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甲壳类水产品中氨基脲的来源及生成机理研究进展*

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摘要 氨基脲(semicarbazide, SEM)通常作为判断水产品中是否滥用呋喃西林的标志物，在动物体内能与蛋白质结合形成稳定的结合物，摄入过多对人体有一定的危害。研究发现，甲壳类水产品未使用呋喃西林仍能检测到 SEM，现已确认的 SEM 来源包括内源存在和外源摄入，外源摄入途径有生长环境和饲料引入、加工过程中使用次氯酸盐消毒和偶氮二甲酰胺的分解产生。对于 SEM 广泛的来源途径，目前，对 SEM 形成机理的研究相对较少。甲壳类水产品中 SEM 的天然存在给呋喃西林药物检测带来了严重的干扰。本文对甲壳类水产品中 SEM 的来源途径进行总结并推测可能的生成机理，可为甲壳类水产品质量控制及内源性 SEM 的生成机理提供理论参考。

关键词 甲壳类水产品；氨基脲；来源；生成机理

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呋喃西林是人工合成的广谱抗菌药物，能破坏细菌的糖代谢和氧化酶系统，早期在水产和畜牧养殖中用来治疗畜禽疾病和防治病虫害。呋喃西林进入动物体内后迅速代谢，其代谢物氨基脲(semicarbazide, SEM)与蛋白质结合后在动物体内长期稳定存在(范清涛等, 2020)。Vass 等(2008a、b)研究发现，动物源性食品中残留的 SEM 可通过食物链传递给人类，长期摄入对人体有致癌、致畸等副作用。对 SD 大鼠(*Rattus norvegicus*)的研究表明，SEM 造成大鼠多个组织器官发生病变，包括子宫、胰脏和甲状腺等，同时，表现出致变性和弱遗传毒性效应(Maranghi *et al*, 2009; 朱乐玫等, 2012)。对妊娠期大鼠腹腔注射 40 mg/kg SEM，21 d 后大鼠腹中胎儿组织和骨骼发生畸变，同时多个脏器出现核酸水平显著降低的现象(李嘉, 2008)。SEM 在组织形态学上导致多种组织器官形态改变，也对神经系统、内分泌系统的功能产生影响。美国、澳大利亚、加拿大、日本、新加坡、欧盟等已禁止在食品工业中使用该类药物，并严格执行对水产品中呋喃西林的残留监测(龚珞军等, 2019)。呋喃西林也已被我国列入首批《兽药地方标准废止目录》中，在《关于开展 2016 年国家产地水产品质量安全监督抽查工作的通知》中，将 SEM 的残留限量值定为 1.0 μg/kg。

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近年来，我国对甲壳类水产品药物残留进行检测发现，SEM 的检出超标率高达 50% (于慧娟等, 2012)。2002—2003 年期间，欧盟食品和饲料快速预警系统(Rapid Alert System for Food and Feed, RASFF)发布了 300 余份来自泰国、文莱、巴西等国家的虾类等 SEM 残留事件的通报，数百吨水产品因此被销毁。SEM 在不同甲壳类水生动物中的本底含量差异较大，几乎在所有甲壳中均不同程度的检出 SEM，包括日本沼虾(*Macrobrachium nipponense*)、罗氏沼虾(*Macrobrachium rosenbergii*)、凡纳滨对虾(*Litopenaeus vannamei*)、克氏原螯虾(*Procambarus clarkii*)、中华绒螯蟹(*Eriocheir sinensis*)等，其壳中 SEM 检出率为 100%，且含量远高于 1.0 μg/kg。在甲壳类肌肉可食组织中，SEM 含量差异较大，如凡纳滨对虾、中华绒螯蟹等肌肉中未检出 SEM，而日本沼虾和罗氏沼虾肌肉中 SEM 检出率极高(于慧娟等, 2012; 张睿等, 2012; 李东利等, 2015; 王鼎南等, 2016; 彭婕等, 2019; 曹爱玲等, 2020; 范清涛等, 2020) (表 1)。SEM 严重超标的现状引发了人们对甲壳类水产品安全性的思考。本文针对甲壳类水产品中 SEM 的不同来源进行总结，概述有关 SEM 来源的研究现状及生成机理，以期为甲壳类水产品中 SEM 的检测提供理论根据。

