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普洱熟茶后发酵酚类物质变化研究进展

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摘要 普洱熟茶的独特品质与健康功效源自其微生物驱动的后发酵过程。在此过程中,酚类物质发生显著转化,构成了其风味特征与功能特性的物质基础。为解析普洱熟茶品质形成机制,本文综述了普洱熟茶发酵过程中酚类物质的变化,包括儿茶素类在微生物胞外酶催化下降解,经氧化、聚合、裂解等反应转化为没食子酸、茶褐素及生物活性增强的新型衍生物(如普洱茶素、羧甲基化儿茶素和Teadenol A);黄酮类物质总量保持稳定,其糖苷水解释放槲皮素等苷元;酚酸组成变化显著,没食子酸与鞣花酸含量上升,并代谢生成赋予陈香风味的甲氧基苯类化合物。此外,发酵过程中形成的茶黄素和茶红素进一步通过酶促聚合及与非酚类成分(如多糖和蛋白质)的络合,最终转化为茶褐素。这些转化奠定了普洱熟茶红褐明亮汤色、醇厚滋味与独特陈香风味的物质基础,并与其调节肠道菌群、抗氧化及调节代谢等健康效益密切相关。未来研究需结合多组学技术,深入解析微生物与酚类物质代谢的互作机制,精准鉴定关键活性衍生物的构效关系,以全面阐释普洱熟茶的品质形成与功能特性。

关键词 普洱熟茶;后发酵;酚类物质;微生物代谢;品质形成
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茶叶是以茶树(*Camellia sinensis*)新梢为原料加工而制成的,是全球消费量仅次于水的第二大饮料[1-2]。根据发酵程度的不同,茶叶分为绿茶(不发酵)、白茶(微发酵)、黄茶(轻发酵)、乌龙茶(半发酵)、红茶(全发酵)和黑茶(后发酵)。茶多酚(或称单宁)是茶叶中最主要的次生代谢产物,占干物质总量的18%～36%,主要包括儿茶素类、黄酮与黄酮苷类、酚酸和缩酚酸类、花青素和花白素类等[3](图1)。这些酚类物质不仅影响茶叶的品质特性,还具有预防心血管疾病、肥胖和糖尿病等健康功效[4-5]。

在茶叶加工过程中,多酚类物质的含量与结构发生显著变化,这一变化对塑造不同茶类独特的感官品质具有关键作用。例如,绿茶在杀青阶段通过高温快速抑制酶促氧化,最大限度地保留了较多原始儿茶素,呈现出清汤绿叶的品质特征[6];而红茶在发酵阶段则主要依赖酶促氧化,使儿茶素聚合生成茶黄素、茶红素和茶褐素等色素,共同构成了红汤红叶的品质特征[7]。

根据国家标准GB/T 22111－2008《地理标志产品 普洱茶》,普洱熟茶(ripened Puer tea)是指以云南大叶种茶树[*Camellia sinensis* (Linn.) var. *assamica* (Masters) Kitmaura]的晒青茶为原料,在国家地理标志保护范围内,经后发酵(post-fermentation)等特定工艺加工形成散茶或紧压茶,其品质特征表现为汤色红浓(褐)、滋味醇厚(和)和陈香显著[8-9]。据《云南省茶叶产业发展报告(2024年)》统计数据,2024年云南普洱茶产量达18.5万t,占全省茶叶总产量的33.03%,已成为高原特色农业的支柱产品。现代研究表明,普洱熟茶富含茶褐素、茶多糖及洛伐他汀等活性成分,可通过调节肠道菌群-胆汁酸轴[10]、抗氧化和抗炎等机制,在代谢综合征(如肥胖和2型糖尿病)的营养干预中发挥出多靶点效应[9-13]。

普洱熟茶的独特品质与健康功效源于其特殊的后发酵工艺体系。该工艺是以晒青茶为原料,通过人工渥堆构建微生物发酵环境,在40～60 d的发酵周期中通过多次翻堆完成的固态发酵过程[14](图2)。

