萝卜硫苷的高效纯化技术研究进展

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摘要：萝卜硫苷（Glucoraphanin，RAA）是广泛存在于十字花科植物中的硫代葡萄糖苷，其代谢产物具有防癌抗癌等功能。但从十字花科植物中提取的RAA纯度较低，降低了其利用率，因此需要对RAA纯化。当前纯化RAA的主要技术为色谱纯化技术，但该技术存在回收率低以及二次污染等问题。此外，因膜纯化技术是分离纯化糖苷类物质最常用的方法，具有设备和操作简单以及无二次污染等特点，故该技术同样是纯化RAA的潜在技术。因此，色谱纯化与膜纯化联合技术可实现RAA的有效回收并提高RAA的纯度，有效规避色谱纯化技术所造成的RAA回收率低及二次污染的缺点。因此，该文主要讨论了目前RAA主要的纯化方法，分析了色谱和膜纯化技术在RAA纯化中联合应用的可行性，为RAA的高效纯化提供方法参考。

关键词：萝卜硫苷；十字花科植物；高效纯化；色谱纯化技术；膜纯化技术

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Research Progress on the Efficient Purification of Glucoraphanin

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Abstract: Glucoraphanin (RAA) is a glucosinolate widely found in cruciferous plants, the metabolites of which have been established to have anti-cancer effects. However, the purity of RAA extracted from cruciferous plants is low, which limits its effective utilization, and consequently, it is necessary to develop an effective process for RAA purification. Although the main technique currently used for the purification of RAA is chromatographic purification, this procedure has notable drawbacks, including low recovery rates and secondary contamination. As an alternative procedure, membrane purification, which is the most commonly used method for the separation and purification of glycosides, requires only simple equipment and entails simple operation. Moreover, it is less prone to secondary contamination. Accordingly, this separation procedure is considered a potential technique for the purification of RAA. It is speculated that combined chromatographic and membrane purification could facilitate the effective recovery of RAA and enhance the purity of the recovered product, thereby overcoming the problems of low

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recovery and secondary contamination of RAA associated with the sole use of chromatographic purification. This study focuses mainly on the main methods currently used for the purification of RAA and assesses the feasibility of the combined application of chromatography and membrane purification techniques for RAA purification, thereby providing a methodological reference for the efficient purification of RAA.

Key words: glucoraphanin; cruciferous plant; efficient purification; chromatographic purification technology; membrane purification technology

萝卜硫苷（Glucoraphanin，RAA）是一种由甲硫氨酸衍生而成的脂肪族硫代葡萄糖苷。RAA 由一个带侧链的 *β*- 硫代葡萄糖苷 N- 羟基硫酸盐和一个 *β*-D- 吡喃葡萄糖残基构成的水溶性物质，其广泛的存在于十字花科植物中[1-3]。RAA 的代谢产物具有抑菌、抗炎和抑制癌症的生理活性，对维护机体健康具有重要作用[4,5]。然而，目前从十字花科植物中提取的 RAA 提取物富含大量的蛋白质、多糖等物质，不利于 RAA 的后期利用，因此需要对 RAA 进行纯化。目前，分离纯化 RAA 的主要方法是色谱纯化技术[6]。色谱纯化技术主要是柱色谱纯化技术和液相色谱纯化技术（Liquid Chromatography，LC）。然而，色谱纯化技术在纯化 RAA 方面有诸多缺点，如色谱纯化技术的纯化效率较低、RAA 的损失率高和 RAA 的回收率低。

为进一步提高 RAA 纯化效率，研究人员开始探究其他纯化技术在 RAA 纯化中应用的可能性。其中研究人员关注最多的技术是膜纯化技术，该技术的原理是利用膜的选择透过性和膜两侧的压力差，将溶液中无法分离的组分分开。由于膜纯化技术是物理纯化技术，因此不会对溶液中的成分造成化学变化，对天然产物具有一定的保护作用[7-9]。在此背景下，膜纯化技术被广泛用于食品加工和制药等行业[10-14]。尽管研究表明膜纯化技术可以实现植物天然产物的有效纯化，但膜纯化技术在 RAA 纯化过程中的纯化效果仍有不足[15-17]。本文主要分析了目前 RAA 纯化的主要技术以及膜纯化技术与色谱纯化技术联合应用在 RAA 纯化领域的可能性，也为进一步拓展 RAA 高效纯化技术提供理论和方法支撑。

