-(4→1)-*α*-*D*-galactopyranoside (**2**), and *α*-*D*-galactopyranosyl-(1→2)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-galactopyranosyl- (1→6) - *α*-*D*-glucopyranosyl- (1→2) - *β*-*D*-fructofuranoside (**3**), raffinose (**4**), stachyose (**5**), verbascose (**6**), ajugose (**7**), umbelliferose (**8**), erlose (**9**), loliose (**10**), *α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranosyl-(1→1)-*α*-*D*-galactopyranoside (**11**), rehmaglupentasaccharide E (**12**), and rehmaglupentasaccharide F (**13**). All oligosaccharides with degrees of polymerization ranging from 3 to 6 were isolated from *Scutellaria baicalensis* Georgi for the first time. Compounds **1**−**3** are new

收稿日期: 2026-02-10;　修回日期: 2026-03-20.

基金项目: 国家重点研发计划—中医药现代化研究 (2023YFC3502804); 国家自然科学基金资助项目 (82274068).

*通讯作者 E-mail: mabaiping@sina.com

DOI: 10.16438/j.0513-4870.2026-0183

compounds belonging to the non-classical raffinose-family oligosaccharides. Furthermore, compounds **11**−**13** are non-classical raffinose-family oligosaccharides and compounds **4**−**7** are raffinose-family oligosaccharides.

Key words: *Scutellaria baicalensis* Georgi; oligosaccharide; isolation; structural elucidation; non-classical raffinose family oligosaccharide

黄芩 (Scutellariae radix) 为唇形科植物黄芩 (*Scutellaria baicalensis* Georgi) 的干燥根, 为我国传统常用清热类中药, 始载于《神农本草经》, 具披针叶, 根茎肉质, 花多紫色, 原产地主要在中国境内。具有平肝泻火、清热解毒、止血、安胎之效[1]。作为中医临床和中成药中最为常用的中药之一, 根据Jia等[2]的统计, 在《中药部颁标准》中有477个成药含有黄芩, 包含主治疾病153种, 因此, 对黄芩的研究一直广受关注。黄芩中所含有的化学成分结构类型复杂多样, 包括黄酮、多糖、三萜、挥发油等, 迄今为止, 已从黄芩中分离鉴定了270余种化学成分[3]。现代药理学研究也表明, 黄芩中的黄酮、多糖和挥发油等是主要活性成分, 具有抗肿瘤、抗炎、抗氧化、抗菌等作用[3-6]。尤其是黄芩多糖在抗结直肠癌和调节肠道菌群等方面有多项研究报道[7-9]。在前期研究中, 本课题组利用长春瑞滨诱导的免疫抑制斑马鱼模型对黄芩寡糖部位进行评价, 发现黄芩寡糖部位显示出抗炎作用, 显著下调TNF-α、IL-1β等炎症因子的水平, 表明该部位能够有效缓解免疫低下斑马鱼炎症。然而, 对于其中的寡糖化学结构至今未见任何报道。

寡糖又称低聚糖, 是2～10个单糖分子通过糖苷键结合而成的直链或支链聚合物, 五碳糖和六碳糖是其主要结构单元。寡糖的主要获取方式有直接提取、多糖降解、化学合成等, 目前中药中寡糖的获取主要还是依靠直接提取。研究表明, 寡糖结构与其生物活性密切相关, 如异麦芽糖因含α-1,6键难以消化, 可作为益生元促进益生菌增殖[10], 果胶低聚糖抗糖基化活性与其GalA∶Rha的比值成正比, 与其分支度成反比, 而其益生元活性则与其Ara∶Rha与Gal∶Rha的比值正相关[11]; 甘露寡糖的免疫活性则与其末端的β-Man密切相关[12]; 葡甘露寡糖的抗氧化活性则与其聚合度有关, 聚合度越低, 清除自由基能力越强[13]。由此可见, 了解寡糖的化学结构信息是探究其构效关系的第一步。基于此, 利用本课题组前期建立的中药寡糖通用表征筛选方法[14], 对系列中药中的寡糖进行表征分析, 发现黄芩含有寡糖, 但对于寡糖的具体结构类型仍不清楚。为了揭示黄芩中所含有的寡糖结构, 本研究对黄芩中的寡糖进行了分离纯化和结构鉴定, 制备得到13个寡糖单体化合物, 包括4个棉子糖家族寡糖, 3个三聚糖的同分异构体, 6个非传统型棉子糖家族寡糖, 其中有3个是新寡糖结构 (图1)。化合物**1**～**13**均为首次从黄芩中分离得到, 不仅扩充了天然寡糖化学结构, 并为寡糖的构效关系以及糖类药物的研发奠定了基础。

结果与讨论

1 结构鉴定

化合物**1**为白色粉末, 红外光谱IR显示化合物**1**结构中存在羟基 (3 381 cm^{-1}), 在1 067 cm^{-1}附近的吸收峰对应C-O-C糖苷键的伸缩振动, 这表明寡糖结构中含有吡喃糖单元; 在925和817 cm^{-1}附近的典型吸收峰表明存在呋喃糖环且含有β-型糖苷键; 而在871 cm^{-1}处的吸收峰则表明存在葡萄糖单元的α-型糖苷键[15]。根据HRMS分析结果显示, 化合物**1** *m*/*z* 827.267 1 $[M-H]^-$ (计算值为827.266 9), 推断其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$, 不饱和度为5。在高能级质谱下, 观察到该化合物持续丢失4个162 Da的碎片离子, 确定化合物**1**为5个六碳糖组成的五聚糖。对其^{1}H NMR谱进行分析, 可以观察到4个明显的端基质子信号δ_H 5.45 (1H, d, *J* = 3.9 Hz)、5.01 (1H, d, *J* = 3.7 Hz) 和4.99 (2H, d, *J* = 3.5 Hz) ppm, 根据HSQC可知其分别与δ_C 94.80、101.27、101.00和101.33相关, 提示该化合物含有4个六碳糖, 缺失的1个质子信号提示还存在1个六碳糖的酮糖形式。

利用选择性激发TOCSY提取端基质子信号可知δ_H 5.45与4.06、3.75、3.58、3.55属于同一糖环质子信号, 结合^{1}H-^{1}H COSY可将其归属于该糖基的H1～H5, 根据δ_H 4.06、3.55与δ_C 68.60存在HMBC相关信号, 而δ_H 4.05、3.68与δ_C 68.60存在HSQC相关, 可将δ_H 4.05、3.68归属于其H6位。结合端基质子δ_H 5.45 (1H, d, *J* = 3.9 Hz) 偶合常数, 将该糖基确定为α-*D*-Glc*p* (Glc)。同样, 选择性激发δ_H 4.23, 结合^{1}H-^{1}H COSY与偶合常数可将δ_H 4.23、4.09、4.06、4.00、3.80分别归属于第2个糖基的H3～H6位, 利用HMBC δ_C 106.87、78.86分别与δ_H 3.68存在强相关信号, 可将δ_H 3.68归属于H1上的质子信号, 最终确定该糖基为β-*D*-Fru*f* (Fru)。选择性激发δ_H 5.01可以观察到δ_H 4.05、3.92、3.82等信号属于同一糖环质子信号, 结合^{1}H-^{1}H COSY可将其归属于该糖基的H1～H4, 但该糖基信号在H4～H5之间传递