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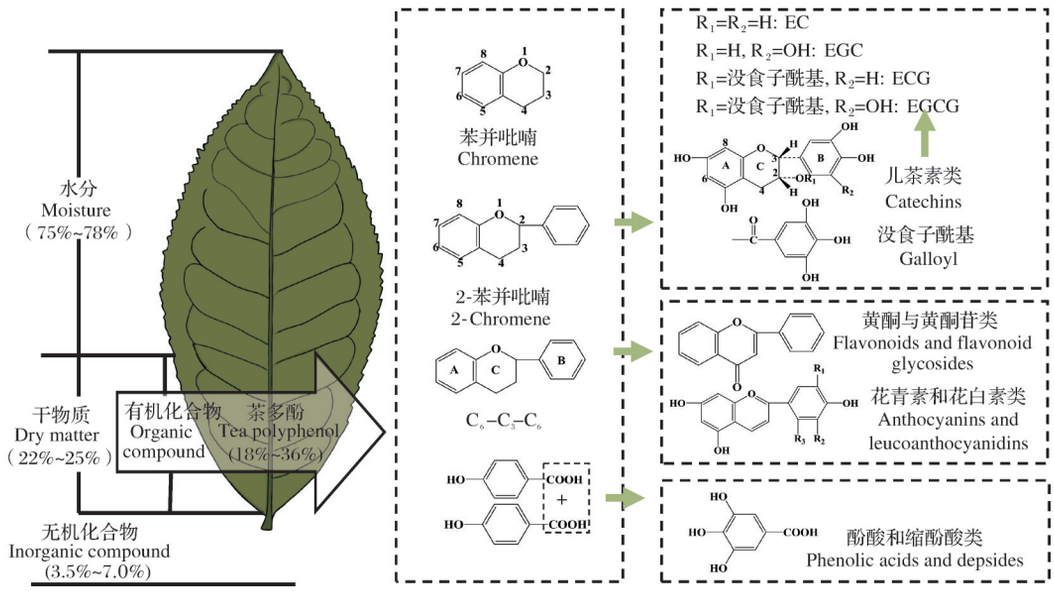

图1 茶叶酚类物质

Fig. 1 Tea polyphenols

后发酵的本质是以晒青茶的内含成分为基质，在微生物胞外酶、呼吸代谢产热及湿热条件的协同作用下，茶多酚发生一系列复杂而剧烈的化学变化，从而形成普洱熟茶特有的色、香、味品质[3]。这一过程涵盖糖基化、羟基化、甲基化、缩合、氧化、降解及结构修饰等多种反应，导致黄酮类化合物、酚酸、嘌呤生物碱、氨基酸和挥发性化合物等发生显著变化，共同塑造其独特品质。因此，深入探究酚类物质在普洱熟茶后发酵过程中的变化，对系统解析其品质形成机制与功能特性具有重要意义。本文重点围绕普洱熟茶发酵过程中儿茶素、黄酮类、酚酸和茶色素等酚类物质的动态变化，综述其降解途径及其产物形成机制，以期为深入解析普洱熟茶的品质形成机制与功能特性提供理论依据。

图2 普洱熟茶加工工艺流程[8]

Fig. 2 Processing technology of ripened Puer tea

1　普洱熟茶后发酵儿茶素类物质的变化

在普洱熟茶的后发酵过程中，儿茶素类物质发生了一系列复杂的代谢转化。作为茶多酚的主要组分，儿茶素约占其总量的60%～80%[15]，可分为非酯型儿茶素[如(＋)-儿茶素(catechin，C)、(－)-表儿茶素(epicatechin，EC)、(－)-表没食子儿茶素(epigallocatechin，EGC)、(＋)-没食子儿茶素(gallocatechin，GC)]和酯型儿茶素[如(－)-儿茶素-3-没食子酸酯(catechin-3-gallate，CG)、(－)-表儿茶素-3-没食子酸酯(epicatechin-3-gallate，ECG)、(－)-没食子儿茶素-3-没食子酸酯(gallocatechin-3-gallate，GCG)、(－)-表没食子儿茶素-3-没食子酸酯(epigallocatechin-3-gallate，EGCG)][15]。在发酵过程中，微生物及其分泌的胞外酶驱动多种生化反应，导致儿茶素类化合物发生降解与结构转化，并生成多种结构新颖、生物活性增强的衍生物。

后发酵显著降低了普洱熟茶中的儿茶素总量。发酵结束后，茶多酚含量(105.8～135.6 mg/g)仅为生茶的一半左右[16-17]。该过程呈现明显的阶段性：发酵初期，微生物分泌的单宁酶(tannase)催化酯型儿茶素(特别是ECG和EGCG)水解，生成非酯型儿茶素(EC、EGC)并释放没食子酸(gallic acid)[18-20]，导致这两类成分含量出现短暂上升；与此同时，儿茶素单体(如C、EC、EGC)和二聚物(如EC-EC和EC-EGC)含量显著降低[8, 21-22]。利用超高效液相色谱-三重四极杆串联质谱(ultra high performance liquid chromatography-triple quadrupole tandem mass spectrometry，UHPLC-QQQ-MS/MS)进行的靶向代谢组学分析进一步证实，儿茶素二聚物在发酵过程中大幅减少，变化趋势与单体一致，且EC-EC二聚物仅在熟茶中被检出[21]。至发酵结束时，非酯型儿茶素、酯型儿茶素及可检出的二聚物含量均显著低于生茶，部分酯型儿茶素(如EGCG、ECG和GCG)在某些样品中甚至无法检出[19]。