表 1　不同品种甲壳类水产品不同检测部位 SEM 含量(μg/kg)

Tab.1　SEM content in different test sites of different crustacean aquatic products (μg/kg)

不同品种 Different breeds		拉丁名 Scientific name	不同检测部位 Different test sites		
			甲壳 Carapace	肌肉 Muscle	其他组织 Other tissues
虾类 Shrimp	日本沼虾	*M. nipponense*	30.00~315.30	1.38~11.87	58.60~81.30
	罗氏沼虾	*M. rosenbergii*	26.38~64.16	1.63~4.41	2.41~6.43
	凡纳滨对虾	*L. vannamei*	1.50~10.27	ND	ND
	中国对虾	*Penaees chinensis*	<1	<1	<1
	克氏原螯虾	*P. clarkii*	3.50±0.09	0.44~0.68	1.97~2.15
	斑节虾	*Penaeus monodon* Fabricius	3.04~15.36	0~0.76	0.88~1.02
蟹类 Crab	中华螯绒蟹	*E. sinensis*	5.48~24.31	0~2.05	ND
	海蟹	*Portunus trituberculatus*	13.80~26.50	ND	ND
	锯缘青蟹	*Scylla serrata*	81.80±7.00	ND	ND
	珍宝蟹	Dungeness crab	46.30±4.80	ND	ND
鳖类 Turtle	中华鳖	*Trionyx sinensis*	1.36±0.04	ND	ND

注：ND：未检出。

Note: ND: Not detected.

1　甲壳类水产品中 SEM 的来源

1.1　甲壳类水产品中内源性 SEM 的来源

赵芸等(2019)研究发现，许多不曾接触呋喃西林药物的养殖甲壳类水生动物体内(以虾蟹为代表)含有 SEM。此外，研究人员多次从生活在天然水域的虾蟹中检测出 SEM，推测 SEM 具有内源性。Saari 等(2004)在未食用呋喃西林的克氏原螯虾中检测到 SEM 最高含量为 12 μg/kg，首次提出了甲壳动物自身可以产生 SEM 的观点。McCracken 等(2013)通过对孟加拉国野生淡水明虾(*Macrobrachium agwi*)研究发现，虾肉和虾壳均有 SEM 检出，相较于虾肉，虾壳中 SEM 含量更高，这与 van Poucke 等(2011)对罗氏沼虾、王鼎南等(2016)对日本沼虾、倪永付等(2012)对微山湖小青虾 SEM 检测结果一致。这些结果证明了甲壳类水产品中内源性 SEM 的存在。彭婕等(2019)在中华绒螯蟹脱壳后新长出的软壳中检测到了 SEM，而蟹肉中未检出 SEM，推测水生动物甲壳可能是其内源性 SEM 的主要来源。

1.2　甲壳类水产品中外源性 SEM 的来源

1.2.1　*生长环境或食物摄入 SEM*　自然界中，甲壳类动物的生存环境会因人类经济活动的影响而受到 SEM 污染。于召强等(2013)研究发现，SEM 作为一种新的水体污染物在水体和沉积物中长时间存在并不断富集，最终进入生物体内。徐英江等(2010)在潮河河口水和河流沉积物中检测到 SEM 大量存在；田秀慧(2018)分别在山东省金城湾、四十里湾和莱州湾西部 3 个水域的水体、沉积物中检测到 SEM 存在，且所监测水域中的贝类、虾蟹等 SEM 均有不同程度的检出，表明水体环境中的 SEM 对水生动物的富集污染。其次，甲壳类水生动物可通过摄食自然界中的藻类或喂食饲料引入 SEM，田秀慧(2018)通过对月菱

形藻(*Nitzschia closterium*)、扁藻(*Platymonas*)和叉鞭金藻(*Dicrateria* sp.)中的 SEM 进行监测，发现 SEM 在藻类中有很强的富集能力，富集系数为 145.3~200.0。同样，Hoenicke 等(2004)在红藻(*Rhodophyta*)、褐藻(*Phaeophyta*)中检测到了 SEM。水生动物食用这些天然食物后，体内会产生 SEM 残留。