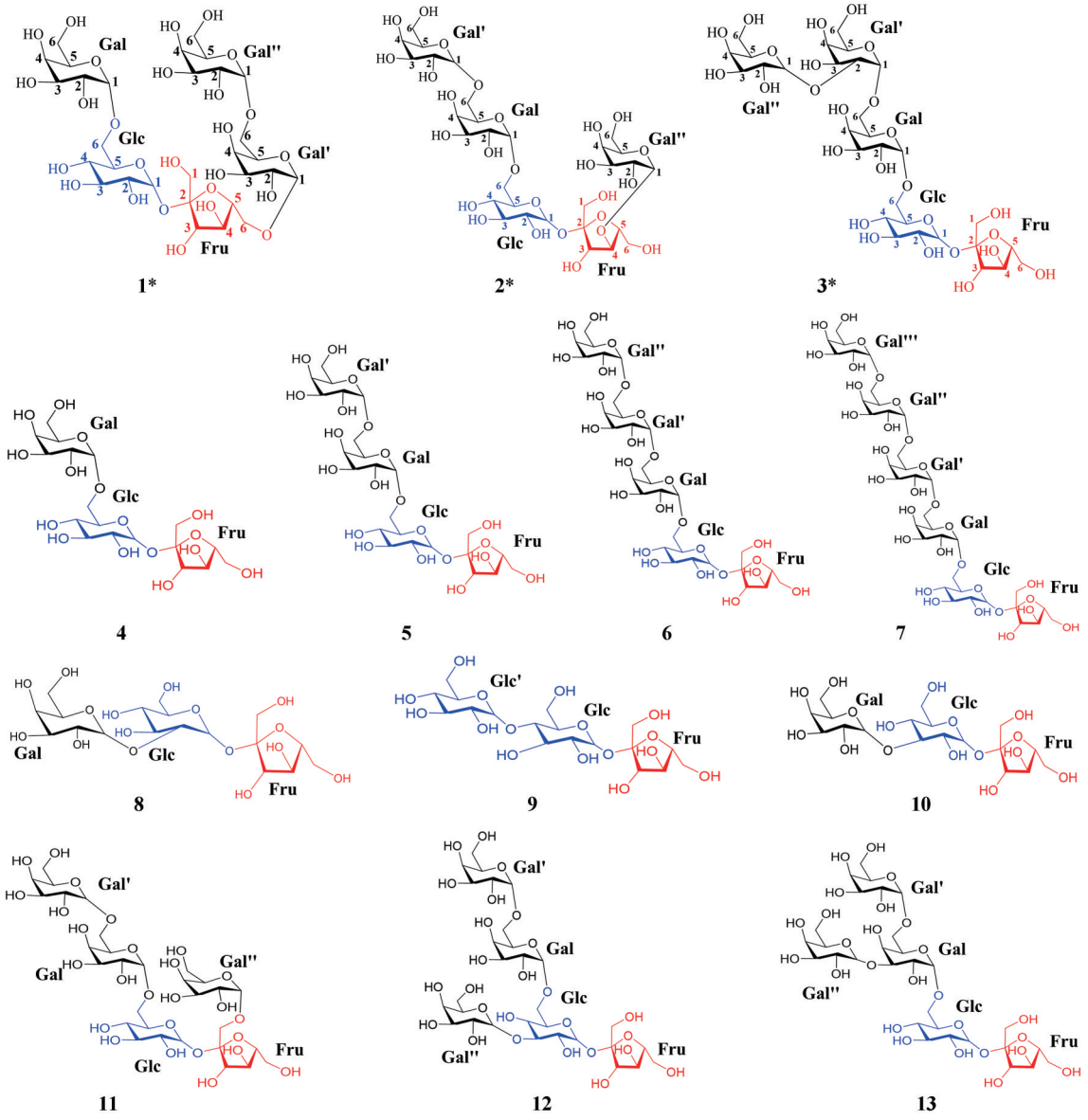


Figure 1 The structures of **1**−**13**. *Novel compounds; Gal: Galactopyranosyl; Glc: Glucopyranosyl; Fru: Fructofuranosyl

时迅速衰减, 未在选择性激发TOCSY中观察到明显信号, 提示其可能为$^{3}J_{H4,H5}$较小的半乳糖。结合HSQC, 利用HMBC观察到δ_C 72.17 (C4)、72.26 (C3)分别与δ_H 4.00存在强相关信号, 可将δ_H 4.00归属于H5上的质子信号。同样, δ_C 72.17 (C4)、73.87 (C5)分别与δ_H 3.75存在HMBC强相关信号, 可将δ_H 3.75归属于H6上的质子信号。结合端基质子偶合常数 (J = 3.7 Hz), 以及4位上质子偶合常数确定该糖基与葡萄糖基不同, 为*α*-*D*-Gal*p* (Gal)。当选择性激发δ_H 4.99时, 发现同时提取出了2套糖基信号, 提示这2个糖基种类相同, 化学位移重叠严重。结合^{1}H-^{1}H COSY、TOCSY以及HMBC, 将δ_H 4.99、4.15、3.99、3.87、3.86、3.82、3.72确定为一个糖环上的质子信号, 将δ_H 4.99、4.01、3.98、3.90、3.84、3.76确定为另一个糖环上的质子信号。结合端基质子偶合常数 (J = 3.5 Hz), 以及4位上质子偶合常数, 确定这2个糖基为*α*-*D*-Gal*p* (分别记为Gal′和Gal″)。

利用HMBC对其连接顺序与位置进行判断 (图2), 首先观察到δ_H 5.45 (Glc-H1)与δ_C 106.87 (Fru-C2)存在相关信号, 确定葡萄糖 (Glc)与果糖 (Fru)为1→2连接; δ_H 5.01 (Gal-H1)与δ_C 68.60 (Glc-C6)存在相关信号, 确定半乳糖 (Gal)与Glc为1→6连接; δ_H 4.99 (Gal′-H1)与δ_C 71.62 (Fru-C6)存在相关信号, 确定Gal′与Fru为1→6连接; δ_H 4.99 (Gal″-H1)与δ_C 69.33 (Gal′-C6)存在相关信号, 确定Gal″与Gal′为1→6连接。

对其^{1}H NMR和^{13}C NMR谱数据进行全归属 (表1), 确定化合物**1**的结构为*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranosyl-(6→1)-*α*-*D*-galactopyranosyl-(6→1)-*α*-*D*-galactopyranoside,

经SciFinder数据库检索, 确定化合物**1**为新化合物, 将其命名为6F-*α*-*D*-digalactosylraffinose。

化合物**2**为白色粉末, 根据HRMS分析结果显示, 化合物**2** *m*/*z* 827.268 4 $[M-H]^-$ (计算值为827.266 9), 推断其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$, 不饱和度为5。在高能级质谱下, 观察到该化合物持续丢失4个162 Da的碎片离子, 确定化合物**1**为5个六碳糖组成的五聚糖。从^{1}H NMR谱中可以观察到4个明显的端基质子信号δ_H 5.44 (1H, d, *J* = 3.8 Hz)、5.00 (1H, d, *J* = 3.8 Hz)、5.33 (1H, d, *J* = 3.7 Hz) 和4.99 (1H, d, *J* = 3.9 Hz) ppm, 根据HSQC可知其分别与δ_C 95.27、100.90、100.81和101.22相关, 提示该化合物含有4个六碳糖, 缺失的1个质子信号提示还存在1个六碳糖的酮糖形式。

化合物**2**的解析过程同化合物**1**, 利用选择性激发TOCSY分别提取4个端基质子信号, 可分别得到与端基质子位于同一糖环上的H2～H4位的质子信号, 利用^{1}H-^{1}H COSY以及HMBC相关信号并结合端基质子偶合常数, 以及4位上质子偶合常数, 可确定化合物**2**中六碳糖的糖基种类分别为3个*α*-*D*-Gal*p* (Gal、Gal′、Gal″) 和1个*α*-*D*-Glc*p* (Glc)。同时通过选择性激发δ_H 4.48, 利用^{1}H-^{1}H COSY以及HMBC相关信号, 可确定化合物**2**中的酮糖为*β*-*D*-Fru*f* (Fru)。

利用HMBC对其连接顺序与位置进行判断 (图2), 首先观察到δ_H 5.44 (Glc-H1) 与δ_C 107.10 (Fru-C2)存在相关信号, 确定Glc与Fru为1→2连接; δ_H 4.99 (Gal-H1) 与δ_C 68.60 (Glc-C6) 存在相关信号, 确定Gal与Glc为1→6连接; δ_H 5.00 (Gal′-H1) 与δ_C 69.39 (Gal-C6) 存在相关信号, 确定Gal′与Gal为1→6连接; δ_H 5.33 (Gal″-H1) 与δ_C 82.35 (Fru-C4) 存在相关信号, 确定Gal″与Fru为1→4连接。

对其^{1}H NMR和^{13}C NMR谱数据进行全归属 (表1), 确定化合物**2**的结构为*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranosyl-(4→1)-*α*-*D*-galactopyranoside, 经SciFinder数据库检索, 确定化合物**2**为新化合物, 将其命名为4F-*α*-*D*-galactosylstachyose。

化合物**3**为白色粉末, 根据HRMS分析结果显示, 化合物**3** *m*/*z* 827.267 9 $[M-H]^-$ (计算值为827.266 9), 推断其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$, 不饱和度为5。在高能级质谱下, 观察到该化合物持续丢失4个162 Da的碎片离子, 确定化合物**1**为5个六碳糖组成的五聚糖。从^{1}H NMR谱可以观察到4个明显的端基质子信号δ_H 5.44 (1H, d, *J* = 3.9 Hz)、5.15 (1H, d, *J* = 3.9 Hz)、5.05 (1H, d, *J* = 2.1 Hz) 和5.00 (1H, d, *J* = 3.9 Hz) ppm, 根据HSQC可知其分别与δ_C 94.98、98.12、100.66和101.28相关, 提示该化合物含有4个六碳糖, 缺失的1个质子信号提示还存在1个六碳糖的酮糖形式。

化合物**3**的解析过程同化合物**1**, 利用选择性激发TOCSY分别提取4个端基质子信号, 可分别得到与端基质子位于同一糖环上的H2～H4位的质子信号, 利用^{1}H-^{1}H COSY以及HMBC相关信号并结合端基质子偶合常数, 以及4位上质子偶合常数, 可确定化合物**3**中4个六碳糖为3个*α*-*D*-Gal*p* (Gal、Gal′、Gal″) 和1个*α*-*D*-Glc*p* (Glc)。同时通过选择性激发δ_H 4.23, 利用^{1}H-^{1}H COSY以及HMBC相关信号, 可确定化合物**3**中的酮糖为*β*-*D*-Fru*f* (Fru)。