在降解的同时，多种胞外酶[包括单宁酶、多酚氧化酶(polyphenol oxidase)、漆酶(laccase)、果胶酶(pectinase)和纤维素酶(cellulase)等]协同催化儿茶素发生羰基化、羧甲基化、异构、酯化、缩合、环化及环裂解等反应，形成结构多样且具有生物活性的新型衍生物，主要包括羧甲基化/羧基化儿茶素(carboxymethylated/carboxylated catechins)，如8-羧甲基-(＋)-儿茶素(图3A)、8-羧甲基-(＋)-儿茶素甲酯(图3A)、6-羧甲基-(＋)-儿茶素(图3A)、8-羧基-(＋)-儿茶素(图3A)、6-羧基-(－)-没食子儿茶素(图3B)、(＋)-儿茶素-8-C-β-D-吡喃葡萄糖苷(图3C)和(－)-表儿茶素-8-C-β-D-吡喃葡萄糖苷(图3D)等[23]。这类物质主要由C、GC等非酯型儿茶素的A环发生裂变、异构、酯化及羧甲基化反应形成。

普洱茶素(puerins)是普洱熟茶中一类特征性衍生物，具有抗氧化、抗炎、延缓细胞衰老及抑制α-葡萄糖苷酶和乙酰胆碱酯酶等生物活性。目前已鉴定出14种，按其核心结构可分为3类：(1)8-C取代黄烷-3-醇类(8-C substituted flavan-3-ols)，如普洱茶素A、B(图3E)，其A环C-7和C-8通过C—C键桥连1个五元内酯环[24]；(2)8-C苯丙烷取代黄烷-3-醇类(8-C phenylpropanoid-substituted flavan-3-ols)，包括源自GC和EGC的普洱茶素C至F(图3F-I)，在A环C-7和C-8位置桥连1个源自苯丙烷单元的六元内酯环[25]；(3)8-C N-乙基-2-吡咯烷酮取代黄烷-3-醇类(8-C N-ethyl-2-pyrrolidinone substituted flavan-3-ols)，包括源自EC和EGC等的普洱茶素Ⅰ至Ⅷ(图3J～Q)，其A环C-8位置的羟基被N-乙基-2-吡咯烷酮基团取代[26]。其中，普洱茶素Ⅰ在发酵后期含量最高可达0.4 mg/g，且普洱茶素Ⅰ和Ⅳ在熟茶中含量显著高于生茶。这些化合物可能源于EC、GC、EGC等非酯型儿茶素A环上的羟基与有机酸、酚酸或茶氨酸中的羧基/氨基发生的亲核反应、缩合及环化反应。

此外，在黑曲霉(*Aspergillus niger*)等优势微生物作用下，非酯型儿茶素的B环发生裂解，形成Teadenol A(图3R)和Teadenol B(图3S)等衍生物[27-28]。普洱熟茶中Teadenol A含量显著提高，可达4.38～8.15 mg/g，较生茶提高10倍以上[27-28]。类似的B环裂解衍生物(如茯砖茶中的茯砖茶素A～F)也存在于其他黑茶(如六堡茶)的后发酵过程中[29]。

2　普洱熟茶后发酵黄酮与黄酮苷类物质的变化

普洱熟茶中的黄酮类物质主要包括黄酮(flavones)、黄烷酮(flavanones)和黄酮醇(flavonols)及其糖苷形式。其中，游离态黄酮醇、黄酮、黄烷酮等含量较低(8.8～9.6 mg/g)，表明黄酮类糖苷主要以糖苷形式存在[18]。黄酮醇苷元以槲皮素(quercetin)、山奈