1.2.2 养殖过程中非法使用呋喃西林引入 SEM

呋喃西林作为广谱抗菌药物，具有良好的抗菌效果和价格低廉等优点。某些养殖户为了降低水产品疾病发生率(比较典型的疾病：赤皮、烂鳃和肠炎)、获得更大的经济利益，违反呋喃西林使用规定。呋喃西林进入动物体内后，可以在弱酸性条件下迅速分解成 SEM (Leitner *et al*, 2001)，从而与蛋白形成难以代谢的结合体。Kwon(2017)研究表明，在混合养殖的过程中，一些养殖户会用从出生开始就被投喂了呋喃西林等抗生素的家禽垫料对池塘施肥，从而对养殖水体造成 SEM 污染进而进入养殖动物体内。索纹纹等(2013)研究发现，通过对养殖斑点叉尾鮰(*Ictalurus punetaus*)的水体进行呋喃西林泼洒后，水体、底泥和鱼体均出现了 SEM 蓄积，水体底泥蓄积量显著高于鱼体(P<0.05)。樊新华等(2010)、蒋原等(2008)、谭志军等(2008)分别对中华绒螯蟹、克氏原螯虾、大菱鲆(*Scophthalmus maximus*)进行不同的呋喃西林给药方式处理，以研究体内 SEM 的蓄积和消除规律，结果发现，无论哪种给药方式，呋喃西林进入动物体内后代谢迅速，而 SEM 残留时间可长达 180 d。丁春燕(2019)、Pak-Sin 等(2008)、黄宣运等(2017)、丁军伟等(2018)发现水生动物摄入含有呋喃西林的饲料后，无法实现完全代谢，代谢物 SEM 会长期残留在动物源性食品中，最终对人体产生毒副作用。

1.2.3 次氯酸盐消毒产生 SEM 次氯酸盐因具有强氧化性广泛用于水产品的卫生消毒(李会生等, 2001)。袁涛等(2011)研究发现，次氯酸盐浸泡的水产品中 SEM 含量显著高于清水浸泡的水产品。杨曦等(2011)、王建(2015)发现水产品中 SEM 含量与次氯酸盐的质量浓度、作用持续时间和食品接触物表面积成正比。Zhang 等(2016)采用次氯酸盐处理凡纳滨对虾、三疣梭子蟹(*Portunus trituberculatus*)和哈氏仿对虾(*Parapenaeopsis hardwickii*)后发现，SEM 含量与次氯酸盐浓度存在剂量依赖性且次氯酸盐对不同水产品的 SEM 含量具有差异。

1.2.4 偶氮二甲酰胺加工产生 SEM 偶氮二甲酰胺(azodicarbonamide, ADC)在人类生产生活中有 2 种用途：一是用作食品添加剂，增强面粉团的柔韧性；二是作为食品级玻璃罐密封垫圈的原材料(黄晓姗等, 2018)。ADC 在高温高压条件下，受热快速分解产生 SEM，对与其接触的食品产生污染。

某些生产厂家为迎合消费者口感需求会对水产品裹粉以促进销售，如面包虾等，使用含 ADC 的面粉作为甲壳类水产品的裹粉原料是导致甲壳类水产品 SEM 超标的原因之一。Pereira 等(2004)在含有 ADC 添加剂的面粉中检出 SEM，含量约为 2~5 μg/kg。胡菏等(2018)、阮莎莎等(2019)等对市售的面粉及面制品中的 ADC 和 SEM 的含量进行监测发现，面粉及面制品中均有 ADC 检出，面制品中 SEM 的含量高于面粉，且面包中 SEM 的含量高达 139~1 288 μg/kg，说明 ADC 经高温反应生成了 SEM。另外，SEM 可通过包装材料对与之接触的食品造成污染。Stadler 等(2004)从水产品罐头、蜂蜜、调味品和婴儿食品罐头中均检测到了 SEM，最高含量可达 25 μg/kg；陈志锋等(2009)研究发现，食品接触垫圈经过加热可分解产生 SEM；赵天祎等(2019)在蜂蜜中检测出 SEM，通过模拟性实验推断是蜂蜜罐垫圈的内溶物外溶所致。Hoenicke 等(2004)将玻璃罐垫圈进行加热并检测 SEM 含量，发现垫圈中的 ADC 在高温条件下降解成 SEM，且 SEM 可从垫圈迁移到食品中。因此，甲壳类水产品在加工运输过程中应当尽量避免与 ADC 接触，以防受到外源性 SEM 的污染。