利用HMBC对其连接顺序与位置进行判断 (图2), 首先观察到δ_H 5.44 (Glc-H1) 与δ_C 106.67 (Fru-C2)存在相关信号, 确定Glc与Fru为1→2连接; δ_H 5.00 (Gal-H1) 与δ_C 68.76 (Glc-C6) 存在相关信号, 确定Gal与Glc为1→6连接; δ_H 5.05 (Gal′-H1) 与δ_C 68.96 (Gal-C6) 存在相关信号, 确定Gal′与Gal为1→6连接; δ_H 5.15 (Gal″-H1) 与δ_C 77.32 (Gal′-C2) 存在相关信号, 确定Gal″与Gal′为1→2连接。由于化合物**3**的碳、氢信号与文献[16]报道的rehmaglupentasaccharide G很接近, 同时第2个Gal′上的H2与H3位质子信号重叠, 再分析HMBC谱中δ_C 77.32 (Gal′-C2) 与δ_H 5.05 (Gal′-H1)、4.24 (Gal′-H4)、3.97 (Gal′-H3) 存在相关信号, 而δ_C 77.32 (Gal′-C2) 与δ_H 3.99 (Gal′-H5) 不存在相关信号, 可判断Gal″与Gal′为1→2连接, 而非1→3连接。

对其^{1}H NMR和^{13}C NMR谱数据进行全归属 (表1), 确定化合物**3**的结构为*α*-*D*-galactopyranosyl-(1→2)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-galactopyranosyl-(1→6)-*α*-*D*-glucopyranosyl-(1→2)-*β*-*D*-fructofuranoside, 经SciFinder数据库检索, 确定化合物**3**为新化合物, 将其命名为2g-*α*-*D*-galactosylstachyose。

2 讨论

黄芩作为传统中药, 其中的黄酮、多糖等类成分[17-21]已有大量研究。然而对于黄芩中的寡糖成分研究至今未见报道。本研究通过多种色谱技术的交叉使用, 克服了寡糖极性大、缺乏生色团与荧光团以及同分异构体多[22,23]导致分离纯化困难的问题, 实现了不同聚合度及同一聚合度同分异构体的分离, 从黄芩中分离得到了13个寡糖单体化合物。同时采用多种核磁技术, 如选择性激发谱等, 实现了寡糖单体确切结构的鉴定。除了4个棉子糖家族寡糖, 作者还发现了3个三聚糖同分异构体以及6个非传统型棉子糖家族寡糖, 其中化合物**1**～**3**为首次发现的非传统型棉子糖家族五聚糖。

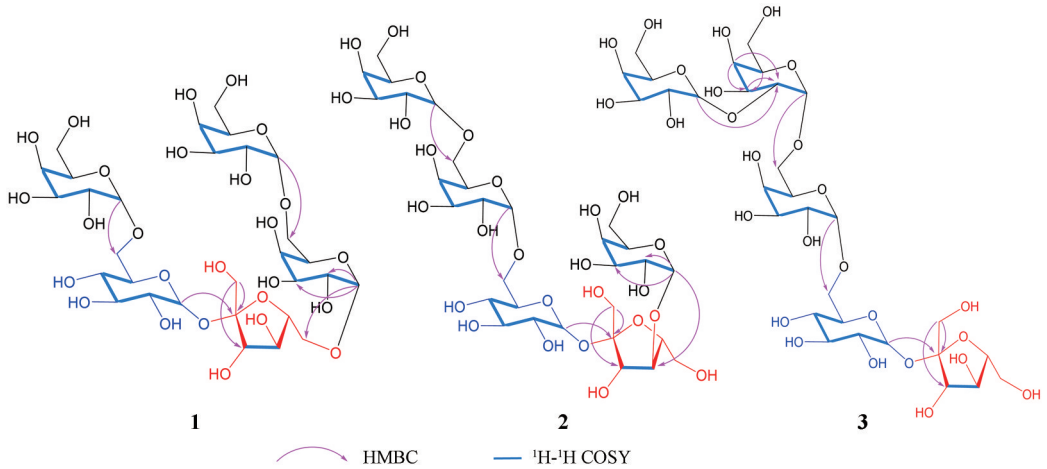


Figure 2 Key ^{1}H-^{1}H COSY and HMBC correlations of **1**−**3**

Table 1 ^{1}H NMR (700 MHz) and ^{13}C NMR (175 MHz) data of **1**−**3** (δ in ppm; measured in D_2O). *These signals overlapped with others

Position		1		2		3	
		δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
Fru	1	3.68, s	64.54	3.69, s	63.89	3.68, s	64.27
	2		106.87		107.10		106.67
	3	4.23, d (8.6)	78.86	4.48, d (8.2)	79.36	4.23, d (8.8)	79.26
	4	4.09, t (8.6)	77.21	4.20, t (8.1)	82.35	4.07, t (8.5)	76.85
	5	4.06, m*	82.20	4.08, br t (3.2)	83.26	3.90, m	84.20
	6	4.00, m*;	71.62	3.89, m;	65.78	3.82, m;	65.34
		3.80, dd (11.1, 2.8)		3.84, m		3.79, m	
Glc	1	5.45, d (3.9)	94.80	5.44, d (3.8)	95.27	5.44, d (3.9)	94.98
	2	3.58, dd (3.9, 9.9)	73.87	3.58, dd (10.1, 3.8)	73.81	3.58, dd (3.9, 10.0)	73.84
	3	3.75, t (9.7)	75.80	3.77, t (9.6)	75.52	3.76, t (9.6)*	75.59
	4	3.55, t (9.3)	72.26	3.55, t (9.5)	72.27	3.54, t (9.5)	72.32
	5	4.06, m*	73.95	4.07, m*	74.22	4.06, m	74.20
	6	4.05, d (12.8);	68.60	4.07, m*;	68.60	4.05, m;	68.76
		3.68, d (12.3)		3.66, d (9.5)		3.67, d (8.0)	
Gal	1	5.01, d (3.7)	101.27	4.99, d (3.9)	101.22	5.00, d (3.9)	101.28
	2	3.82, m*	71.18	3.84, dd (10.2, 3.7)	71.00	3.84, dd (10.5, 3.3)	71.29
	3	3.92, tt (10.3, 3.5, 3.5)	72.26	3.91, dd (10.7, 3.4)	72.28	3.92, dd (10.3, 3.3)	72.25
	4	4.05, m*	72.17	4.04, d (3.8)	72.23	4.04, d (3.4)	72.11
	5	4.00, m*	73.87	4.15, dd (7.6, 3.8)	71.68	4.16, t (6.3)	71.30
	6	3.75, m*	64.01	3.88, m;	69.39	3.87, m;	68.96
				3.72, dd (10.3, 4.6)		3.76, m*	
Gal′	1	4.99, d (3.5)	101.00	5.00, d (3.8)	100.90	5.05, d (2.1)	100.66
	2	3.82, m*	71.16	3.82, dd (10.4, 3.7)	71.15	3.97, br d (1.3)*	77.32
	3	3.86, dd (10.0, 3.7)	72.36	3.85, dd (10.5, 3.3)	72.37	3.97, br d (1.3)*	69.63
	4	3.99, d (3.3)	72.11	3.99, br t (3.3)	72.11	4.24, br d (3.5)	68.46
	5	4.15, br t (6.1)	71.68	3.94, t (6.0)	74.44	3.99, br d (6.1)	73.66
	6	3.87, dd (7.0, 3.7);	69.33	3.74, t (5.4)*	64.06	3.76, d (6.0)	64.02
		3.72, dd (9.9, 4.4)					
Gal″	1	4.99, d (3.5)	101.33	5.33, d (3.7)	100.81	5.15, d (3.9)	98.12
	2	3.84, m*	71.35	3.84, dd (10.2, 3.7)	71.32	3.87, dd (10.3, 3.9)	71.09
	3	3.90, tt (10.3, 3.5, 3.5)*	72.29	3.87, dd (10.4, 3.1)	72.00	3.95, dd (10.4, 3.4)	72.19
	4	4.01, br t (3.7)*	72.00	3.99, br t (3.3)*	72.10	4.02, br t (3.3)	72.13
	5	3.98, br t (6.5)	73.78	4.00, br t (5.9)	73.87	4.19, t (6.2)	73.77
	6	3.76, m*	63.79	3.74, t (5.4)*	64.06	3.76, d (6.2)	64.00

棉子糖家族寡糖作为大众所熟知寡糖系列之一, 其结构特点是半乳糖糖基以α-(1→6) 连接方式在蔗糖的葡萄糖基上进行不同个数的延伸; 而非传统型棉子糖家族寡糖, 其结构特点则是半乳糖糖基以α-(1→1)、或α-(1→3)、或α-(1→4)、或α-(1→6) 连接方式在棉子糖的半乳糖基或果糖基上进行不同个数糖基的延伸[24]。本研究首次发现了基于棉子糖结构在果糖基上以α-(1→6) 延伸2个半乳糖的五聚糖 (**1**)、基于棉子糖结构在半乳糖基以α-(1→6) 和果糖基上以α-(1→4) 分别延伸1个半乳糖的五聚糖 (**2**), 以及基于棉子糖结构在半乳