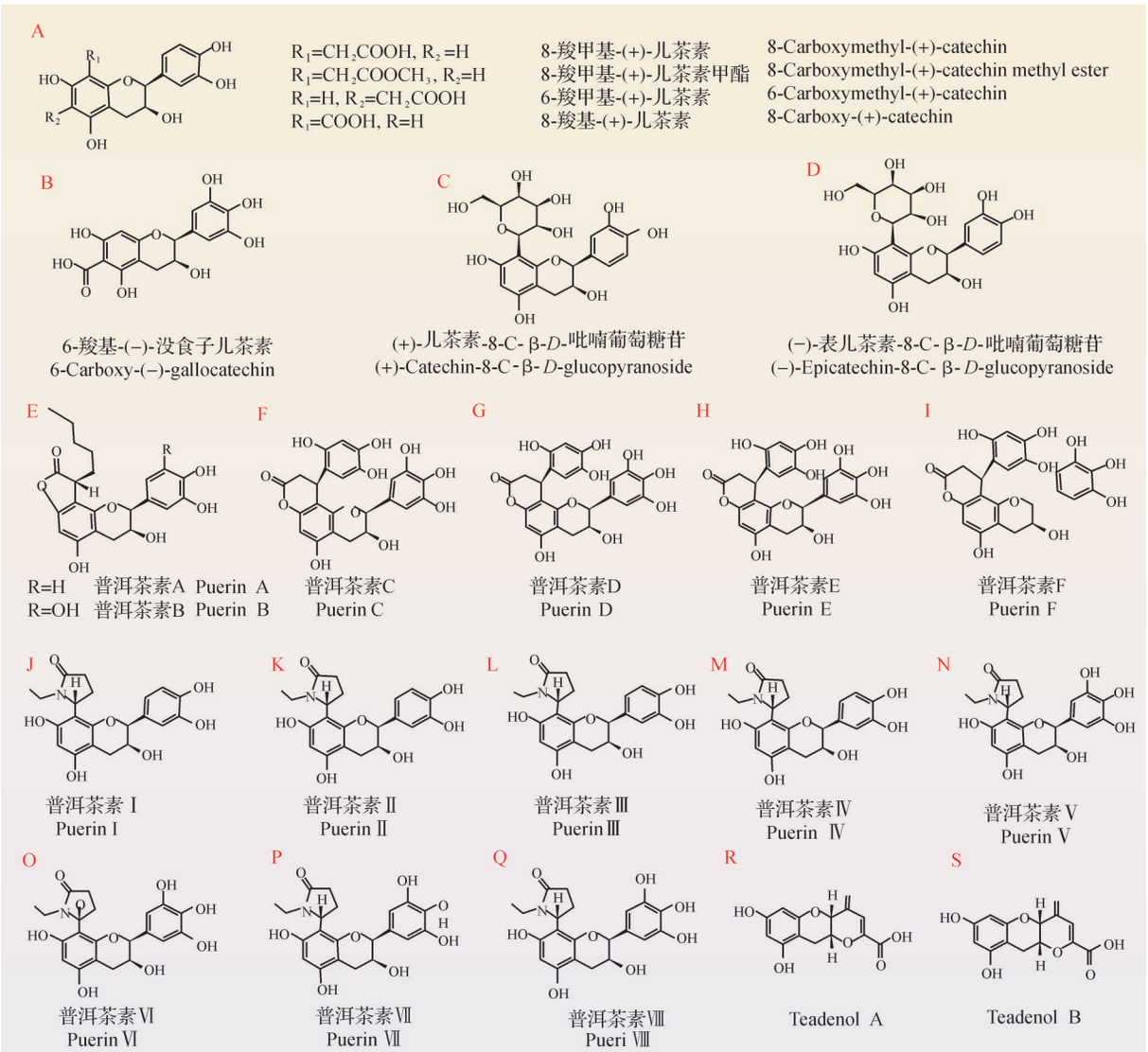

图3 普洱熟茶中已鉴定的儿茶素衍生物[8, 14]

Fig.3 Catechin derivatives identified in ripened Puer tea

酚(kaempferol)和杨梅素(myricetin)为主;而黄烷酮苷元如花旗松素(taxifolin)及黄酮苷元如木犀草素(luteolin)的含量则显著低于普洱生茶[18]。值得注意的是,与儿茶素类(属黄烷醇)在发酵过程中剧烈降解不同,黄酮醇、黄烷酮等黄酮类物质的总量变化相对稳定,整体降幅通常不超过50%[18]。普洱熟茶中较高含量的槲皮素等黄酮醇苷元,可能与潜在的健康益处如延缓记忆力衰退相关[30]。

目前已从普洱熟茶中鉴定出上百种结构多样的黄酮类糖苷,其苷元类型丰富,包括山奈酚、槲皮素、杨梅素、花旗松素、木犀草素、芹菜素(apigenin),以及3′,4′,5-三羟基-7-甲氧基黄酮和3′,4′,7-三羟基-5-甲氧基黄酮等[8,18]。依据糖苷键类型(C-糖苷键或O-糖苷键)及其连接位置,这些糖苷可分为黄酮C-糖苷和黄酮醇O-糖苷两大类。

黄酮C-糖苷的苷元多为芹菜素、柚皮素(naringenin)等,糖基通过稳定的C—C键连接在黄酮骨架的C-6或C-8位。代表性化合物包括夏佛塔苷(schaftoside)、异夏佛塔苷(isoschaftoside)、牡荆素(vitexin)、异牡荆素(isovitexin)、维采宁-2(vicenin-2)以及(2*R*)/(2*S*)-异柚葡糖苷(isohemiphloin)等。这类C-糖苷在后发酵过程中通常表现出较高的稳定性,含量变化较小[8,18]。黄酮醇O-糖苷的苷元包括山奈酚、槲皮素、杨梅素和草质素(herbacetin)等,糖基通过O-糖苷键连接在苷元的C-3-O或C-7-O位。其种类繁多,主要包括:山奈酚衍生物,如紫云英苷(astragalin,即山奈酚-3-O-葡萄糖苷)、山奈酚3-O-洋槐糖苷(biorobin)、山奈酚-3-O-芸香糖苷(nicoti-

florin）；槲皮素衍生物，如芦丁（rutin，即槲皮素-3-O-芸香糖苷）、槲皮素-3-O-β-*D*-吡喃葡萄糖苷、槲皮素-3-O-β-*D*-半乳糖苷、槲皮素-3-O-洋槐糖苷；杨梅素衍生物，如杨梅素-3-O-β-*D*-吡喃葡萄糖苷、杨梅素-3-O-β-*D*-半乳糖苷、杨梅素-3-O-芸香糖苷；以及草质素衍生物，如草质素-7-O-α-鼠李糖苷等[8, 18]。

