doi: 10.12301/spxb202300264 文章编号: 2095-6002(2023)03-0028-13
引用格式: 陶永胜,李娜. 葡萄酒中香气物质研究进展[J]. 食品科学技术学报,2023,41(3):28-40.
TAO Yongsheng, LI Na. Research progress on aroma compounds in wine[J]. Journal of Food Science and Technology, 2023,41(3):28-40.

葡萄酒中香气物质研究进展

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摘 要: 香气是葡萄酒感官评价的重要指标,也是影响葡萄酒质量风格和消费者导向的重要因素。各种风格特色的葡萄酒中具有的香气成分复杂多样,葡萄品种、发酵工艺、陈酿条件等因素均会影响其最终香气。保持品种典型性、提高发酵香气并改善陈酿风味一直是葡萄酒风味研究追求的目标,因此,全面分析葡萄酒中香气物质的形成途径和呈香机制至关重要。从发酵调控角度重点论述了品种和发酵香气成分的生成规律及酿造工艺对葡萄酒香气物质生成的调控机制,深入介绍相关风味酶和香气前体物质同香气物质的关系;探讨陈酿香气的生成路径并总结不同橡木制品和陈酿技术对葡萄酒陈酿香气特征的影响机理;简要阐述了香气物质的检测技术和香气物质间感知协同作用的研究方法,分析关键香气物质相互作用及基质效应对葡萄酒风味感知的影响。最后对未来研究方向和趋势提出展望,以期为建立以风味导向为基础的葡萄酒工艺调控手段提供理论依据和技术支持。

关键词: 葡萄酒; 香气物质; 分析技术; 协同呈香; 基质效应
中图分类号: TS201.2 **文献标志码:** A

葡萄酒香气释放引起的嗅觉、味觉与三叉神经感觉,是驱动消费者对葡萄酒选择和接受的关键因素,其中嗅觉在风味识别和情绪唤起中起到重要作用[1]。葡萄酒的香气物质主要由源于葡萄果皮的品种香气物质[2],酵母在发酵过程中代谢与积累的发酵香气[3],橡木成分转移形成的陈酿香气物质[4]组成。为了应对葡萄果实品质的差异,冷浸渍[5]、添加外源风味酶[6]、混菌发酵[7]、优选橡木陈酿[8]等工艺可以有效调控葡萄酒中的香气物质达到增香酿造的效果。对挥发性香气物质进行精准定性定量分析并综合其香气活性值和香气稀释因子,找到对葡萄酒整体香气有贡献的关键香气物质,对葡萄酒风味的研究意义重大[9]。

葡萄酒中各种挥发性香气化合物经由嗅觉神经系统传导到大脑嗅觉皮层进而触发对气味的识别[10],形成葡萄酒馥郁优雅的风味特征感知。但不同葡萄酒独特的香气轮廓并非不同香气化合物之间的简单加和,而是基于嗅觉系统不同阶段可能发生的各种定性和定量感知相互作用的结果[11]。气味物质之间以及嗅觉受体感受器上来自不同受体信号的相互作用使气味混合物产生了协同、加成、掩盖等效应[12]。此外,葡萄酒基质成分也对香气化合物的表现有显著的影响[13]。

本研究系统阐述了葡萄酒中主要香气物质的代

收稿日期: 2023-05-04
基金项目: 陕西省科技创新团队项目(2023-CX-TD-59);陕西省杰出青年科学基金项目(2020JC-22);国家自然科学基金面上项目(31972199)。
Foundation: Shaanxi Science and Technology Innovation Team Project(2023-CX-TD-59); Shaanxi Science Fund for Distinguished Young Scholars (2020JC-22); National Natural Science Foundation of China(31972199).
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谢与生成途径，介绍风味酶和前体物质对葡萄酒香气的贡献，探讨发酵菌种、调控因子和橡木制品对葡萄酒香气物质形成的影响，分析香气的感知互作机制及非挥发性成分的基质效应，展望未来葡萄酒香气的研究热点，希望可为葡萄酒风味研究提供理论和技术指导。

1　葡萄酒中香气物质来源

葡萄酒香气物质根据来源不同可分为品种香气物质[2]、发酵香气物质[3]和陈酿香气物质[4]三类，葡萄酒总体香气物质轮廓的大部分是由发酵香气物质组成。挥发性香气化合物在葡萄酒发酵和陈酿过程中的变化极其复杂，分析其代谢与生成规律并进行精准调控对于改善葡萄酒风味有重要意义。