2 甲壳类水产品中 SEM 的生成机理

2.1 内源性 SEM 生成机理

甲壳类水产品中壳的 SEM 含量普遍大于肉，而壳的主要成分是甲壳素(几丁聚糖)。因此，相关研究对内源性 SEM 是否来源于甲壳中的甲壳素进行了论证。

周萍等(2008)研究发现，未使用任何药物的蜂蛹在生长后期体内的 SEM 含量随着甲壳素含量的增加而逐渐增加，推测内源性 SEM 的形成或与内源甲壳素有关。McCracken 等(2013)研究发现，在虾壳和虾肉之间存在着一层分泌甲壳素的单细胞表皮层，靠近该表皮层虾肉的 SEM 含量是内层虾肉检出量的 3 倍以上，由此推断虾肉中的 SEM 主要来自于产生甲壳素的细胞表皮层。然而，彭婕等(2015)通过对中华绒螯蟹蟹壳中的甲壳素研究发现，内源性 SEM 的产生与甲壳素无关，可能是蟹壳中的结合蛋白水解后，产生了在一定条件下能转化为 SEM 的氨基酸。对于以上实验结果，彭婕等(2019)进一步研究了不同蟹壳中

的主要成分与 SEM 残留的相关性，发现不同部位蟹壳中甲壳素含量与 SEM 残留水平呈明显的正相关性，蛋白质含量及氨基酸组成与 SEM 残留水平呈负相关性，这可能是甲壳素和氨基酸在之前处理过程中产生了 SEM，是导致中华绒螯蟹中内源性 SEM 残留的原因。

目前，关于甲壳类水产品内源性 SEM 的形成机理已有一定进展。一种被认可的说法是内源性 SEM 形成可能与甲壳中的结合蛋白及氨基酸有关。曹爱玲等(2019、2020)研究发现，中华鳖壳中 SEM 含量随着烘干温度的上升而上升，但其蛋白含量随烘干温度的上升而下降，对其丰度差异蛋白质进行筛选，发现球蛋白、角蛋白等 13 种蛋白与 SEM 含量的变化显著相关，此类蛋白涉及细胞碳代谢、焦点黏附等生物过程，由此猜测这些蛋白随热能的增加转化成了 SEM。Samsonova 等(2008)对动物体内含有 SEM 残基的蛋白进行鉴定，发现白蛋白中含有高浓度 SEM 残基，并且在以谷胱甘肽 S-转移酶为主要成分的蛋白质混合物中也发现含有高浓度的 SEM 残基，表明 SEM 的形成可能与 SEM 结合的谷胱甘肽有关联。谢冬冬等(2014)研究表明，甲壳类水产品中内源 SEM 不仅与样品中的蛋白质有关，而且与样品中的氨基酸组成有关联。Noonan 等(2008)证实甲壳类水产品中含量最丰富的氨基酸是精氨酸。精氨酸酶可将精氨酸水解为鸟氨酸和尿素进入尿素循环，尿素和 SEM 在结构上有一定的相似性。Hoenicke 等(2004)认为 SEM 是由含氮物质(如精氨酸、组氨酸、瓜氨酸和肌酐)与酰胺或尿素反应形成。Abernethy 等(2015)研究表明，肼作为参与尿素循环的重要中间物质，可与酸根离子反应生成 SEM，因此，某些高氨氮(NH_4^+-N)含量的食品可在酸性条件下形成 SEM。由此推测，精氨酸可能是动物内源性 SEM 的前体。Yu 等(2019)在凡纳滨对虾生长期间对参与尿素循环的相关物质含量进行检测后认为，虾体内的精氨酸等物质通过尿素循环最终形成 SEM。

精氨酸是内源性 SEM 形成的重要潜在前体。精氨酸等参与甲壳类水生动物的尿素循环，通过恶嗪啶中间体产生了 SEM，结合尿素循环中主要物质的含量变化分析，内源性 SEM 的形成与精氨酸的胍基和酰胺基、瓜氨酸和尿素的酰胺结构密切相关，内源性 SEM 可能的生成机理如图 1 所示。