黑曲霉、溜曲霉（*Aspergillus tamarii*）和烟曲霉（*Aspergillus fumigatus*）等优势菌株分泌的多种酶，如α-葡萄糖苷酶（α-glucosidase）、β-葡萄糖苷酶（*β*-glucosidase）、6-磷酸葡糖酸脱氢酶（6-phosphogluconate dehydrogenase）、α-葡萄糖醛酸酶（α-glucuronidase）等糖苷水解酶，以及黄酮醇3-O-糖基转移酶（flavonol 3-O-glucosyltransferase）、黄酮醇*L*-鼠李糖基转移酶（flavonol *L*-rhamnosyltransferase）、黄酮8-C-糖基转移酶（flavone 8-C-glycosyltransferase）等糖苷转移酶，共同催化黄酮类糖苷的水解过程[20]，促进槲皮素、山柰酚、杨梅素等黄酮醇苷元的释放[31]。后发酵过程中发生的去羟基化、O-甲基化、糖苷化、β-糖苷水解、异构化以及氧化和缩合等反应，显著影响了黄酮类物质的组成与含量[32]，其具体转化机制仍有待深入研究。

3　普洱熟茶后发酵酚酸和缩酚酸类物质的变化

酚酸类物质是普洱熟茶中重要的风味与功能活性成分，其组成与含量在后发酵过程中发生显著变化。基于超高效液相色谱-四极杆飞行时间质谱（ultra high performance liquid chromatography-quadrupole-time-of-flight/mass spectrometry，UHPLC-Q-TOF/MS）技术，目前已从普洱熟茶中鉴定出至少20余种酚酸类物质[20]。这些变化主要源于微生物酶促反应及非酶促热降解对前体物质（如酯型儿茶素和缩酚酸类）的转化。

普洱熟茶与生茶在酚酸组成上存在显著差异。没食子酸和3-没食子酰基奎宁酸（theogallin）分别是熟茶与生茶中最主要的酚酸，其中熟茶的没食子酸含量显著上升，范围在0.25～30.2 mg/g[33]。与生茶相比，熟茶中多种特征酚酸含量较高，包括没食子酸、鞣花酸（ellagic acid）[34]、原儿茶酸（protocatechuic acid）、4-对羟基苯乙酸（4-hydroxyphenylacetic acid）、3-（4-羟基苯基）丙酸[（3-（4-hydroxyphenyl）propionic acid）]、对香豆酸（*p*-coumaric acid）及咖啡酸（caffeic acid）等[33, 35]。而绿原酸（chlorogenic acid）、二羟基苯戊酸（dihydroxyphenyl valeric acid）和羟基苯戊酸（hydroxyphenyl valeric acid）等在生熟茶之间含量相对稳定，无显著差异[35]。值得注意的是，受发酵工艺和检测方法的影响，部分普洱熟茶样品中鞣花酸或咖啡酸的含量可能超过没食子酸，成为最主要的酚酸成分。

普洱熟茶中关键酚酸的形成与转化路径较为明确。没食子酸主要来源包括：（1）黑曲霉等优势菌株分泌的单宁酶特异性催化酯型儿茶素（如EGCG、ECG）的酯键水解，直接释放没食子酸[36]；（2）3-没食子酰基奎宁酸（theogallin）水解也可生成没食子酸。已积累的没食子酸在发酵环境中进一步转化：通过环裂解、还原、脱羧、脱甲基等反应，生成2,5-二羟基苯甲酸（2,5-dihydroxybenzoic acid）、间苯三酚（phloroglucinol）、邻苯三酚（pyrogallic acid）、没食子酸甲酯（methyl gallate）、水杨酸（salicylic acid）、3,4-二羟基苯甲酸（3,4-dihydroxybenzoic acid，即原儿茶酸）及2,3,4-三羟基苯甲酸（2,3,4-trihydroxybenzoic acid）等衍生物[37-38]。在发酵后期，部分衍生物（特别是原儿茶酸）经甲基化与脱羧反应转化为关键香气成分，例如1,2,3-三甲氧基苯（1,2,3-trimethoxybenzene）和1,2,4-三甲氧基苯（1,2,4-trimethoxybenzene），这些物质被认为是普洱熟茶“陈香”风味的重要物质基础[37-38]。鞣花酸则主要来源于非酶促热降解反应：缩酚酸类物质［如木麻黄素（strictinin）］发生热解，同步生成没食子酸与鞣花酸[39]。该过程导致木麻黄素在熟茶中几乎消失，而鞣花酸成为熟茶的特征性成分之一[34, 39]。