1.1　品种香气物质

品种香气源于葡萄果实中以香气糖苷形式存在的风味前体物质（图 1），由于存在共轭糖分子结构，糖苷类物质只有被酸解或酶解后释放出挥发性香气物质才能被嗅觉感知[14]，糖苷水解的过程中还会发生分子重排、氧化、还原和降解反应[15]。考虑到结合态香气糖苷在葡萄浆果中的含量是游离态香气物质的 2 ~ 8 倍，糖苷物质的水解程度与葡萄酒品种香气质量的提升与否密切相关[16]。

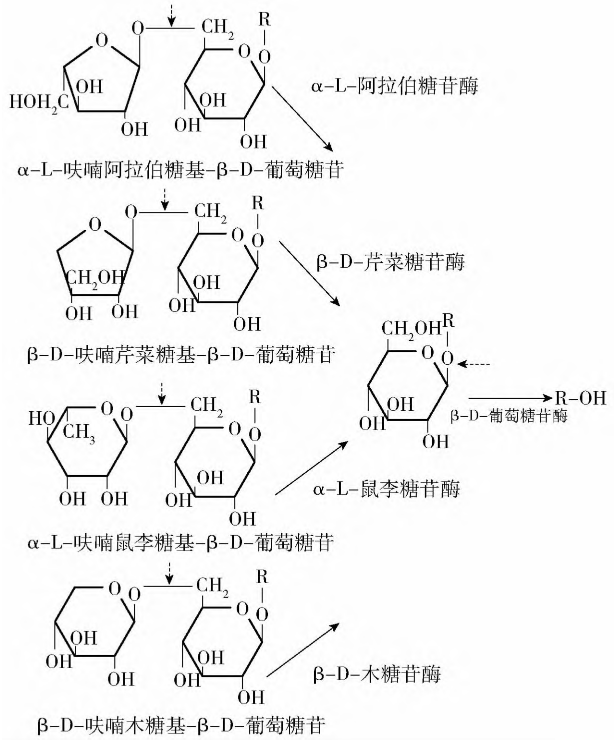


图 1　双糖苷类香气前体物质的酶解方式

Fig. 1　Enzymatic hydrolysis of disaccharidic aroma precursors

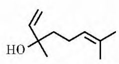
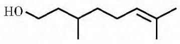
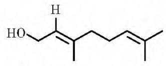
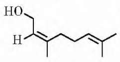
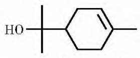
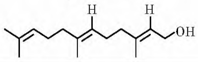
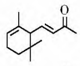
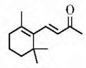
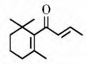
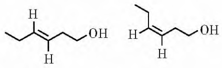
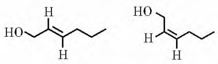
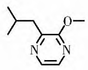
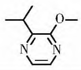
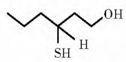
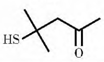
葡萄酒酿造过程中，90% 的糖苷类物质被酵母菌产生的糖苷酶水解，品种香气物质在葡萄酒中有较低的感官阈值，是花香、果香等特征的主要来源[8]。因此，提高发酵醪中香气糖苷的含量并促进糖苷物质的水解是提高品种香气的有效途径，如发酵前冷浸渍和发酵中添加外源糖苷酶[5,16]。研究表明，非酿酒酵母（*non-Saccharomyces*，NS）可以产生活性更高的糖苷酶[17]，提取 NS 胞外糖苷酶参与发酵或将 NS 与酿酒酵母（*Saccharomyces cerevisiae*，SC）混合发酵可有效改善葡萄酒品种香气[18]。混菌发酵过程中糖苷酶活性与发酵体系内酵母的生物量呈正相关[2]，高拮抗性能 SC 可以通过细胞互作显著提高 NS 糖苷酶活性[19]。同理，部分乳杆菌（如 *Lactobacillus plantarum*，*Lactobacillus brevis*）也可以产生高活性的糖苷酶[20]，参与混菌发酵能够诱导品种香气物质产生。