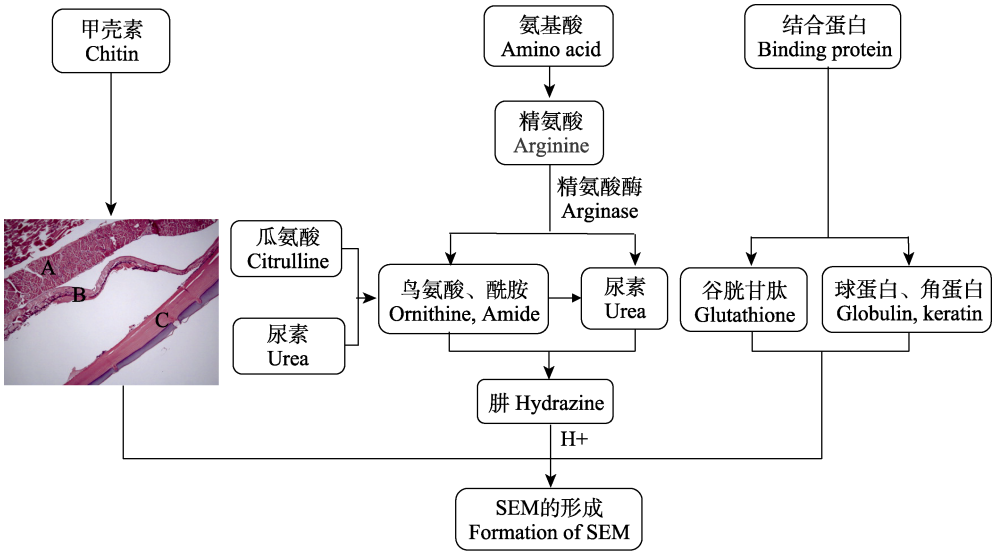

图 1　内源性 SEM 在甲壳类水产品中可能的生成机理

Fig.1　Possible formation mechanism of endogenous SEM in crustacean aquatic products

A: 虾肉；B: 虾表皮层；C: 虾壳。

A: Shrimp meat; B: Shrimp epidermal layer; C: Shrimp shell.

2.2　外源性 SEM 生成机理

2.2.1　*次氯酸盐引入 SEM 生成机理*　　Hoenicke 等(2004)研究不同浓度的次氯酸盐对北海虾、鱼制品、蛋白粉、红藻、鸡肉和蜂蜜的 SEM 检出的影响发现，随着有效氯含量不断增加，6 种样品的 SEM 含量均有不同程度的增加，其中，以蛋白粉最为显著，检出量为 20 μg/kg。考虑到水产品中富含的精氨酸、组氨酸、瓜氨酸、肌酸酐等多种具有胍基或脲基结构的含

氮化学物质结构与 SEM 化学结构相近，Hoenickek 等(2004)认为这些含氮化学物质经过次氯酸盐溶液的处理后，发生降解反应最终形成了 SEM。Abernethy 等(2015)推测次氯酸盐溶液中的氨基甲酸根离子可能与水产品中的氨或酸性酰胺反应生成肼，肼通过尿素循环与尿素及其他化合物反应生成 SEM。Bendall (2009)认为 SEM 是次氯酸盐和尿素在一定条件下发生霍夫曼反应产生的。由此推测，水产品中的 SEM 可能来自体内以及次氯酸盐中的氨，次氯酸盐引入 SEM 可能生成机理见图 2。

2.2.2 ADC 生成 SEM 机理　温度可能对 SEM 的生成有影响。Pereira 等(2004)研究发现，在面粉中添加 10 μg/kg 的 ADC，所检样品的 SEM 含量为 12 μg/kg，转化率约为 0.1%。Ye 等(2011)研究发现，经高温烘焙后，面粉中添加的 ADC 会分解成 SEM，且面制品外部的 SEM 含量要高于内部，说明温度对 SEM 的生成有积极影响。姚敬等(2016)、蒋志红等(2014)通过实验证明了 ADC 在湿热条件下可生成 SEM。Noonan 等(2008)研究 ADC 面粉及面制品中的 SEM 生成情况时发现，生面团不含 SEM，而面制品中有 SEM 检出，进一步研究发现 SEM 含量与温度成正比。