糖基上以α-(1→6)和α-(1→2)延伸2个半乳糖的五聚糖(**3**),这3个新寡糖结构的揭示为深入了解非传统型棉子糖家族寡糖的结构提供了线索,证明了在棉子糖家族寡糖外,半乳糖基以不同连接方式、不同延伸个数所形成的非传统型棉子糖家族寡糖具有多种可能性。继地黄[16]、银柴胡[25]中发现非传统型棉子糖家族以来,作者又发现了这类寡糖的存在,这不仅填补了该类型寡糖在糖类化学研究领域的空白,亦为探究黄芩中活性成分提供了新的物质基础。

实验部分

Vanquish Core高压高效液相色谱仪配备有CAD检测器、VFC分流阀与自动馏分收集系统、Vanquish Flex超高压高效液相色谱仪配备有CAD检测器、Hypercarb色谱柱(150 mm × 10 mm, 5 μm)、Nicolet IS5 FT-IR红外光谱仪、色谱乙腈(美国Thermo Fisher公司); Hannon Newstyle NP700 Serial制备液相(江苏汉邦科技有限公司); 示差折光检测器Shodex RI-102(日本Showa Denko group); 中压纯化系统Pure C-850(瑞士BUCHI公司); Waters synapt G2-Si包括四极杆飞行时间质谱与ACQUITY primer H-class液相(美国Waters公司); BP-211D十万分之一天平(德国Sartorius公司); RE-2020A旋转蒸发仪(上海亚荣生化仪器厂); Bruker Avance III HD 700 MH核磁共振仪(德国Bruker公司); Claricep Flash NH2色谱柱、Cleanert Pesti Carb色谱柱(天津博纳艾杰尔科技有限公司); Asahipak NH2P-50 10E色谱柱(250 mm × 10 mm, 5 μm, 日本Shodex公司); 95%乙醇(分析纯, 北京现代东方科技发展有限公司); 乙腈(分析纯, 常州科莱玛生物科技有限公司)。

实验所用黄芩药材购于北京同仁堂,经同仁堂药师鉴定为唇形科植物黄芩*Scutellaria baicalensis* Georgi的干燥根药材,留样100.0 g保存于军事科学院军事医学研究院。

1 黄芩寡糖的提取与初步分离

称取500 g黄芩(HQ),加入50%乙醇进行回流提取(每次用12 L溶剂,提取2 h),重复操作3次。将提取液合并后过滤,减压浓缩至900 mL, 4 ℃下静置24 h,离心分离得到上清液及沉淀,将上清液减压浓缩,干燥。取部分已干燥的上清用蒸馏水溶解,所得溶液经SP825大孔吸附树脂柱,并采用水、10%乙醇、50%乙醇、95%乙醇进行依次洗脱,得到上样流出部位(17.79 g)、水洗脱部位(58.25 g)、10%乙醇洗脱部位(24.06 g)、50%乙醇洗脱部位(43.70 g)、95%乙醇洗脱部位(6.12 g)。其中,水洗脱部位经冻干处理,共获得58.25 g黄芩粗寡糖粉末,用于后续纯化。取黄芩粗寡糖粉末(54 g),溶于50%乙腈–水溶液,上样至中压快速制备系统进行进一步纯化。随后,使用Claricep Flash NH2色谱柱(40 g),以乙腈–水(85∶15 → 65∶35 → 55∶45 → 50∶50)进行梯度洗脱,流速为32 mL·min^{-1},并通过蒸发光散射检测器监测,共收集到6个组分。所得组分经冻干后,分别记为HQ-F1 (4.90 g), HQ-F2 (12.55 g), HQ-F3 (10.86 g), HQ-F4 (6.75 g), HQ-F5 (10.32 g)与HQ-F6 (2.15 g)。

2 黄芩寡糖的进一步分离纯化

2.1 半制备高效液相色谱分离 半制备高效液相色谱采用半制备Asahipak NH2P-50 10E色谱柱(250 mm × 10 mm, 5 μm)对HQ-F4 (6.75 g)进行进一步分离纯化。色谱分离以70%乙腈水溶液作为流动相,流速为2 mL·min^{-1}。通过示差折光检测器在线监测,根据色谱峰形手动收集目标流份。经减压浓缩与冻干后,最终得到5个流份,分别命名为HQ-F4-1 (704.46 mg)、HQ-F4-2 (231.22 mg)、HQ-F4-3 (606.71 mg)、HQ-F4-4 (155.77 mg)与HQ-F4-5 (173.15 mg)。

以74%乙腈水溶液作为流动相,流速为2 mL·min^{-1}对HQ-F5进行分离,通过示差折光检测器在线监测,根据色谱峰形手动收集目标色谱峰。经减压浓缩与冻干后,最终从HQ-F5 (10.32 g)中分离得到化合物**5** (1.06 g)。

2.2 石墨化碳固相萃取柱分离 采用石墨化碳固相萃取柱(2 g/12 mL)对样品HQ-F4-1与HQ-F6进行分级分离。样品均以50 mg·mL^{-1}的浓度溶解于50%乙腈水溶液后上样。色谱柱预先经8 BV乙腈活化后,分别采用不同梯度的水–乙腈溶液进行洗脱。

对于HQ-F4-1,固相萃取柱使用4 BV去离子水平衡。上样后,依次以4 mL去离子水,以及5%、6%、7%、8%、9%、10%、12%的乙腈水溶液进行洗脱,共收集到8个组分,依次命名为HQ-F4-S1至HQ-F4-S8。

对于HQ-F6,固相萃取柱则采用4 BV的5%乙腈水溶液平衡。上样后,依次使用20 mL的5%、8%、10%、12%、15%和30%乙腈水溶液进行洗脱,最终获得6个组分,分别记为HQ-F6-S1至HQ-F6-S6。

2.3 电雾式检测器(CAD)触发自动馏分收集器的高效液相色谱分离 实验室前期基于石墨化碳色谱柱(Hypercarb, 150 mm × 10 mm, 5 μm)利用高效液相色谱仪采用CAD,通过搭配分流阀与自动收集模块(FC),建立了寡糖单体的梯度条件在线检测与制备分离系统[26]。利用该系统对组分HQ-F4-S2以及HQ-F6-S4进行寡糖单体的制备分离,实现了多个寡糖单体的制备级分离。其中,组分HQ-F4-S2 (254 mg)以乙腈–水(0∶100 → 12∶88, 0～95 min)为流动相,在2 mL·min^{-1}的流速下进行梯度洗脱,经分离纯化得到4个单体,命

名为化合物**4** (137.3 mg)、**8** (0.54 mg)、**9** (1.08 mg)、**10** (0.72 mg); 组分HQ-F6-S4 (260 mg) 以乙腈−水 (8∶92 → 15∶85, 0～35 min) 为流动相, 在2 mL·min^{-1}的流速下进行梯度洗脱, 分离获得了8个单体, 相应记为化合物**1** (12.41 mg)、**2** (2.93 mg)、**3** (0.88 mg)、**6** (56.84 mg)、**7** (4.98 mg)、**11** (7.37 mg)、**12** (0.8 mg)、**13** (0.48 mg)。

3 结构鉴定

化合物**4**为白色粉末, ESI-MS *m*/*z* 503.169 7 [M−H]$^-$, 其分子质量为504 Da, 分子式为$C_{18}H_{32}O_{16}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.43 (1H, d, *J* = 3.9 Hz, Glc-H1), 4.99 (1H, d, *J* = 3.8 Hz, Gal-H1), 4.23 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.06 (1H, d, *J* = 8.6 Hz, Fru-H4), 4.06 (1H, d, *J* = 8.6 Hz, Glc-H5), 4.03 (1H, t, *J* = 3.9 Hz, Gal-H4), 4.00 (1H, d, *J* = 3.4 Hz, Gal-H6b), 3.95 (1H, t, *J* = 6.4 Hz, Gal-H3), 3.90 (1H, m, Fru-H5), 3.88 (1H, d, *J* = 3.3 Hz, Gal-H2), 3.85 (1H, m, Fru-H6b), 3.83 (1H, m, Gal-H5), 3.79 (1H, d, *J* = 7.4 Hz, Glc-H3), 3.77 (1H, d, *J* = 9.5 Hz, Glc-H6a), 3.75 (1H, d, *J* = 5.1 Hz, Fru-H6a), 3.75 (1H, d, *J* = 5.1 Hz, Gal-H6a), 3.69 (1H, m, Glc-H6b), 3.67 (2H, s, Fru-H1), 3.57 (1H, dd, *J* = 3.9, 10.1 Hz, Glc-H2), 3.54 (1H, d, *J* = 9.5 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.23 (Fru-C1), 106.63 (Fru-C2), 79.17 (Fru-C3), 76.82 (Fru-C4), 84.18 (Fru-C5), 65.29 (Fru-C6), 94.94 (Glc-C1), 73.80 (Glc-C2), 75.50 (Glc-C3), 74.23 (Glc-C4), 73.89 (Glc-C5), 68.73 (Glc-C6), 101.31 (Gal-C1), 71.32 (Gal-C2), 72.24 (Gal-C3), 72.05 (Gal-C4), 72.29 (Gal-C5), 63.96 (Gal-C6), 以上数据与文献[27,28]报道对照基本一致, 故鉴定化合物**4**为棉子糖。