萜烯类是葡萄酒品种香气物质中占比最大的一类挥发性物质，葡萄中的结合态单萜类糖苷经酸解或酶解产生游离态单萜醇[14]。单萜类的里哪醇、香叶醇、橙花醇等是重要的香气活性化合物，在葡萄酒中呈现出花香、果香和柑橘类香气[21]。萜烯类物质在发酵以及陈酿过程中均会自发进行分子重排，改变葡萄酒的香气特征[16]。发酵过程中里哪醇通过脱氢反应转化为香茅醇，或在酶的作用下和乙酰乙酸乙酯发生酯化反应生成香叶基丙酮，香叶基丙酮仍可进一步转化为橙花醇[21]。陈酿过程中里哪醇、橙花醇和香叶醇在酸作用下脱氢环化为萜品油烯，橙花醇和香叶醇还能异构化为里哪醇[22]。此外，当 pH 值和温度相对稳定时，萜烯的重排更容易发生且产物更丰富，其含量随着陈酿逐渐稳定[23]。

品种香气物质还包括 C_{13}-去甲类异戊二烯、C_6 化合物、甲氧基吡嗪、硫醇等。其中，C_{13}-去甲类异戊二烯是类胡萝卜素发生水解后在酸性条件下分子重排形成的[24]，是葡萄酒花香的重要贡献者。C_6 化合物在酒精发酵期间由多种酶解反应生成[25]，赋予葡萄酒青草、草药等生青气味。甲氧基吡嗪是由氨基酸代谢产生的含氮杂环物质，其较低的阈值赋予葡萄酒浓郁的青椒、芦笋，甚至泥土味[8]。由半胱氨酸和谷胱甘肽转化生成的硫醇类化合物通常与葡萄酒感官缺陷有关[26]。葡萄酒中典型品种香气化合物见表 1。

表 1 葡萄酒中典型品种香气化合物

Tab. 1 Typical varietal aroma compounds in wine

序号	化合物	结构式	阈值*/(μg·L^{-1})	感官描述
	萜烯类			
1	里哪醇		15	柑橘味、薰衣草味、玫瑰味
2	香茅醇		100	柠檬味、柑橘味
3	香叶醇		30	玫瑰味、花香
4	橙花醇		15	柑橘味、柠檬味、玫瑰味
5	α-萜品醇		250	花香、丁香花味
6	法尼醇		1 000	花香
	C_{13}-去甲类异戊二烯类			
7	α-紫罗兰酮		0.09	甜果味
8	β-紫罗兰酮		0.09	紫罗兰味
9	β-大马酮		0.05	花香、蜂蜜味、甜香味
	C_6化合物类			
10	1-己醇		8 000	青草味、生青味
11	(*Z*/*E*)-3-己烯-1-醇		400	青草味、生青味
12	(*Z*/*E*)-2-己烯-1-醇		4	青草味、生青味
	甲氧基吡嗪类			
13	2-甲氧基-3-异丁基吡嗪		0.005	青椒味、芦笋味、泥土味
14	2-异丙基-3-甲氧基吡嗪		0.002	青椒味、豌豆味、泥土味
	硫醇类			
15	3-巯基己醇		0.06	蔬菜味、西番莲味
16	4-巯基-4-甲基戊酮		0.000 8	黄杨木味、百香果味、草莓味

* 阈值参考文献[8]和[27]。

1.2 发酵香气物质

发酵香气物质是由酵母菌在酒精发酵过程中产生的挥发性副产物，是构成葡萄酒香气的重要方面(图 2)[3]。重要的发酵香气物质有酯类、高级醇、脂肪酸、苯乙基类化合物等，尤其是酯类物质，它们甚至是某些酒的呈香主体。葡萄酒中酯类物质具有典型的花香和果香特征[28]，根据结构中醇和酸类物质的不同，酯类可分为乙酸酯与脂肪酸乙酯两种，其中乙酸酯和 C_4 ~ C_{10} 脂肪酸乙酯对果香贡献度更大[29]，被称为果香酯。此外，基于酯类与其他香气物质的协同作用，即使在低于阈值时也会对葡萄酒香气产生显著影响[30]，尤其是化学结构相似的酯类物质在数量和质量上都参与调节葡萄酒果香特征[12]。不同酯类间的协同呈香还使得多种酯类混合后比单一酯类的香气强度更高，阈值附近酯类浓度的微小变化会影响葡萄酒香气[31]。