ADC 在高温条件下先降解为联二脲，联二脲再经过水解反应转化为 SEM (李金强等, 2009)。考虑到呋喃西林与联二脲分子结构的差异性，可排除呋喃西林代谢产生联二脲的推测。从现有的研究看，ADC 是联二脲的唯一生物来源，因此，可将联二脲作为 ADC 相应的目标检出物，ADC 引入 SEM 生成机理见图 2。

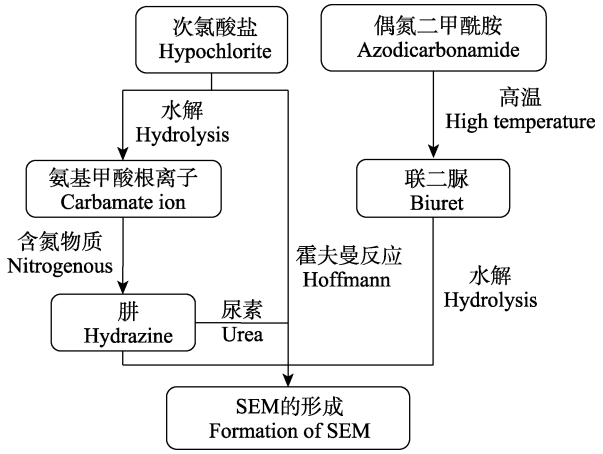

图 2　外源性 SEM 在甲壳类水产品中可能的生成机理

Fig.2　Possible formation mechanism of exogenous SEM in crustacean aquatic products

3　结论与展望

SEM 在自然界中的来源广泛，甲壳类水产品中检出的 SEM 非呋喃西林唯一代谢产生，水体环境及加工过程的污染等均可导致 SEM 超标。对于 SEM 的生成机理，目前研究相对较少，当前对于内源性 SEM 的生成机理有 2 种推测：一是富含蛋白质的甲壳类水产品中的含氮物质如精氨酸等参与尿素循环等过程形成 SEM；二是来源于单细胞表皮层的甲壳素转化。对于外源性 SEM 的生成机理也有 2 种推断：一是甲壳类水产品经次氯酸盐的处理生成的肼进入尿素循环，增加了 SEM 生成量；二是加工过程中外加的 ADC 经高温降解为 SEM，导致 SEM 过量残留。深入分析研究甲壳类水产品中 SEM 的主要来源及形成作用机理对于保障我国水产养殖业健康发展具有重大意义。对甲壳类水产品内源性 SEM 的形成机理进行研究，可为我国制定甲壳类水产品中 SEM 最大残留限量提供科学数据。

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Progress on the Origin and Formation Mechanism of Semicarbazide in Crustacean Aquatic Products

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Abstract Nitrofurazone is a synthetic antimicrobial drug developed by the Eaton Institute in the United States in the 1950s. Nitrofurazone can play an inhibitory or bactericidal role by interfering with the glucose metabolism process and oxidase system in bacteria. Due to its strong bactericidal ability, wide antibacterial spectrum, and low price, it was widely used in animal husbandry and aquaculture. Nitrofurazone is detected in animals because it is rapidly metabolized, with a half-life of only a few hours. Semicarbazide (a typical metabolite of nitrofurazone) is detected in food-borne products in a linear proportion to the amount of nitrofurazone added to the animal. Semicarbazide binds to animal proteins to generate stable residues and is difficult to metabolize completely. The United States, European Union, China, and other countries detect and monitor semicarbazide as a marker of nitrofurazone drugs. Nitrofurazone (and its metabolite semicarbazide) have teratogenic and carcinogenic effects on the human body. Any residues in animal-derived foods can be transmitted to humans through the food chain. Long-term intake of semicarbazide in humans will cause anemia, liver necrosis, neuritis, and damages the eyeball and DNA. Therefore, the United States, the European Union, and other countries have explicitly banned its use in the food industry. China has listed nitrofurazone as a banned drug and specified that nitrofurazone and its metabolites should not be detected in animal-derived foods. Over the years, the detection of semicarbazide has been limited by the detection methods and instruments. The Ministry of Agriculture has stated the residual limit of semicarbazide as 1.0 μg/kg and assigned a supervision and sampling inspection program.