化合物**5**为白色粉末, ESI-MS *m*/*z* 665.213 6 [M−H]$^-$, 其分子质量为666 Da, 分子式为$C_{24}H_{42}O_{21}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.44 (1H, d, *J* = 3.9 Hz, Glc-H1), 4.99 (1H, d, *J* = 3.2 Hz, Gal′-H1), 4.99 (1H, d, *J* = 3.8 Hz, Gal-H1), 4.23 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.14 (1H, ddd, *J* = 7.9, 4.6, 1.2 Hz, Gal-H5), 4.07 (1H, d, *J* = 8.7 Hz, Fru-H4), 4.06 (1H, d, *J* = 8.6 Hz, Glc-H5), 4.05 (1H, m, Glc-H6a), 4.05 (1H, m, Gal-H4), 4.01 (1H, d, *J* = 6.4 Hz, Gal′-H5), 3.98 (1H, d, *J* = 3.1 Hz, Gal′-H4), 3.91 (1H, d, *J* = 3.3 Hz, Gal-H3), 3.92 (1H, m, Fru-H5), 3.88 (1H, d, *J* = 10.0 Hz, Gal-H6b), 3.85 (1H, d, *J* = 3.0 Hz, Gal′-H3), 3.85 (1H, d, *J* = 3.0 Hz, Fru-H6a), 3.82 (1H, d, *J* = 3.7 Hz, Gal-H2), 3.82 (1H, d, *J* = 3.7 Hz, Gal′-H2), 3.78 (1H, d, *J* = 7.5 Hz, Glc-H3), 3.76 (1H, m, Fru-H6b), 3.75 (2H, d, *J* = 6.1 Hz, Gal′-H6), 3.72 (1H, d, *J* = 4.6 Hz, Gal-H6a), 3.68 (2H, s, Fru-H1), 3.68 (1H, br s, Glc-H6b), 3.58 (1H, dd, *J* = 3.9, 10.0 Hz, Glc-H2), 3.54 (1H, t, *J* = 9.6 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.26 (Fru-C1), 106.66 (Fru-C2), 79.18 (Fru-C3), 76.84 (Fru-C4), 84.20 (Fru-C5), 65.31 (Fru-C6), 94.95 (Glc-C1), 73.84 (Glc-C2), 75.57 (Glc-C3), 72.36 (Glc-C4), 74.13 (Glc-C5), 68.70 (Glc-C6), 101.22 (Gal-C1), 71.29 (Gal-C2), 72.33 (Gal-C3), 72.22 (Gal-C4), 71.65 (Gal-C5), 69.33 (Gal-C6), 100.88 (Gal′-C1), 71.14 (Gal′-C2), 72.36 (Gal′-C3), 72.09 (Gal′-C4), 73.80 (Gal′-C5), 64.00 (Gal′-C6), 以上数据与文献[27,29]报道对照基本一致, 故鉴定化合物**5**为水苏糖。

化合物**6**为白色粉末, ESI-MS *m*/*z* 827.259 8 [M−H]$^-$, 其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.44 (1H, d, *J* = 3.9 Hz, Glc-H1), 5.01 (1H, br d, *J* = 3.2 Hz, Gal-H1), 5.00 (1H, d, *J* = 3.8 Hz, Gal″-H1), 4.99 (1H, d, *J* = 3.8 Hz, Gal′-H1), 4.23 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.16 (1H, dd, *J* = 7.8, 4.5 Hz, Gal-H5), 4.15 (1H, dd, *J* = 7.8, 4.5 Hz, Gal′-H5), 4.09 (1H, m, Glc-H5), 4.07 (1H, t, *J* = 8.5 Hz, Fru-H4), 4.04 (1H, m, Glc-H6a), 4.04 (1H, m, Gal″-H4), 4.02 (1H, br d, *J* = 6.1 Hz, Gal″-H5), 4.00 (1H, d, *J* = 3.1 Hz, Gal-H4), 3.99 (1H, d, *J* = 3.1 Hz, Gal′-H3), 3.92 (1H, d, *J* = 3.1 Hz, Gal″-H3), 3.91 (1H, d, *J* = 3.4 Hz, Gal-H3), 3.90 (1H, m, Fru-H5), 3.86 (1H, m, Gal′-H6b), 3.85 (1H, d, *J* = 3.1 Hz, Gal′-H4), 3.84 (1H, br d, *J* = 3.6 Hz, Gal″-H2), 3.82 (1H, d, *J* = 3.7 Hz, Gal-H2), 3.82 (1H, br d, *J* = 3.7 Hz, Gal′-H2), 3.82 (1H, d, *J* = 3.7 Hz, Fru-H6a), 3.79 (1H, d, *J* = 3.9 Hz, Fru-H6b), 3.76 (1H, t, *J* = 6.3 Hz, Glc-H3), 3.76 (2H, d, *J* = 6.2 Hz, Gal″-H6), 3.72 (1H, d, *J* = 4.5 Hz, Gal′-H6a), 3.68 (1H, m, Glc-H6b), 3.68 (2H, s, Fru-H1), 3.67 (2H, m, Gal-H6), 3.58 (1H, dd, *J* = 3.9, 10.0 Hz, Glc-H2), 3.54 (1H, t, *J* = 9.2 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.39 (Fru-C1), 106.81 (Fru-C2), 79.33 (Fru-C3), 76.98 (Fru-C4), 84.37 (Fru-C5), 65.46 (Fru-C6), 95.11 (Glc-C1), 73.95 (Glc-C2), 75.74 (Glc-C3), 72.39 (Glc-C4), 74.25 (Glc-C5), 68.70 (Glc-C6), 100.78 (Gal-C1), 71.26 (Gal-C2), 72.39 (Gal-C3), 72.24 (Gal-C4), 71.82 (Gal-C5), 69.29 (Gal-C6), 101.34 (Gal′-C1), 71.16 (Gal′-C2), 72.24 (Gal′-C3), 72.50 (Gal′-C4), 71.68 (Gal′-C5), 69.45 (Gal′-C6), 100.95 (Gal″-C1), 71.43 (Gal″-C2), 72.24 (Gal″-C3), 72.39 (Gal″-C4), 73.96 (Gal″-C5), 64.15 (Gal″-C6), 以上数据与文献[27,30]报道对照基本一致, 故鉴定化合物**6**为毛蕊花糖。

化合物**7**为白色粉末, ESI-MS *m*/*z* 989.321 9 [M−H]$^-$, 其分子质量为990 Da, 分子式为$C_{36}H_{62}O_{31}$。

^{1}H NMR (D_2O, 700 MHz) δ_H: 5.44 (1H, d, *J* = 3.9 Hz, Glc-H1), 5.01 (1H, d, *J* = 3.7 Hz, Gal‴-H1), 5.00 (1H, d, *J* = 3.9 Hz, Gal″-H1), 4.99 (1H, d, *J* = 3.9 Hz, Gal′-H1), 4.98 (1H, d, *J* = 3.9 Hz, Gal-H1), 4.21 (1H, m, Gal′-H5), 4.20 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.20 (1H, m, Gal-H5), 4.15 (1H, dd, *J* = 5.9, 2.3 Hz, Gal″-H5), 4.07 (1H, m, Glc-H5), 4.07 (1H, t, *J* = 8.5 Hz, Fru-H4), 4.05 (1H, m, Glc-H6b), 4.04 (1H, m, Gal″-H4), 4.04 (1H, m, Gal′-H4), 4.02 (1H, d, *J* = 3.4 Hz, Gal-H4), 4.00 (1H, m, Gal‴-H5), 3.99 (1H, d, *J* = 3.9 Hz, Gal‴-H4), 3.92 (1H, t, *J* = 3.3 Hz, Gal′-H3), 3.90 (1H, m, Gal″-H6a), 3.90 (1H, m, Gal-H6a), 3.90 (1H, m, Fru-H5), 3.87 (1H, dd, *J* = 3.6, 10.0 Hz, Gal″-H3), 3.87 (1H, m, Gal′-H6b), 3.87 (1H, dd, *J* = 10.0, 3.6 Hz, Gal‴-H3), 3.87 (1H, dd, *J* = 10.0, 3.6 Hz, Gal-H3), 3.85 (1H, dd, *J* = 3.9, 10.3 Hz, Gal′-H2), 3.84 (1H, dd, *J* = 10.2, 3.7 Hz, Gal‴-H2), 3.84 (1H, dd, *J* = 10.2, 3.7 Hz, Gal″-H2), 3.84 (1H, dd, *J* = 3.9, 10.3 Hz, Gal-H2), 3.82 (1H, d, *J* = 4.4 Hz, Fru-H6a), 3.79 (1H, d, *J* = 4.9 Hz, Fru-H6b), 3.75 (2H, m, Gal‴-H6), 3.75 (1H, t, *J* = 9.6 Hz, Glc-H3), 3.73 (1H, d, *J* = 4.8 Hz, Gal′-H6a), 3.69 (1H, m, Gal-H6b), 3.68 (1H, m, Glc-H6a), 3.68 (1H, m, Gal″-H6b), 3.68 (2H, s, Fru-H1), 3.58 (1H, dd, *J* = 10.0, 3.8 Hz, Glc-H2), 3.54 (1H, t, *J* = 9.6 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.27 (Fru-C1), 106.67 (Fru-C2), 79.20 (Fru-C3), 76.84 (Fru-C4), 84.21(Fru-C5), 65.34 (Fru-C6), 94.97 (Glc-C1), 73.82 (Glc-C2), 75.60 (Glc-C3), 72.35 (Glc-C4), 74.12 (Glc-C5), 68.66 (Glc-C6), 100.66 (Gal-C1), 71.32 (Gal-C2), 72.39 (Gal-C3), 72.35 (Gal-C4), 71.62 (Gal-C5), 69.37 (Gal-C6), 101.22 (Gal′-C1), 71.17 (Gal′-C2), 72.29 (Gal′-C3), 72.23 (Gal′-C4), 71.46 (Gal′-C5), 69.31 (Gal′-C6), 100.65 (Gal″-C1), 71.17 (Gal″-C2), 72.37 (Gal″-C3), 72.23 (Gal″-C4), 71.74 (Gal″-C5), 69.15 (Gal″-C6), 100.85 (Gal‴-C1), 71.32 (Gal‴-C2), 72.38 (Gal‴-C3), 72.14 (Gal‴-C4), 73.87 (Gal‴-C5), 64.02 (Gal‴-C6), 以上数据与文献[31]报道对照基本一致, 故鉴定化合物**7**为筋骨草糖。