1 色谱技术在RAA纯化过程中的应用

1.1 柱色谱技术在RAA纯化过程中的应用

由于 RAA 结构中存在离子化的硫酸盐和亲水性的硫代葡萄糖残基等结构，导致萝卜硫苷的辛醇—水分配系数较低，使得难以从 RAA 粗提取物中分离纯化得到 RAA 纯品[6]。目前，分离纯化 RAA 的主要技术是柱色谱技术（图 1）。Toribio 等[18]利用硫酸基团与烷基铵离子配对原理成功构建了一种强离子交换离心分配色谱（Strong Ion-Exchange Centrifugal Partition Chromatography，SIX-CPC）。RAA 粗提取物经 SIX-CPC 分离纯化后，粗提取物中大部分的蛋白质、多糖等大分子物质被去除，得到 RAA 纯化物，并且分离纯化后 RAA 纯度为 98%。由于 SIX-CPC 可以获得高纯度的 RAA，研究人员开始探究柱色谱技术在 RAA 纯化中应用前景。

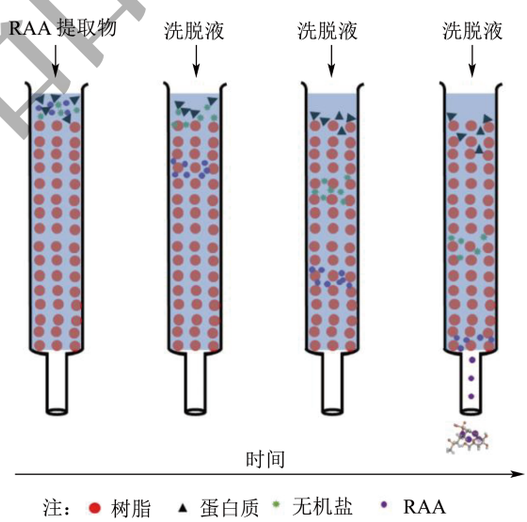

图 1 柱色谱技术纯化 RAA 机制

Fig.1 Mechanism of purification of RAA by column chromatography

近年来，研究人员[19]发现，以 D261 强碱性阴离子交换树脂为柱色谱填充材料同样可以实现纯化 RAA 的目的。自印度芥菜籽中提取的 RAA 在 D261 强碱性阴离子交换色谱纯化后的纯度是 58.37%，且萝卜硫苷的回收率是 79.82%。尽管该条件下的 RAA 回收率较高，但是 RAA 的纯度较低，不利于 RAA 的后续利用。因此，为进一步提高 RAA 的纯

度，Wang 等[20]以大孔阴离子树脂色谱纯化黑芥子苷后发现大孔阴离子树脂色谱纯化后的黑芥子苷纯度为 95%，黑芥子苷回收率约 77.38%。然而，另有研究人员在此基础上结合树脂改性技术构建了另一种纯化 RAA 的大孔树脂纯化技术[21]。该色谱技术以聚甲基丙烯酸缩水甘油酯（Poly Glycidyl Methacrylate，PGMA）和强碱性三乙胺改性 PGMA 为填充材料，通过该色谱技术纯化 RAA 的色度显著降低，且纯化后 RAA 的纯度为 75%，回收率为 81%。但是，基于大孔离子树脂的色谱纯化技术无法同时实现高 RAA 纯度和高回收率的目标。

因此，为提高 RAA 纯度和回收率，Chen 等[22]将硅胶色谱纯化技术应用于 RAA 纯化，且纯化后的 RAA 纯度为 91.7%，回收率为 5.5 g/100 g 种子。同时，Chen 等的结果同样表明，传统的柱色谱技术可以从十字花科植物粗提取液中分离纯化得到 RAA，但是无法同时兼顾 RAA 的纯度和回收率。另外，色谱柱的吸附和解吸能力有限，在柱色谱纯化过程中会损失大量的 RAA。另外，柱色谱的洗脱液为无机盐溶液，导致 RAA 溶液中无机盐离子浓度较高，导致 RAA 终产物中含有无机盐离子，影响 RAA 的生产和应用。

1.2 LC纯化技术在RAA纯化过程中的应用

随着研究的深入，LC 技术已成为有机物分离纯化的首选方法（表 1）。LC 技术可以纯化大分子有机物和小分子有机物。随着材料科学的发展，符合食品工业标准的 LC 填充材料不断被研发[23]。因此，从总硫代葡萄糖苷提取物中分离纯化 RAA 的 LC 技术得到迅速发展并成为目前纯化 RAA 的主要技术之一。