酒精发酵过程中，酯类在酵母细胞内由酰基转移酶或酯合成酶催化生成，其净累积量取决于酵母

中合成酯类的酶和酯酶之间的平衡[32]。酯类的生成还与其前体物高级醇、脂肪酸的浓度线性相关，高级醇是乙酸酯生成的限制性前体，在发酵体系补充中链脂肪酸可显著提高脂肪酸乙酯产量[33]。目前常采用添加外源酶或 NS 参与发酵来促进酯类生成，实现葡萄酒的增香酿造[27]。外源酶处理主要是从促进酵母代谢的角度进行调控[6,34]，较高的酯酶活性还可提高中链脂肪酸的水平[18]。当酵母生长达到稳定期时酯酶活性通常达到最大值，可以在发酵旺盛的香气物质半生成期对酯类进行调控[35]。高产风味酶的 NS 参与混合发酵也能改善发酵体系中的酯酶活性，如发酵毕赤酵母(*Pichia fermentans*)参与发酵可提高酯酶和酯合成酶的累积活性并影响酯类生成[7]。但其调控效果受接种策略影响，如胶红酵母(*Rhodotorula mucilaginosa*)参与的发酵中酯类含量与 NS 接种比例正相关[36]。此外，NS 对苹果酸-乳酸发酵(malo-lactic fermentation，MLF)中乳酸菌的生长和活性有促进作用，进而改善特定香气属性。利用酿酒酵母、发酵毕赤酵母、酒类酒球菌(*Oenococcus oeni*)顺序接种发酵梅尔诺葡萄酒，诱导了葡萄酒中高水平的 3-甲基乙酸丁酯、己酸乙酯和辛酸乙酯等脂肪酸乙酯，乳酸菌的代谢主要提高了支链酯类的浓度[37]。

发酵时添加外源可同化氮也可提高中链脂肪酸乙酯和乙酸酯含量，尤其是在补充氮素营养前确定葡萄汁的营养状况并由此调整氨基酸的组成。精准氮调控促进酯类合成的机制与酵母碳代谢流分配的变化有关，补氮显著提高了高级醇和脂肪酸水平[38]。研究发现，混菌发酵中酵母细胞间的接触可以增加谷氨酸的消耗以及组氨酸、甘氨酸、脯氨酸等与细胞生长有关氨基酸的生物合成，进而提高酯类产量[19]。氧化还原电位也是影响酵母中链脂肪酸乙酯代谢水平的重要因素，对其调控能够显著改变酵母碳通量分布和酯相关基因的表达[39]。