化合物**8**为白色粉末, ESI-MS *m*/*z* 503.163 8 [M−H]$^-$, 分子质量为504 Da, 分子式为$C_{18}H_{32}O_{16}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.69 (1H, d, *J* = 3.6 Hz, Glc-H1), 5.17 (1H, d, *J* = 3.9 Hz, Gal-H1), 4.23 (1H, d, *J* = 8.9 Hz, Fru-H3), 4.17 (1H, t, *J* = 6.3 Hz, Gal-H5), 4.11 (1H, t, *J* = 8.6 Hz, Fru-H4), 4.02 (1H, d, *J* = 3.5 Hz, Gal-H4), 3.94 (1H, m, Glc-H5), 3.91 (1H, dd, *J* = 10.3, 3.3 Hz, Gal-H3), 3.89 (1H, t, *J* = 9.5 Hz, Glc-H3), 3.86 (1H, m, Gal-H2), 3.86 (1H, m, Fru-H5), 3.84 (1H, m, Fru-H6a), 3.83 (1H, m, Glc-H6a), 3.81 (1H, m, Glc-H6b), 3.81 (1H, m, Fru-H6b), 3.75 (2H, d, *J* = 6.3 Hz, Gal-H6), 3.75 (2H, s, Fru-H1), 3.68 (1H, dd, *J* = 9.9, 3.7 Hz, Glc-H2), 3.51 (1H, t, *J* = 9.6 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.64 (Fru-C1), 107.07 (Fru-C2), 79.11 (Fru-C3), 76.56 (Fru-C4), 83.98 (Fru-C5), 64.91 (Fru-C6), 92.43 (Glc-C1), 78.40 (Glc-C2), 74.14 (Glc-C3), 72.07 (Glc-C4), 74.97 (Glc-C5), 63.11 (Glc-C6), 99.33 (Gal-C1), 71.00 (Gal-C2), 72.19 (Gal-C3), 71.93 (Gal-C4), 73.87 (Gal-C5), 63.85 (Gal-C6), 以上数据与文献[32,33]报道对照基本一致, 故鉴定化合物**8**为umbelliferose。

化合物**9**为白色粉末, ESI-MS *m*/*z* 503.163 2 [M−H]$^-$, 分子质量为504 Da, 分子式为$C_{18}H_{32}O_{16}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.42 (1H, d, *J* = 3.9 Hz, Glc′-H1), 5.42 (1H, d, *J* = 3.9 Hz, Glc-H1), 4.22 (1H, d, *J* = 8.8, 4.1 Hz, Fru-H3), 4.04 (1H, t, *J* = 8.7 Hz, Fru-H4), 4.03 (1H, t, *J* = 9.5 Hz, Glc-H3), 3.98 (1H, td, *J* = 9.9, 2.9 Hz, Glc-H5), 3.90 (1H, m, Fru-H5), 3.87 (1H, m, Glc′-H6b), 3.84 (2H, m, Glc-H6), 3.82 (2H, m, Fru-H6), 3.77 (1H, d, *J* = 5.2 Hz, Glc′-H6a), 3.74 (1H, m, Glc′-H5), 3.71 (1H, m,Glc-H4), 3.68 (1H, t, *J* = 9.5 Hz, Glc′-H3), 3.68 (2H, s, Fru-H1), 3.60 (1H, dd, *J* = 9.5, 3.9 Hz, Glc-H2), 3.59 (1H, dd, *J* = 9.5, 3.5 Hz, Glc′-H2), 3.43 (1H, t, *J* = 9.5 Hz, Glc′-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.17 (Fru-C1), 106.48 (Fru-C2), 79.33 (Fru-C3), 76.87 (Fru-C4), 84.22 (Fru-C5), 65.20 (Fru-C6), 94.80 (Glc-C1), 74.63 (Glc-C2), 75.85 (Glc-C3), 79.60 (Glc-C4), 73.68 (Glc-C5), 63.02 (Glc-C6), 102.60 (Glc′-C1), 73.66 (Glc′-C2), 75.76 (Glc′-C3), 72.17 (Glc′-C4), 75.52 (Glc′-C5), 63.32 (Glc′- C6), 以上数据与文献[28]报道对照基本一致, 故鉴定化合物**9**为erlose。

化合物**10**为白色粉末, ESI-MS *m*/*z* 503.170 3 [M−H]$^-$, 分子质量为504 Da, 分子式为$C_{18}H_{32}O_{16}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.44 (1H, d, *J* = 3.9 Hz, Glc-H1), 5.38 (1H, d, *J* = 4.0 Hz, Gal-H1), 4.26 (1H, t, *J* = 6.3 Hz, Gal-H5), 4.21 (1H, d, *J* = 8.7 Hz, Fru-H3), 4.06 (1H, t, *J* = 8.6 Hz, Fru-H4), 4.01 (1H, d, *J* = 3.6 Hz, Gal-H4), 3.92 (1H, dd, *J* = 10.2, 8.3 Hz, Glc-H3), 3.90 (1H, dd, *J* = 10.2, 3.3 Hz, Gal-H3), 3.89 (1H, m, Fru-H5), 3.88 (1H, m, Glc-H5), 3.85 (1H, dd, *J* = 10.5, 4.0 Hz, Gal-H2), 3.83 (2H, m, Glc-H6), 3.82 (2H, m, Fru-H6), 3.72 (1H, dd, *J* = 10.2, 8.6, Glc-H4), 3.72 (2H, m, Gal-H6), 3.69 (2H, s, Fru-H1), 3.67 (1H, dd, *J* = 10.2, 3.7 Hz, Glc-H2); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.33 (Fru-C1), 106.53

(Fru-C2), 79.58 (Fru-C3), 76.92 (Fru-C4), 84.24 (Fru-C5), 65.20 (Fru-C6), 95.19 (Glc-C1), 72.60 (Glc-C2), 82.54 (Glc-C3), 72.36 (Glc-C4), 75.04 (Glc-C5), 62.73 (Glc-C6), 102.14 (Gal-C1), 71.50 (Gal-C2), 72.25 (Gal-C3), 72.04 (Gal-C4), 73.64 (Gal-C5), 63.84 (Gal-C6), 以上数据与文献[34]报道的化合物SX对照基本一致, 故鉴定化合物**10**为已知化合物, 并根据结构鉴定为loliose[35]。