研究表明，逆流色谱（Countercurrentchromatography，CCC）作为一种液－液分配色谱技术可以利用固定相和流动相对各组分分配系数（KD）的不同来实现 RAA 的分离纯化（图 2）。纯化过程中，KD 低的组分先被分离，从而实现不同组分的分离纯化[28]。有研究人员利用高速逆流色谱（High-Speed Countercurrent Chromatography，HSCCC）纯化 RAA，纯化后 RAA 的纯度为 98%，回收率约为 90%[24]。结果表明，HSCCC 可以同时实现 RAA 纯度高和高回收率两个目标，与柱色谱技术纯化 RAA 的效率相比有明显提高。因此，结合盐析理论的 HSCCC 可进一步提高 RAA 的纯度[25]。

表 1 色谱法纯化RAA

Table 1 Purification of RAA by chromatography

纯化方法	原理	原料	洗脱液	回收率/产量	纯度/%	优点	缺点	参考文献
SIX-CPC	硫酸基团与烷基铵离子配对	西兰花种子	碘化钠溶液	2.6 g/25 g 种料	98	纯度高	产量低	[18]
大孔离子交换色谱	RAA 的带电性	印度芥菜籽	氯化钾溶液	79.82%	58.37	回收率高	纯度低、盐离子浓度高	[19]
		大蒜芥种子	氨水	80.63%	74.39	回收率高、盐离子浓度低	纯度低	[21]
硅胶色谱法	硅胶对不同物质的吸附能力不同	辣木种子	乙酸乙酯和甲醇的混合溶液	5.5 g/100 g 种料	91.7	纯度高、盐离子浓度低	产量低	[22]
HSCCC	溶剂分配系数的不同	西兰花种子	正丙醇－乙腈－硫酸铵－水混合物	90%	98	回收率高、纯度高	高溶剂消耗量，盐离子浓度高	[24]
		金银花	正丁醇硫酸铵溶液和正丁醇乙腈硫酸铵溶液	65.7%	98	纯度高		[25]
反相色谱法	RAA 的离子性质	板蓝根	硝酸钾溶液	ND	98	纯度高	产量低、无机盐离子污染	[26]
半制备型 HPLC	利用高压、高流量和高分辨率色谱柱	板蓝根	乙腈	ND	ND	分离不同构型的硫代葡萄糖苷	产量低	[27]

注：未检测（ND）。

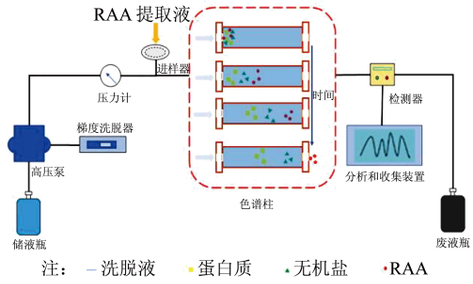

图 2 液相色谱技术纯化 RAA 机制

Fig.2 Mechanism of purification of RAA by liquid chromatography

由于 LC 技术的发展，研究人员探究了反相 LC 技术在纯化 RAA 中的效果。Xie 等[26] 以 ODS-BP 为固定相，结合反相 LC 纯化技术，实现了 RAA 的纯化。反相 ODS-BP LC 技术利用 RAA 的离子特性，实现不同硫代葡萄糖苷同分异构体的分离，在此条件下，RAA 的纯度为 98%。也有研究者采用半制备型 HPLC 纯化 RAA，该研究以乙腈为洗脱液，葡聚糖凝胶柱 Sephadex lh-20 (MeOH) 为脱盐处理条件，发现经该方法处理之后 RAA 的纯度和回收率明显提升，无机盐离子含量降低[27]。通过超高效液相 - 质谱联用 / 质谱分析表明，从板蓝根提取液中同时分离纯化出 4 种硫代葡萄糖苷（Progoitrin、Epprogoitrin、Gluconapin 和 Neoglucobrassicin）。但是，由于半制备 HPLC 洗脱液类型为有机溶剂，严重影响了该技术在食品工业中的应用。

虽然 LC 纯化技术可以从总硫代葡萄糖苷中分离纯化 RAA，但该过程需要大量的高浓度无机盐溶液和高极性溶液。因此，液相色谱纯化技术会消耗大量的时间和溶剂。同时，部分纯化溶剂有毒，不适合食品级产品的开发利用。但基于目前的工业基础，LC 纯化技术的设备要求和技术工艺要求高，且在 LC 纯化过程中，RAA 的损失比较大，因此 LC 无法达到规模纯化的程度。