4　普洱熟茶后发酵花青素和花白素类物质的变化

花青素和花白素在普洱熟茶中含量较低，约占总多酚的1%。目前已检测出包括锦葵色素（malvidin）、矢车菊色素（pelargonidin）、飞燕草色素（cyanidin）在内的6种花青素。发酵后花青素含量普遍下降[40]，这可能与其对光、热和pH条件敏感的特性有关，也可能源于微生物酶催化的氧化或降解反应。然而，其具体代谢途径、转化产物及对品质的贡献仍有待深入研究。

5　普洱熟茶后发酵茶色素类物质的变化

在普洱熟茶的后发酵过程中，酚类物质发生以

氧化聚合为主导的化学转化。儿茶素类、花色素、原花色素、黄酮醇类以及酚酸等多种酚类物质经氧化聚合形成复杂的水溶性色素，主要包括茶黄素（theaflavins）、茶红素（thearubigins）和茶褐素（theabrownins）[41-42]。后发酵显著改变这3类色素的含量与结构，其中茶褐素作为终产物和特征成分，对普洱熟茶的感官品质与功能属性起主导作用。

在普洱熟茶发酵过程中，茶色素组成发生显著变化。茶黄素含量显著降至3.5 mg/g以下，茶红素含量维持在约10 mg/g，均明显低于普洱生茶及滇红等其他茶类[32]；而茶褐素成为主导成分，含量在122.8～190.7 mg/g（表1），显著高于普洱生茶及其他黑茶［如六堡茶：（99.6±9.1）mg/g；茯砖茶：（69.5±8.7）mg/g］[43]。随着发酵进程，茶褐素含量从原料中的3.23%持续增加至10%以上，而茶黄素和茶红素含量则逐渐降低[44]。值得注意的是，茶褐素的增加量显著大于茶黄素和茶红素的减少量，表明茶褐素的形成不仅源于茶黄素和茶红素的转化，还涉及多糖、蛋白质、生物碱等非色素成分的络合与聚合[45-46]。

茶褐素的形成机制复杂，其本质是儿茶素、茶黄素、茶红素等酚类物质在微生物及其分泌酶催化下，经氧化聚合并与茶多糖、蛋白质、氨基酸、生物碱等络合形成的高分子质量（4～100 ku以上）褐色复合物[47]，该过程涉及酶促与非酶促反应的协同作用。酶促氧化聚合作为主导途径，其核心在于多酚氧化酶、过氧化物酶、漆酶等胞外酶催化酚类底物（如EGCG）生成醌类中间体，进而驱动氧化缩合与聚合反应[45, 48]。从微生物来源看，曲霉属真菌［黑曲霉（*Aspergillus tubingensis*）、塔宾曲霉、琉球曲霉（*Aspergillus luchuensis*）、烟曲霉］是产多酚氧化酶和过氧化物酶的关键菌株[49-55]，埃默森罗萨氏菌（*Rasamsonia emersonii*）、分枝横梗霉（*Lichtheimia ramosa*）和汉逊德巴利酵母（*Debaryomyces hansenii*）等则通过同时产过氧化物酶和漆酶参与转化[56]，而酵母菌［如产朊假丝酵母（*Candida utilis*）］贡献较弱[57]。

茶色素形成路径可能依次为：（1）多酚氧化酶（如漆酶、酪氨酸酶、儿茶酚氧化酶[58-59]）催化酚类氧化为活性醌；（2）醌类经氧化聚合形成茶黄素和茶红素[58, 60]；（3）茶黄素、茶红素及其他酚类（如没食子酸、槲皮素及其糖苷等）在酶的持续作用下，与多糖、蛋白质、生物碱等通过氧化、聚合、耦合反应形成大分子茶褐素[41, 58, 61-62]。这一过程可被葡萄糖、没食子酸、邻苯二酚等物质促进和诱导[63]（图4）。然而，其具体反应机制与茶褐素结构有待深入研究。

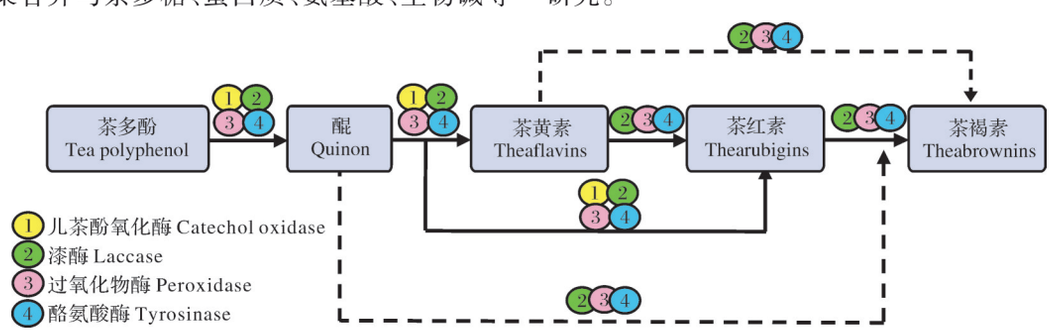

图4 茶色素的形成途径推导[51]