化合物**11**为白色粉末, ESI-MS *m*/*z* 827.250 5 [M−H]$^-$, 其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.48 (1H, d, *J* = 3.9 Hz, Glc-H1), 5.06 (1H, d, *J* = 3.8 Hz, Gal″-H1), 5.00 (1H, d, *J* = 3.6 Hz, Gal′-H1), 5.00 (1H, d, *J* = 3.6 Hz, Gal-H1), 4.30 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.16 (1H, dd, *J* = 7.6, 4.8 Hz, Gal-H5), 4.08 (1H, t, *J* = 8.6 Hz, Fru-H4), 4.07 (1H, m, Glc-H6b), 4.06 (1H, m, Glc-H5), 4.04 (1H, m, Gal-H4), 4.00 (1H, m, Gal″-H4), 4.00 (1H, m, Gal′-H5), 3.99 (1H, d, *J* = 3.3 Hz, Gal′-H4), 3.95 (1H, m, Gal″-H5), 3.95 (1H, m, Fru-H5), 3.91 (1H, d, *J* = 3.4 Hz, Gal-H3), 3.90 (1H, dd, *J* = 10.3, 3.4 Hz, Gal″-H3), 3.88 (1H, m, Gal-H6a), 3.88 (1H, m, Fru-H1b), 3.86 (1H, m, Gal′-H3), 3.84 (1H, dd, *J* = 10.4, 3.8 Hz, Gal-H2), 3.84 (1H, dd, *J* = 3.8, 10.4 Hz, Gal″-H2), 3.84 (1H, m, Fru-H6a), 3.82 (1H, m, Gal′-H2), 3.79 (1H, d, *J* = 7.4 Hz, Fru-H6b), 3.74 (2H, m, Gal″-H6), 3.75 (2H, m, Gal′-H6), 3.75 (1H, dd, *J* = 10.0, 9.1 Hz, Glc-H3), 3.73 (1H, m, Gal-H6b), 3.68 (1H, m, Fru-H1a), 3.66 (1H, m, Glc-H6a), 3.57 (1H, dd, *J* = 10.0, 3.9 Hz, Glc-H2), 3.54 (1H, t, *J* = 9.4 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 69.15 (Fru-C1), 106.38 (Fru-C2), 79.33 (Fru-C3), 76.56 (Fru-C4), 84.08 (Fru-C5), 65.14 (Fru-C6), 95.41 (Glc-C1), 73.83 (Glc-C2), 75.58 (Glc-C3), 72.31 (Glc-C4), 74.16 (Glc-C5), 68.62 (Glc-C6), 101.21 (Gal-C1), 71.19 (Gal-C2), 72.27 (Gal-C3), 72.23 (Gal-C4), 71.68 (Gal-C5), 69.39 (Gal-C6), 100.90 (Gal′-C1), 71.19 (Gal′-C2), 72.37 (Gal′-C3), 72.12 (Gal′-C4), 73.87 (Gal′-C5), 64.04 (Gal′-C6), 101.59 (Gal″-C1), 71.31 (Gal″-C2), 72.20 (Gal″-C3), 72.10 (Gal″-C4), 74.26 (Gal″-C5), 64.06 (Gal″-C6), 以上数据与文献[25]报道SDO-Va基本一致, 故鉴定化合物**11**为已知化合物, 并命名为6g-*α*-*D*-galactosyllychnose。

化合物**12**为白色粉末, ESI-MS *m*/*z* 827.260 1 [M−H]$^-$, 其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.46 (1H, d, *J* = 3.9 Hz, Glc-H1), 5.36 (1H, d, *J* = 4.0 Hz, Gal″-H1), 5.00 (1H, d, *J* = 3.7 Hz, Gal′-H1), 5.00 (1H, d, *J* = 3.7 Hz, Gal-H1), 4.26 (1H, t, *J* = 6.3 Hz, Gal″-H5), 4.23 (1H, d, *J* = 8.8 Hz, Fru-H3), 4.16 (1H, dd, *J* = 7.7, 4.5 Hz, Gal-H5), 4.10 (1H, m, Glc-H5), 4.07 (1H, d, *J* = 12.0 Hz, Glc-H6b), 4.07 (1H, t, *J* = 8.6 Hz, Fru-H4), 4.04 (1H, d, *J* = 3.4 Hz, Gal-H4), 4.01 (1H, d, *J* = 3.2 Hz, Gal″-H4), 3.99 (1H, m, Gal′-H5), 3.98 (1H, d, *J* = 3.7 Hz, Gal′-H4), 3.93 (1H, t, *J* = 9.4 Hz, Glc-H3), 3.92 (1H, dd, *J* = 3.4, 10.4 Hz, Gal-H3), 3.91 (1H, dd, *J* = 10.3, 3.3 Hz, Gal″-H3), 3.90 (1H, m, Fru-H5), 3.88 (1H, d, *J* = 3.8 Hz, Gal-H6a), 3.87 (1H, dd, *J* = 3.9, 10.4 Hz, Gal″-H2), 3.84 (1H, d, *J* = 3.1 Hz, Gal′-H3), 3.84 (1H, d, *J* = 12.2 Hz, Fru-H6a), 3.83 (1H, dd, *J* = 10.3, 3.6 Hz, Gal-H2), 3.82 (1H, dd, *J* = 10.3, 3.6 Hz, Gal′-H2), 3.79 (1H, t, *J* = 9.6 Hz, Glc-H4), 3.78 (1H, d, *J* = 12.2 Hz, Fru-H6b), 3.75 (2H, d, *J* = 6.0 Hz, Gal′-H6), 3.73 (2H, d, *J* = 6.3 Hz, Gal″-H6), 3.72 (1H, *J* = 6.0 Hz, Gal-H6b), 3.70 (1H, dd, *J* = 9.8, 4.0 Hz, Glc-H2), 3.68 (2H, s, Fru-H1), 3.65 (1H, m, Glc-H6a); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.27 (Fru-C1), 106.66 (Fru-C2), 79.52 (Fru-C3), 76.92 (Fru-C4), 84.21 (Fru-C5), 65.32 (Fru-C6), 95.06 (Glc-C1), 72.60 (Glc-C2), 83.15 (Glc-C3), 72.63 (Glc-C4), 73.89 (Glc-C5), 68.33 (Glc-C6), 101.15 (Gal-C1), 71.31 (Gal-C2), 72.37 (Gal-C3), 72.24 (Gal-C4), 71.67 (Gal-C5), 69.37 (Gal-C6), 100.83 (Gal′-C1), 71.16 (Gal′-C2), 72.37 (Gal′-C3), 72.24 (Gal′-C4), 73.84 (Gal′-C5), 64.02 (Gal′-C6), 102.34 (Gal″-C1), 71.53 (Gal″-C2), 72.09 (Gal″-C3), 72.24 (Gal″-C4), 73.70 (Gal″-C5), 63.86 (Gal″-C6), 以上数据与文献[16]报道对照基本一致, 故鉴定化合物**12**为rehmaglupentasaccharide E。

化合物**13**为白色粉末, ESI-MS *m*/*z* 827.251 8 [M−H]$^-$, 其分子质量为828 Da, 分子式为$C_{30}H_{52}O_{26}$。^{1}H NMR (D_2O, 700 MHz) δ_H: 5.44 (1H, d, *J* = 4.1 Hz, Glc-H1), 5.18 (1H, d, *J* = 3.9 Hz, Gal″-H1), 5.03 (1H, d, *J* = 3.8 Hz, Gal-H1), 5.01 (1H, d, *J* = 3.8 Hz, Gal′-H1), 4.31 (1H, d, *J* = 3.1 Hz, Gal-H4), 4.23 (1H, d, *J* = 8.9 Hz, Fru-H3), 4.19 (1H, t, *J* = 6.3 Hz, Gal″-H5), 4.15 (1H, dd, *J* = 5.3, 7.7 Hz, Gal-H5), 4.10 (1H, d, *J* = 12.0 Hz, Glc-H6b), 4.06 (1H, m, Glc-H5), 4.04 (1H, m, Gal′-H5), 4.04 (1H, dd, *J* = 3.0, 10.3 Hz, Gal-H3), 4.04 (1H, t, *J* = 8.6 Hz, Fru-H4), 4.02 (1H, d, *J* = 3.9 Hz, Gal″-H4), 3.99 (1H, d, *J* = 3.3 Hz, Gal′-H4), 3.99 (1H, dd, *J* = 10.5, 3.8 Hz, Gal-H2), 3.96 (1H, dd, *J* = 10.5, 3.4 Hz, Gal″-H3), 3.90 (1H, d, *J* = 3.3 Hz, Gal-H6a), 3.90 (1H, dd, *J* = 7.5, 3.3 Hz, Fru-H5), 3.87 (1H, dd, *J* = 3.9, 10.3 Hz, Gal″-H2), 3.86 (1H, dd, *J* = 10.1, 3.3 Hz, Gal′-H3), 3.85 (1H, m, Fru-H6a), 3.82 (1H, dd, *J* = 10.3, 3.7 Hz, Gal′-H2), 3.78 (1H,

d, J = 12.1 Hz, Fru-H6b), 3.76 (1H, t, J = 9.5 Hz, Glc-H3), 3.75 (1H, d, J = 2.6 Hz, Gal-H6b), 3.75 (1H, m, Gal′-H6a), 3.75 (1H, m, Gal″-H6a), 3.68 (1H, s, Fru-H1), 3.68 (1H, d, J = 12.0 Hz, Glc-H6a), 3.67 (1H, m, Gal′-H6b), 3.67 (1H, m, Gal″-H6b), 3.55 (1H, dd, J = 9.9, 4.1 Hz, Glc-H2), 3.54 (1H, t, J = 9.6 Hz, Glc-H4); ^{13}C NMR (D_2O, 175 MHz) δ_C: 64.21 (Fru-C1), 106.72 (Fru-C2), 79.18 (Fru-C3), 76.87 (Fru-C4), 84.24 (Fru-C5), 65.35 (Fru-C6), 95.05 (Glc-C1), 73.85 (Glc-C2), 75.66 (Glc-C3), 72.17 (Glc-C4), 74.12 (Glc-C5), 68.32 (Glc-C6), 101.06 (Gal-C1), 69.77 (Gal-C2), 76.83 (Gal-C3), 68.46 (Gal-C4), 71.55 (Gal-C5), 69.32 (Gal-C6), 100.91 (Gal′-C1), 71.16 (Gal′-C2), 72.35 (Gal′-C3), 72.00 (Gal′-C4), 73.89 (Gal′-C5), 64.00 (Gal′-C6), 97.90 (Gal″-C1), 71.11 (Gal″-C2), 72.25 (Gal″-C3), 72.19 (Gal″-C4), 73.75 (Gal″-C5), 64.00 (Gal″-C6), 以上数据与文献[16]报道对照基本一致, 故鉴定化合物 **13** 为 rehmaglupentasaccharide F。

作者贡献: 张宇婷为本文第一作者, 进行化合物分离、鉴定、数据处理以及文章撰写; 宋娟进行实验指导、结构解析以及稿件修改; 刘思参与部分提取分离和结构鉴定工作; 王睿哲、陈晓娟、梁海珍参与提取分离实验; 马百平对研究工作进行设计、监督、指导以及稿件的修改, 承担研究工作各方面的责任。

利益冲突: 所有作者声明不存在利益冲突。

References

[1] Chinese Pharmacopoeia Commission. Pharmacopoeia of the People's Republic of China (中华人民共和国药典) [S]. Beijing: Chinese Medical Science and Technology Press, 2020.