2 膜纯化技术在RAA纯化过程中应用

膜纯化是利用膜的选择透过性原理，通过外加压力，使高于膜截留分子量的物质被截留在膜表面，低于膜截留分子量的物质通过滤膜，从而使液体中的成分实现分离的方法。根据膜孔径的大小依次可以将过滤膜分为微滤膜、超滤膜和纳滤膜等。由于所使用的过滤膜种类和性质的不同，膜纯化法可以分为微滤法（Microfiltration，MF）、超滤法（Ultrafiltration，UF）、纳滤法（Nanofiltration，NF）和反渗透（Reverse Osmosis，RO）等，且基于膜的纯化技术（UF 和 NF 等）已被证明能够实现大规模的生物活性物质的回收、分离和纯化（表 2）[29,30]。

表 2 食品工业常用的膜纯化技术

Table 2 Membrane purification technology commonly used in food industry

滤膜	过滤方式	原料	截留分子量/膜孔径	目标物质	回收率/%	纯度/%	文献
NF	NS	乳糖水解混合物	≥500 u	半乳糖	87	72	[34]
RO	错流过滤	酸性乳清废液	NS	乳酸	ND	90~95	[36]
NF	错流过滤	青茶花	400 u，500 u	儿茶素	ND	72	[45]
NS	NS	红茶	3.2~3.6 nm	茶多酚	70~90	ND	[40]
NS	NS	绿茶粗提物	0.73 μm	茶多酚	94.38	ND	[42]
MF	NS	茶饮料	NS	茶多酚	91.2~100.5	ND	[43]
UF	NS	玉米水煮液	100 ku	总酚	75.9	ND	[44]
UF	NS	栗色玫瑰汁	100 ku，5 ku	总黄酮	84.19	ND	[46]
RO	NS	番茄	0.1 μm	番茄红素	88.5	ND	[48]
UF	NS	维生素 B12 水溶液	NS	维生素 B12	>92	ND	[49]
UF	错流过滤	玉米纤维碱性提取物	50，100，150 ku	阿魏酸、阿拉伯木聚糖	0，98	ND	[51]
NF	NS	麦麸水解物	600~800 g/mol	阿魏酸、糖类	95，42~49	ND	[52]
RO	错流过滤	模拟生产液	NS	醋酸	44	ND	[53]
UF，NF	NS	油/溶剂混合物	5 000 u，400 u	脂肪酸	58.2，56	ND	[56]
MF	错流过滤	病毒样液	NS	艾滋病毒	100	ND	[64]
NS	NS	水	NS	噬菌体、细菌	100	ND	[65]

注：未具体说明（NS），未检测（ND）.

研究表明，膜纯化技术是分离纯化乳制品中脂类、寡糖和蛋白胶束等大分子物质最常用的纯化技术[31-33]。在纯化乳清中的蛋白质过程中发现，膜纯化技术对乳制品中的天然物质也具有分离纯化作用[34-36]。随着膜纯化技术研究的不断深入，膜纯化技术被应用于植物天然产物的分离纯化[37-39]。研究人员证明膜纯化技术对多酚具有很高的纯化效率[40-45]。同时，膜纯化技术对黄酮类[46]、类胡萝卜素[47,48]、维生素[49]、有机酸[50-53]、氨基酸[54,55]和脂肪酸[56]等天然物质也有较高的纯化效率。随着时间的发展，膜纯化技术在纯化水[57-63]和医药制造[64-68]中也有广泛的应用。

陶瓷膜具有稳定性高、抗污染能力强等优点，在物质的分离和纯化中有着广泛的应用[69-73]。由于陶瓷管式超滤膜可以去除杂质物质，Sjolin 等[74]用陶瓷管式滤膜纯化蔗糖。结果表明，采用陶瓷管纯化技术可以得到高纯度蔗糖，且蔗糖的材料结构没有发生变化。但是研究人员发现，单一的陶瓷膜纯化系统的纯化效果不是十分理想，且纯化效率较慢。因此，研究人员将两种截留分子量不同的超滤膜（100 ku 和 1 ku）组合集成膜纯化系统，并用该集成膜纯化系统实现了自甜叶菊的水提取物中纯化甜菊皂苷 A（Rebaudioside A，Reb A）的目的[16]。集成膜纯化后 Reb A 的颜色得到了进一步纯化，但是该集成膜纯化系统纯化 Reb A 的时间较长，严重制约了集成膜系统的纯化效率。