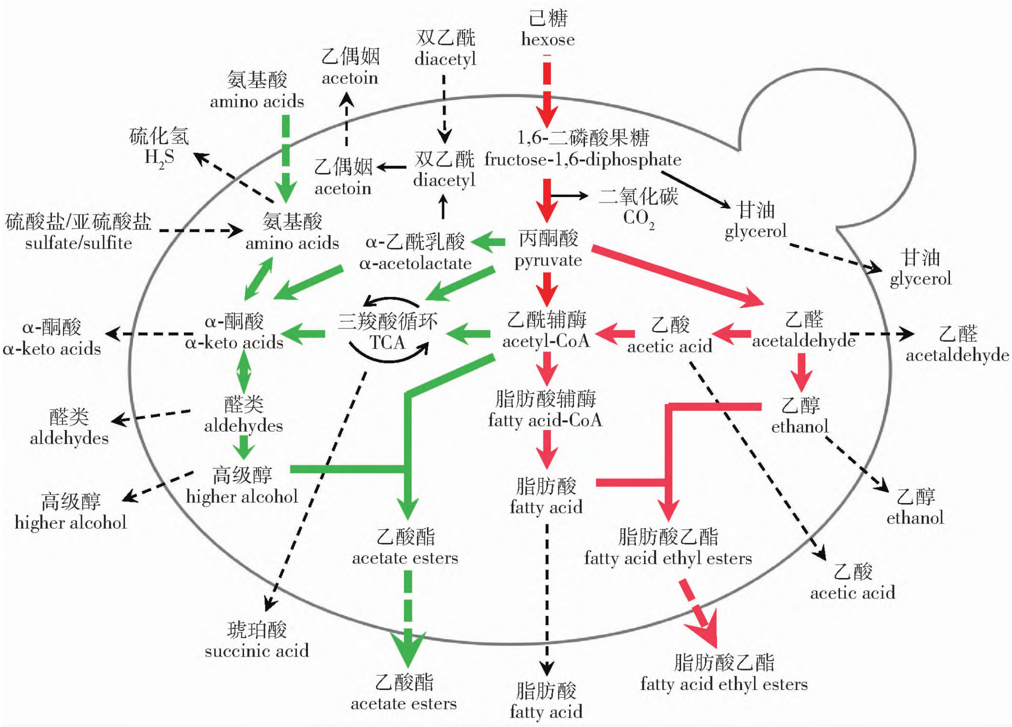


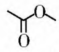
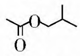
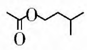
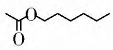
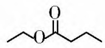
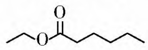
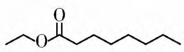
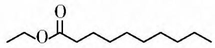
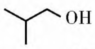
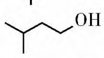
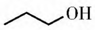
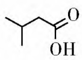
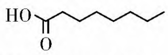
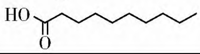
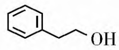
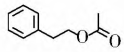
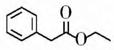
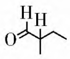
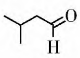
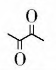
图 2　酵母细胞内香气化合物和相关代谢产物的合成途径

Fig. 2　Synthesis pathway of aroma compounds and related metabolites in yeast cells

高级醇是酒精发酵过程中产生的含量最多的一类挥发性物质，是由糖酵解或氨基酸在生物合成及分解代谢中的中间产物 α-酮酸脱羧还原而成[40]，只有质量浓度低于 300 mg/L 的高级醇才会增加葡萄酒的复杂性[3]。发酵过程中，促进酯类形成的条件也会利于对应脂肪酸的形成，但只有适量的脂肪酸物质才能赋予葡萄酒奶酪般香气[7]。苯乙基类化合物赋予葡萄酒果香和浓郁玫瑰花香，尤其是苯乙乙酯、乙酸苯乙酯等苯乙基酯类物质[2]。浓度合适的支链醛类化合物可以提高葡萄酒干果香气[41]，丁二酮、辛酮和壬酮等酮类化合物也对增加葡萄酒果香有积极作用[42]。葡萄酒中典型发酵香气化合物见表 2。

表 2 葡萄酒中典型发酵香气化合物

Tab. 2 Typical fermentative aroma compounds in wine

序号	化合物	分子式	阈值*/(μg·L⁻¹)	感官描述
	乙酸酯类			
1	乙酸乙酯		7 500	果香、酯香
2	乙酸异丁酯		1 600	草莓味、果香、花香
3	乙酸异戊酯		30	香蕉味、果香
4	乙酸己酯		670	果香、梨味
	脂肪酸乙酯类			
5	丁酸乙酯		20	草莓味、苹果味
6	己酸乙酯		14	青苹果味、果香
7	辛酸乙酯		5	苹果味、花香、啤酒味
8	癸酸乙酯		200	果香、玫瑰味、脂肪味
	高级醇类			
9	异丁醇		40 000	酒精味、杂醇味
10	异戊醇		30 000	苦杏仁味、涩味
11	1-丙醇		50 000	酒精的清香
	脂肪酸类			
12	异戊酸		700	酸败味
13	辛酸		500	奶酪味、酸败味、冰淇淋味
14	癸酸		1 000	脂肪味、奶酪味、异味
	苯乙基类			
15	β-苯乙醇		14 000	玫瑰味、蔷薇味
16	乙酸苯乙酯		250	花香
17	苯乙酸乙酯		73	玫瑰味、花香
	醛酮类			
18	2-甲基丁醛		16	咖啡味、可可味、干果味
19	异戊醛		4.6	苹果味、桃味
20	2,3-丁二酮		100 000	甜香、奶香

* 阈值参考文献[27]。

1.3 陈酿香气物质

在陈酿过程中葡萄酒发生氧化、还原、酯化作用等化学反应，使酯类、醇类、醛类和酸类等达到新的平衡[4]，而葡萄酒与橡木桶中的化合物相互作用，或创新的陈酿技术（橡木制品或微氧化技术），产生了陈酿香气[8]。陈酿过程中橡木成分转移到葡萄酒中，其中感官阈值较低的香草醛以及丁子香酚等挥发性酚对葡萄酒的感官品质起主要作用[43]。酚醛和挥发性酚类物质来自木质素的热降解，赋予葡萄酒烟熏、香草和咖啡的香气[44]。呋喃类物质来自多糖的热降解，提供烤杏仁、坚果、焦糖等香气，并能增强内酯类的香气[45]。橡木内酯由橡木中的酸脱水产生，具有椰子和木头的气味[46]。此外，橡木还能释放出部分其他香气物质，如β-大马酮、丁酸和