Existing studies have identified the semicarbazide detected in crustacean aquatic products combines the residue caused by nitrofurazone metabolism and other obvious sources of semicarbazide, which include: 1) the presence of endogenous sources in crustacean aquatic animals; 2) the growth environment and feed intake; and 3) aquatic product processing. Previously, semicarbazide residues were generally considered to be the result of excessive nitrofurazone drug use by farmers. In recent years, the farmers state they have not used nitrofurazone during aquaculture. However, semicarbazide has been present in seafood. In 2004, Saari *et al*. detected semicarbazide in *Procambarus clarkii* that did not consume nitrofurazone and provided the first report that crustaceans may naturally produce semicarbazide, which is causing the detection of semicarbazide in many cultured crustacean aquatic animals that have not been fed nitrofurazone drugs (represented by shrimp and crab). This research confirms the presence of endogenous semicarbazones in crustacean aquatic products. In addition, the natural living environment of crustacean aquatic animals is polluted with semicarbazide due to economic human activities. Many scientists have detected the presence of semicarbazide in the waters and sediments in various regions. Concurrently,

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semicarbazides also contaminate aquatic plants. Semicarbazide is a new water pollutant that exists in water bodies and plants, which is continuously enriched and enters organisms. Nitrofurazone is a commonly used antibiotic for aquaculture products and is often detected when the amino residues exceed the standard levels due to illegal addition by farmers. Studies have shown that semicarbazide is also introduced through processing aquatic products, such as sodium hypochlorite disinfection resulting in an increase in the levels of semicarbazide, by azodicarboxamide through thermal decomposition producing semicarbazide and so on. The biological toxicity of semicarbazide and the food chain transfer effect have ensured semicarbazide is now an important environmental and food pollutant.

In the current aquatic trade in China, the presence of endogenous semicarbazide in crustacean aquatic products has serious impacts and interferes in the detection of nitrofurazone drugs, resulting in an inability to accurately determine semicarbazide sources. It is of great importance to thoroughly analyze and understand the main sources and formation mechanism of SEM in crustacean aquatic products to ensure the healthy development of the aquaculture industry in China. At present, there are two statements on the formation mechanism of endogenous semicarbazide: arginine is involved in the urea cycle of crustacean aquatic animals and semicarbazide is produced through the oxadine intermediate. An analysis of content changes in the main substances of the urea cycle revealed the formation of endogenous semicarbazide is closely related to the guanidinyl and amide groups of arginine, citrulline, and the amide structure of urea. Arginine is a potentially important factor in the formation of endogenous semicarbazide; secondly, SEM is derived from a single cell epidermis that produces chitin. There is a single cell epidermal layer secreting chitin between the shrimp shell and shrimp meat, and the detection level of semicarbazide in the shrimp meat close to this epidermal layer was more than three times higher than the inner shrimp meat. Therefore, the semicarbazide in shrimp meat mainly originates from the epidermal layer cells producing chitin. Two inferences on the formation mechanism of exogenous semicarbazide are: the carbamate ions in hypochlorite solution may react with ammonia or acid amide in aquatic products to generate hydrazine, and hydrazine reacts with urea and other compounds through the urea cycle to generate semicarbazide, increasing the production of semicarbazide; the azodicarbonamide added in processing is degraded to biurea at high temperatures, and biurea is then converted to semicarbazide by the hydrolysis reaction. Considering the different molecular structures between nitrofurazone and biurea, the speculation that nitrofurazone is metabolized to produce biurea can be ruled out. From existing studies, azodicarbonamide is the only biological source of biurea, so biurea can be used as the corresponding target detector of azodicarbonamide. To solve the problem that endogenous and exogenous semicarbazide cannot be distinguished in aquatic products in China, the endogenous and exogenous pathways of semicarbazide and the corresponding possible formation mechanisms are reviewed in this paper. The formation pathways of endogenous semicarbazide are speculated to help solve the formation mechanism of semicarbazide in crustacean aquatic products and provide scientific data for the standardization of semicarbazide residue limits in China.

Key words Crustacean aquatic products; Semicarbazide; Source pathways; Generation mechanism