[2] Jia Q, Shen D, Tang SH, et al. Analysis on medication regularity of Chinese patent medicines containing *Scutellaria baicalensis* [J]. China J Chin Mater Med (中国中药杂志), 2014, 39: 634-639.

[3] Liu XJ. Research progress on chemical composition and pharmacological effects of *Scutellaria baicalensis* and predictive analysis of quality markers [J]. Chin Arch Tradit Chin Med (中华中医药学刊), 2026. https://link.cnki.net/urlid/21.1546.R.20250506.1510.059.

[4] Chanchal DK, Singh K, Bhushan B, et al. An updated review of Chinese skullcap (*Scutellaria baicalensis*): Emphasis on phytochemical constituents and pharmacological attributes [J]. Pharmacol Res Mod Chin Med, 2023, 9: 100326.

[5] Zheng YF, Wang JJ, Fu CM, et al. Research progress on chemical constituents and pharmacological effects of *Scutellaria baicalensis* [J]. Chin Tradit Pat Med (中成药), 2016, 38: 141-147.

[6] Li W, Jia ZC, Xu W, et al. Chemical composition, pharmacological action and clinical application of *Scutellaria baicalensis* [J]. J Shanxi Datong Univ Nat Sci Ed (山西大同大学学报 自然科学版), 2024, 40: 85-90.

[7] Cui L, Guan X, Ding W, et al. *Scutellaria baicalensis* Georgi polysaccharide ameliorates DSS-induced ulcerative colitis by improving intestinal barrier function and modulating gut microbiota [J]. Int J Biol Macromol, 2021, 166: 1035-1045.

[8] Cui L, Wang W, Luo Y, et al. Polysaccharide from *Scutellaria baicalensis* Georgi ameliorates colitis *via* suppressing NF-*κ*B signaling and NLRP3 inflammasome activation [J]. Int J Biol Macromol, 2019, 132: 393-405.

[9] Xiong S, Li N, Shi S, et al. Structural characterization of a polysaccharide from *Scutellaria baicalensis* Georgi and its immune-enhancing properties on RAW264.7 cells [J]. Int J Biol Macromol, 2024, 283: 137890.

[10] Villéger R, Pinault E, Vuillier-Devillers K, et al. Prebiotic isomaltooligosaccharide provides an advantageous fitness to the probiotic *Bacillus subtilis* CU1 [J]. Appl Sci, 2022, 12: 6404.

[11] Zhu RG, Wang CY, Zhang LJ, et al. Pectin oligosaccharides from fruit of *Actinidia arguta*: Structure-activity relationship of prebiotic and antiglycation potentials [J]. Carbohydr Polym, 2019, 217: 90-97.

[12] Paulovičová E, Paulovičová L, Farkaš P, et al. Importance of *Candida* antigenic factors: Structure-driven immunomodulation properties of synthetically prepared mannooligosaccharides in RAW264.7 macrophages [J]. Front Cell Infect Microbiol, 2019, 9: 378.

[13] Yang WD. Preparation of konjac oligoglucomannans with different molecular weights and their *in vitro* and *in vivo* antioxidant activities [J]. Open Life Sci, 2020, 15: 799-807.

[14] Liu Y, Song J, Liu S, et al. A universal method for profiling and characterization of oligosaccharides in traditional Chinese medicines [J]. J Pharm Biomed Anal, 2024, 244: 116-129.

[15] He L, Yan B, Yao C, et al. Oligosaccharides from *Polygonatum cyrtonema* Hua: Structural characterization and treatment of LPS-induced peritonitis in mice [J]. Carbohydr Polym, 2021, 255: 117392.

[16] Liu YF, Zhou J, Zhang WQ, et al. Seven new pentasaccharides from the roots of *Rehmannia glutinosa* [J]. J Asian Nat Prod Res, 2024, 26: 280-292.

[17] Woo KJ, Lim JH, Suh SI, et al. Differential inhibitory effects of baicalein and baicalin on LPS-induced cyclooxygenase 2 expression through inhibition of C/EBP *β* DNA-binding activity [J]. Immunobiology, 2006, 211: 359-368.

[18] Bao QL, Tao F, Yao DY, et al. Flavonoid baicalin inhibits HIV-1 infection at the level of viral entry [J]. Biochem Biophys Res Commun, 2000, 276: 534-538.

[19] Guo SY, Cheng FF, Zhong XG, et al. Antioxidative effects of baicalin *in vitro* [J]. J Lishizhen Med Mater Med Res (时珍国医国药), 2011, 22: 9-11.

[20] Zhang L, Wang HD, Cong ZX, et al. Wogonoside induces autophagy-related apoptosis in human glioblastoma cells [J]. Oncol Rep, 2014, 32: 1179-1187.

[21] Li L, Zeng YY, Huang XY, et al. Effect of baicalin on T lymphocyte proliferation and cell cycle *in vitro* in mice [J]. Chin J Cell Mol Immunol (细胞与分子免疫学杂志), 2009, 25: 75-78.

[22] Xu C, Li J, Sun M, et al. Research progress on methods for isolation, purification and identification of oligosaccharides [J]. Chin Tradit Herb Drugs (中草药), 2023, 54: 6531-6542.

[23] Guo H, Me R, Fan J, et al. Research progress on extraction, isolation, structural identification and analytical methods of oligosaccharides from Chinese herbal medicine [J]. Chin J Pharm Anal (药物分析杂志), 2025, 45: 361-369.

[24] Zu H, Yan X, Wu J, et al. Application of an *α*-galactosidase from *Bacteroides fragilis* on structural analysis of raffinose family oligosaccharides [J]. Carbohydr Polym, 2024, 346: 122661.

[25] Zhao Z, Wu J, Xu X, et al. Oligosaccharides from *Stellaria dichotoma* L. var. *lanceolate* bind to galectin-3 and ameliorate effects of colitis [J]. Carbohydr Polym, 2024, 345: 122551.

[26] Song J, Liu S, Sun M, et al. Isolation and structural elucidation of immunomodulatory oligosaccharides from *Trillium tschonoskii* [J]. Glycoconjugate J, 2026, 43: 8.

[27] Song J, Liu Y, Yin X, et al. Isolation and structural elucidation of prebiotic oligosaccharides from Ziziphi Spinosae Semen [J]. Carbohydr Res, 2023, 534: 108948.

[28] Seibel J, Moraru R, Götze S, et al. Synthesis of sucrose analogues and the mechanism of action of *Bacillus subtilis* fructosyltransferase (levansucrase) [J]. Carbohydr Res, 2006, 341: 2335-2349.

[29] MyIntyre DD, Vogel HJ. Complete assignment of the ^{1}H NMR spectrum of stachyose by two-dimensional NMR spectroscopy [J]. J Nat Prod, 1989, 52: 1008-1014.

[30] Pan WD, Li YJ, Mai LT, et al. Studies on chemical constituents of the roots of *Lantana camara* [J]. Acta Pharm Sin, 1992, 27: 515-521.

[31] Kotiguda G, Peterbauer T, Mulimani VH. Isolation and structural analysis of ajugose from *Vigna mungo* L [J]. Carbohydr Res, 2006, 341: 2156-2160.

[32] Ishida M, Ohara R, Miyagawa F, et al. Umbelliferose isolated from *Cuminum cyminum* L. seeds inhibits antigen-induced degranulation in rat basophilic leukemia RBL-2H3 cells [J]. Molecules, 2022, 27: 4101.

[33] Pistelli L, Marsili A, Morelli I, et al. Umbelliferose from *Cachrys ferulacea* seeds: Determination of the sugar sequence by NMR 2D-COLOC technique [J]. Planta Med, 1990, 56: 230-231.

[34] Abe T, Kikuchi H, Aritsuka T, et al. Structural confirmation of novel oligosaccharides isolated from sugar beet molasses [J]. Food Chem, 2016, 202: 284-290.

[35] Amiard V, Morvan-Bertrand A, Billard JP, et al. Fructans, but not the sucrosyl-galactosides, raffinose and loliose, are affected by drought stress in perennial ryegrass [J]. Plant Physiol, 2003, 132: 2218-2229.