苯乙醇等[47]。

橡木是葡萄酒陈酿最常用的桶材，橡木桶或橡木制品中挥发性香气物质转移到葡萄酒的过程取决于橡木品种、产地、加工方式(烘烤方法和强度)，橡木和葡萄酒的接触时间，以及橡木使用次数等[48]。目前最广泛使用的橡木品种是美洲的白橡(*Quercus alba*)、法国的无柄橡(*Q. petraea*)和有柄橡(*Q. robur*)，白橡木桶中陈酿的葡萄酒橡木内酯含量较高[8]，与白橡木片接触的葡萄酒显示出更多的香草醛、糠醛和挥发性酚[49]。加工方式中，自然干燥和高烘烤水平的橡木赋予葡萄酒更高浓度的陈酿香气物质[50-51]。来自橡木的香气物质浓度还随着陈酿时间的推移而增加，但陈酿时间过长时呋喃醛和酚醛会被还原成相应的醇[52]。此外，香气物质的数量和提取率随桶体的使用逐年减少，并产生“马厩”等异味[48]。

除了橡木的特性外，葡萄品种和葡萄酒成分也影响陈酿香气[52]，高酒精度和酸度有利于木质素的醇解，从而释放出更多的香草醛和愈创木酚，但内酯类物质的浓度与酒精度、酸度呈负相关[48]。此外，酒糟的存在也会改变陈酿香气特征，几乎全部陈酿香气物质会与酒糟结合进而降低其在葡萄酒中的浓度[53]。因此，酒糟的存在减弱了橡木品质对葡萄酒陈酿香气的影响[54]。此外，葡萄酒在成熟过程中会发生氧化作用，从橡木中萃取的香气物质含量与葡萄酒耗氧量密切相关，香气物质与氧气间的互作还受到橡木类型、陈酿条件的影响[55]。根据物理化学性质和供氧能力选择橡木制品类型和相应处理，是葡萄酒获得特征性陈酿香气的决定性因素[8]。葡萄酒中典型木桶陈酿香气化合物见表3。

2　葡萄酒中香气物质分析检测方法

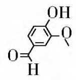
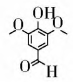
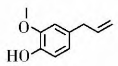
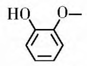
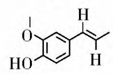
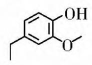
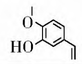
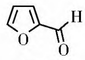
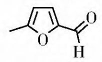
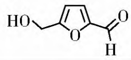
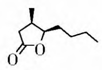
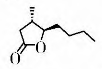
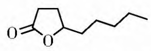
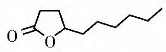
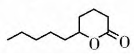
葡萄酒中众多的香气物质，其浓度从mg级到ng级不等，对葡萄酒香气物质分析的前提是对其精确地定性与定量。葡萄酒前处理包括液液萃取、顶空萃取、搅拌棒萃取、固相微萃取以及溶剂辅助风味蒸发萃取等方法[3]。这些方法各有优缺点，如液液萃取操作简单、重复性好，但试剂用量大、耗时长；顶空萃取所需样品量少、分析速度快，但灵敏度较低[56]。虽然目前顶空固相微萃取凭借其快捷和无须溶剂萃取的优势较多地应用于葡萄酒香气物质分析中，但溶剂辅助风味蒸发萃取作为一种相对温和的挥发性成分提取方式，其提取的香气物质更接近真实样品[57]。