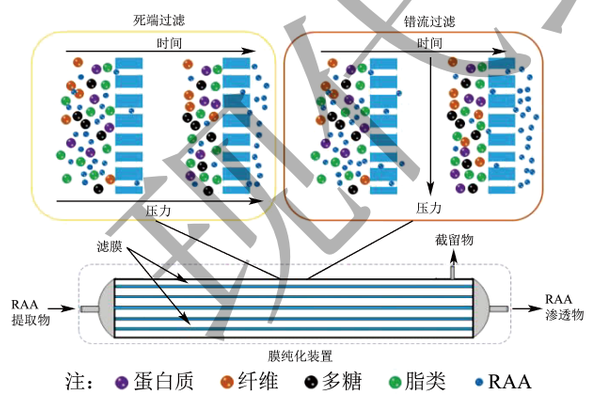

图 3 膜纯化技术纯化 RAA 机制

Fig.3 Purification mechanism of RAA by membrane purification technology

同时，研究人员[16,74]发现膜纯化技术是蔗糖最佳的纯化技术，且同为葡萄糖衍生物的 Reb A 同样可以通过膜纯化技术进行纯化，而且膜纯化后的蔗糖和 Reb A 表现出较高的稳定性、纯度以及回收率。由于 RAA 同样是葡萄糖衍生物，与 Reb A 具有相似的葡萄糖残基，因此膜纯化技术可用于 RAA 纯化。超滤法作为以酸性氧化铝填充材料的制备色谱法纯化硫代葡萄糖苷的除杂技术，用来除去亚麻籽提取物中的蛋白质[75]。Eder 等[76]以 10 ku 聚醚砜超滤膜纯化多糖，多糖回收率为 90%。因此，膜纯化技术目前被广泛应用于多糖的纯化[77,78]。近年来，死端过滤技术被应用于 RAA 的纯化，在 1 ku 超滤膜纯化条件下，果汁中的大部分杂质（蛋白质和胶体）被除去，果汁中的硫代葡萄糖苷纯度从 35.2% 提高到 90.1%，且 RAA 没有降解（图 3）[15]。但研究人员同时发现，死端过滤在纯化 RAA 一段时间后的纯化效率会降低，主要是大部分的杂质被截留于超滤膜表面，阻塞膜孔，限制了死端过滤纯化 RAA 的效率。

因此，膜纯化技术具有以下特点：可控的温度和压力操作条件能够保持目标物质的功能性；无需其他化学试剂或添加助剂，从而避免了目标物质的二次污染；对特定化合物具有极高的选择性，对重金属离子和无机盐离子的去除效果较好[9,30,79]。基于膜纯化的优势，祝亚辉等[80]通过膜过滤技术将粗提液中 RAA 的纯度由 34.96% 成功提升至 54.89%。然而，膜纯化技术在分离纯化过程中仍存在一些不足，如该技术需要外加压力会导致滤膜的结晶化并降低其机械强度，进而导致膜纯化的效率降低；纯化过程中需要多级膜纯化设备，得到的产品纯度无法达到色谱纯化技术的效果[81]。

因此，色谱纯化技术和膜纯化技术各有的优缺点，故为了进一步提高 RAA 的纯化效率及效果，今后可以开展膜纯化技术和色谱纯化技术的联合应用。通过膜纯化技术将 RAA 纯度提升至 50% 以上之后，再次利用色谱纯化技术对 RAA 粗提液进一步纯化，可有效提高 RAA 的回收率以及纯度。能够一定程度上规避色谱纯化过程中因有机试剂的添加造成 RAA 二次污染的问题，缩短利用色谱纯化技术获得高纯度 RAA 的时间，提升 RAA 纯化效率。

3 展望

RAA 纯化的主要技术为色谱纯化技术，但该技术无法实现高效且规模化的 RAA 纯化，且该技术具有二次污染和低回收率的缺点。此外，因膜纯化技术具有规避二次污染和实现规模化纯化的特点而被视为一种潜在的纯化 RAA 技术，其可在一定程

度克服色谱纯化技术的不足，为 RAA 纯化提供新的解决方案。因此，利用色谱纯化和膜纯化联用技术对 RAA 进行纯化可有效提升 RAA 的回收率以及纯度，提升 RAA 纯化效率。此外，色谱纯化和膜纯化联用技术在食品工业中同样具有广阔的应用前景。

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