Fig. 4 The derivative formation pathway of tea pigment[51]

表1 普洱生茶和普洱熟茶中的酚类物质及其含量

Table 1 Phenolic compounds and their contents in raw and ripened Puer teas mg/g

酚类物质类别 Types of phenolic compounds	酚类物质名称 Name of phenolic compounds	普洱生茶 Raw Puer tea	普洱熟茶 Ripened Puer tea
茶多酚 Tea polyphenols[16-17]	茶多酚 Tea polyphenols	215.6～278.6	105.8～135.6
儿茶素 Catechins[9, 16-17, 22]	（+）-儿茶素（+）-Catechin	6.46～11.66	0.19～1.70
	（−）-表儿茶素（−）-Epicatechin	16.09～18.45	1.02～6.42
	（−）-表没食子儿茶素（−）-Epigallocatechin	14.86～28.26	0.40～0.44
	（+）-没食子儿茶素（+）-Gallocatechin	31.07	6.90
	（−）-儿茶素-3-没食子酸酯（−）-Catechin-3-gallate	0.57	0.20
	（−）-没食子儿茶素-3-没食子酸酯（−）-Gallocatechin-3-gallate	38.64	17.02
	（−）-表儿茶素-3-没食子酸酯（−）-Epicatechin-3-gallate	37.81～39.94	0.24～0.48

续表 1 **Continued Table** 1

酚类物质类别 Types of phenolic compounds	酚类物质名称 Name of phenolic compounds	普洱生茶 Raw Puer tea	普洱熟茶 Ripened Puer tea
儿茶素 Catechins[9, 16-17, 22]	(－)-表没食子儿茶素-3-没食子酸酯 (－)-Epigallocatechin-3-gallate	46.02～47.51	0.08～0.09
儿茶素二聚物 Catechin dimer[22]	1型 EC-EC	0.032～0.035	ND
	2型EC-EC	0.10～0.11	0.025～0.035
	3型EC-EC	0.41～0.43	0.05～0.06
	1型EC-EGC	0.036～0.042	ND
	2型EC-EGC	0.08～0.087	ND
	1型EC-ECG	0.45～0.50	ND
	2型EC-ECG	0.22～0.25	ND
普洱茶素等儿茶素衍生物 Puerin and other catechin derivative[22]	普洱茶素Ⅰ Puerin Ⅰ	0.12～0.15	0.25～0.40
	普洱茶素Ⅱ Puerin Ⅱ	0.07～0.08	0.07～0.08
	普洱茶素Ⅲ Puerin Ⅲ	0.07～0.08	0.07～0.08
	普洱茶素Ⅳ Puerin Ⅳ	0.07～0.08	0.18～0.24
	普洱茶素Ⅴ Puerin Ⅴ	0.08～0.11	0.09～0.12
	普洱茶素Ⅵ Puerin Ⅵ	0.06～0.08	0.06～0.08
	普洱茶素Ⅶ Puerin Ⅶ	0.06～0.065	0.06～0.065
	普洱茶素Ⅷ Puerin Ⅷ	0.07～0.08	0.07～0.08
	Teadenol A	0.25～1.28	4.38～8.15
酚酸 Phenolic acids [16-17, 22,39]	没食子酸 Gallic acid	1.1～6.01	0.25～30.2
	鞣花酸 Ellagic acid	0.51～17.01	0.11～21.36
	咖啡酸 Caffeic acid	63.04～91.75	66.54～84.91
	绿原酸 Chlorogenic acid	2.72～3.94	0.00; 3.08～3.96
	3-没食子酰基奎宁酸 3-Galloylquinic acid	0.4～8.5	ND
	木麻黄素 Casuarictin	2.0～7.5	ND
黄酮、黄烷酮、黄酮醇等黄酮类 Flavones, flavanones, flavonols and other flavonoids [16-17, 22]	槲皮素 Quercetin	0.57～5.34	0.03～2.72
	杨梅素 Myricetin	0.22～0.51	0.01～0.31
	山奈酚 Kaempferol	0.02～2.22	0.01～0.73
	木犀草素 Luteolin	0.02～0.10	0.01～0.03
	花旗松素 Taxifolin	0.83～3.99	0.11～0.38
黄酮类糖苷 Flavonoid glycosides [21, 64]	杨梅素 3-O-半乳糖苷 Myricetin 3-O-galactoside	6.50～7.10	0.50～0.60
	山奈酚-3-O-芸香糖苷 Kaempferol-3-O-rutinoside	2.20～2.35	0.25～0.30
	夏佛塔苷 Schaftoside	0.67～0.73	0.50～0.55
	芦丁 Rutin	7.06～8.07、1.51、6.60	0.32～1.02、1.13
	异夏佛塔苷 Isoschaftoside	0.008～0.011	0.007～0.008
	山奈酚-葡萄糖-鼠李糖-葡萄糖 Kaempferol-glucose-rhamnose-glucose	0.076～0.087	ND
	1型山奈酚-葡萄糖 Kaempferol-glucoside (Type 1)	0.14～0.15	ND
	2型山奈酚-葡萄糖 Kaempferol-glucoside (Type 2)	0.83～0.92	0.14～0.16
	杨梅素-葡萄糖 Myricetin-glucoside	0.54～0.58	ND
	杨梅素-鼠李糖-葡萄糖 Myricetin-rhamnose-glucose	0.18～0.23	0.03～0.04
	槲皮素-葡萄糖 Quercetin-glucoside	2.7～3.0	0.2～0.3
	槲皮素-葡萄糖-鼠李糖 Quercetin-glucose-rhamnose	0.17～0.18	0.22～0.24
	槲皮素-葡萄糖-鼠李糖-葡萄糖 Quercetin-glucose-rhamnose-glucose	0.006～0.007	0.002～0.002
茶色素 Tea pigment[16-17]	茶黄素 Theaflavins	5.9～7.1	3.0～3.5
	茶红素 Thearubigins	20.1～53.3	5.8～6.1
	茶褐素 Theabrownins	21.3～41.4	122.8～190.7