气相色谱分析香气成分是葡萄酒鉴定、分类、品质控制的主要手段，气相色谱可通过偶联多种检测器对各类挥发性物质进行精确分析。氢离子火焰检测器可以检测葡萄酒中大部分香气物质，但难以对微量或痕量成分精准分析，而质谱检测器的低检测限可提高分析精确度且不依赖标准品定性[58]。对于含硫的硫醇类化合物和含氮的吡嗪类化合物，则采用专门的脉冲火焰光度检测器和氮磷检测器测定[59]。在此基础上，二维气相色谱质谱、离子迁移质谱、时间飞行质谱等灵敏度更高的仪器正在成为有效分离葡萄酒香气混合物的强大工具[13]。此外，色谱结合模拟人体感觉器官的“电子鼻”在葡萄酒快速分类和整体香气鉴别上具有重要作用[60]。色谱分离得到香气化合物后需使用标准品进行定性定量，未知化合物的保留时间、保留指数、质谱信息以及香气特征等须与标准品完全一致[59]。香气物质的定量方法包括外标法、内标法与稳定同位素稀释法等，后者是消除基质效应影响最有效的方法[61]。

葡萄酒中气味化合物对整体香气具有不同的贡献[9]，其中关键香气物质为葡萄酒提供独特的香气特征，且其浓度的变化显著影响香气特征强度[62]。通常把香气活性值(odor activity values，OAVs)大于等于1的香气物质作为对整体香气有贡献的成分，挥发性物质的香气稀释因子(flavor dilution，FD)越大，其气味贡献也越大[63]。但在葡萄酒等复杂体系中，浓度高于阈值也并非判断关键香气物质的充要条件[5,64]。因此，葡萄酒风味研究中加入了香气重组、缺失实验形成分子感官科学，通过重现特征性香气轮廓，检验筛选结果来验证关键香气物质的准确性[56]。分子感官科学的主体是气相色谱-嗅闻仪分析(gas chromatography-olfactometry，GC-O)，色谱将香气物质分离的同时品评人员进行嗅闻，进而识别贡献度较大的香气成分[63]。GC-O可结合强度、频率、稀释等进行关键香气物质筛选，如Charm分析、香气萃取稀释分析、香气萃取浓缩分析、Osme技术等[59]。分子感官科学已经验证了果香酯类物质也是形成户太8号桃红葡萄酒典型香气特征的关键香气物质[64]，β-大马酮和酯类物质对我国威代尔冰酒香气的显著贡献[65]，β-大马酮还和丁香酚、愈创木酚等挥发性酚类物质一起显著影响马瑟兰葡萄酒香气轮廓[66]。

表 3　葡萄酒中典型木桶陈酿香气化合物

Tab. 3　Typical aging aroma compounds from oak barrel in wine

序号	化合物	分子式	阈值*/(μg·L⁻¹)	感官描述
	酚醛类			
1	香草醛		320	香草味
2	丁香醛		50 000	香料味、烟熏味
	挥发性酚类			
3	丁子香酚		6	丁香味、蜂蜜味、香料味
4	愈创木酚		33	甜香、烟熏味
5	异丁子香酚		6	花香味、丁香花味、木香
6	4-乙基愈创木酚		47	烟熏味、皮革味
7	4-乙烯基愈创木酚		40	丁香花味
	呋喃类			
8	糠醛		20 000	杏仁味
9	5-甲基糠醛		45 000	烤杏仁味
10	5-羟甲基糠醛		100 000	杏仁味
	内酯类			
11	*cis*-橡木内酯		74	木头味、椰子味、香草味
12	*trans*-橡木内酯		320	木头味、椰子味、香料味
13	γ-壬内酯		30	桃味
14	γ-癸内酯		88	桃味、内酯味
15	δ-癸内酯		386	桃味、可可味

* 阈值参考文献[8]。

3　葡萄酒中香气物质呈香机制

人类对气味的感知依赖于嗅觉神经系统对气味分子的捕捉、检测及识别[10]，而香气感知是人对香气化合物的化学刺激、生理反应以及心理作用的总和[67]。气味分子与嗅觉受体结合的同时嗅觉刺激转化为电信号，从嗅球开始逐次传递到嗅觉皮层，最终激活嗅觉神经元并触发嗅觉的感知[68]。嗅觉系统可根据生理需求或动机事件对空间中有效稀疏性的气味进行元素编码、合成编码，或者两者兼有[62]。

3.1　香气感知互作

混合气味分子的感知是基于嗅觉系统不同阶段可能发生的各种定性定量感知相互作用的结果[11]。由于嗅觉系统本身对化学信号的编码识别及大脑对这些信号的处理的特性，会产生协同、加成、掩盖等感知相互作用，使得这些挥发性气味分子的混合物以非线性方式被感知[69]。气味成分间的相互作用研究，可分为微观和宏观两个层面。微观层面气味感知相互作用的神经生理学方法以细胞测量和神经成像技术为主。细胞测量技术可探究混合香气在动物外围嗅觉神经系统水平上的相互作用[70]，包括嗅觉受体神经元的电生理记录、嗅觉电图的响应分析、