注 Note：ND：未检出 Not detected.

6 结论与展望

普洱熟茶的后发酵是一个由微生物及其胞外酶驱动的复杂生化过程，其核心是酚类物质的深度转化。本文综述了该过程中酚类物质的变化：儿茶素类经水解、氧化及缩合等反应发生显著降解，生成茶褐素、没食子酸以及普洱茶素、羧基化儿茶素和Teadenols等一系列结构新颖、生物活性增强的特征性衍生物；黄酮类物质总量相对稳定，但其糖苷发生水解，导致游离苷元含量增加；酚酸组成发生显著改变，没食子酸和鞣花酸显著积累，并进一步转化为贡献“陈香”风味的关键挥发性成分；茶色素组成发生显著转变，茶褐素通过酶促氧化聚合及与非酚类物质络合作用成为核心成分。同时，本文还总结归纳了普洱生茶与熟茶中酚类物质的含量差异（表1）。这些酚类物质的定向转化与协同作用，共同构成了普洱熟茶“红浓、醇厚和陈香”的品质特征，并奠定了其多靶点健康功能的物质基础。

尽管普洱熟茶发酵中酚类物质研究已取得显著进展，未来研究仍需关注以下方向：(1)综合利用代谢组学、蛋白组学与宏基因组等多组学技术，精准解析酚类物质转化途径、关键功能微生物菌株（如黑曲霉、塔宾曲霉）及其特异性胞外酶（如单宁酶、漆酶等）的贡献机制；(2)深入鉴定普洱茶素、Teadenols等新型活性衍生物的精确结构、形成机制、绝对含量及其与感官品质和健康功能的量效与构效关系；(3)阐明茶褐素复杂大分子的结构、组成特性、空间构象及功能属性；(4)探究工艺参数对酚类物质代谢路径的调控规律，实现基于目标风味与功能的精准发酵调控；(5)开展黑茶类比较研究，揭示不同黑茶后发酵中酚类代谢的共性与个性规律。这些研究将深化对普洱熟茶品质形成机制的认知，为提升产品质量标准化水平和开发高附加值产品提供科学依据。

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Progress on changes in phenolic compounds during post-fermentation of ripened Puer tea

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Abstract　The unique quality and health benefits of ripened Puer tea stem from its microbial post -fermentation process. Phenolic compounds undergo significant transformation during this process to form the material basis for their flavor and functional characteristics. This article reviews the changes in phenolic compounds including catechins degraded by microbial extracellular enzymes and converted into gallic acid，theaflavins，and novel biologically active derivatives such as Puer catechins，carboxymethylated catechins，and Teadenol A through the oxidation，polymerization，cleavage，and other reactions during the fermentation process of ripened Puer tea to study the changes in phenolic compounds during the fermentation process of ripened Puer tea and analyze the mechanism of quality formation. The total amount of flavonoids remains stable，and the hydrolysis of glycoside in flavonoids releases quercetin and other aglycones. The composition of phenolic acids changes significantly，with an increase in the content of gallic acid and tannic acid further being metabolized into aroma-contributing compounds like methoxybenzenes. Furthermore，theaflavins and thearubigins formed during fermentation are subsequently converted into theabrownins via enzymatic polymerization and complexation with non-phenolic components such as polysaccharides and proteins. These transformations underpin the characteristic reddish-brown infusion color，mellow taste，and distinctively aged flavor of ripened Puer tea and are closely associated with its health benefits including the regulation of gut microbiota，antioxidant activity，and metabolic modulation. Studies in the future should integrate multi-omics to deeply analyze the interactions between microorganisms and phenolic metabolism，accurately identify the structure-activity relationships of key bioactive derivatives to comprehensively elucidate the quality formation and functional characteristics of ripened Puer tea.

Keywords　ripened Puer tea；post-fermentation；phenolic compounds；microbial metabolism；quality formation

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