光学成像、钙成像等技术。神经成像技术则探索大脑水平的气味分子间的相互作用[71]，包括正电子发射断层扫描、功能磁共振成像和脑电图记录。研究发现嗅觉神经系统外围混合物的相互作用水平取决于各气味的比例，气味浓度比可以驱动其结构与元素感知[72]。

宏观层面气味感知互作的研究方法有阈值法、S 型曲线法、OAV 法、σ−τ 图法等，这些方法通过香气成分组合前后阈值、OAV、强度值等的变化，判定成分间的协同水平[62]。阈值法和 S 型曲线法发现 2-甲基丁醛和 3-甲基丁醛、乙酸异丁酯和乙酸异戊酯等结构、香气相似的成分具有协同或加成作用，而结构或香气差异明显的成分具有掩盖作用[12,73]。尤其是当组分的香气特征差异显著时，不良气味物质对整体香气会产生强烈抑制[74]。OAV 法表明混合物中香气成分的个数越多则相互作用偏向于加成或掩盖[10]。σ−τ 图法还考虑了化合物浓度与强度的影响，不同浓度水平高级醇的协同水平具有显著的差异，中等浓度呈现协同作用，高浓度表现掩盖作用，且混合物中各组分香气强度相近时也呈现协同作用[73]。但果香酯类物质间的相互作用水平受浓度影响较小，主要由物质结构和香气特征决定[74]。此外，Olfactoscan 技术可以将气味分子与背景香气进行结合分析香气分子间的感知相互作用[62]。宏观层面气味协同研究通常与感官分析相结合，传统的描述分析与区别检验方法多被用于气味感知变化的研究[75]。图 3 是香气混合物感知示意[62]。

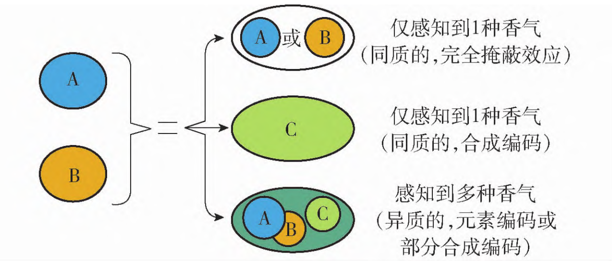


图 3　香气混合物感知示意

Fig. 3　Schematic of aroma mixture perception

3.2　基质效应

葡萄酒中香气物质的释放和感知不仅取决于所涉及的挥发性化合物，还取决于非挥发性物质的基质效应。多酚类物质在葡萄酒香气物质挥发和鼻后感知中发挥着重要作用[76]，研究表明酚酸显著抑制游离萜烯类物质的挥发，影响葡萄酒的香气感知。由于萜烯中的羟基、酚酸中的羧基和羟基有利于氢键的形成，萜烯与酚酸之间的骨架堆积有利于分散性相互作用[77]。因此，酚酸通过氢键和色散力等分子间的非共价相互作用与萜烯及其糖苷自发结合，影响糖苷和萜烯的存在形式，进而调控葡萄酒香气特征，酚酸与萜烯及其糖苷的非共价相互作用见图 4[78]。此外，酚酸对乙酸乙酯等酯类的挥发也有抑制作用，该作用是由疏水效应驱动的自发放热反应，受酚酸浓度和结构的影响[79]。橡木内酯与表儿茶素的部分质子共振信号发生低频场移也会降低其顶空浓度，挥发性酚的苯环则与酚类的没食子酰基环通过 π−π 堆积相互作用，降低挥发性[80]。此外，考虑到葡萄酒陈酿阶段，由于高疏水性和热力学不稳定性，酯类物质会逐渐水解为高级醇和脂肪酸等前体物质，导致果香特征丢失[81]。多糖与香气物质间存在氢键或疏水作用等分子互作关系，对稳定陈酿中葡萄酒的酯类物质和保护葡萄酒风味典型性有一定的作用[82]。此外，混菌发酵，尤其是高拮抗酵母参与的混菌发酵也可以提高发酵体系中的多糖水平[83]。单宁、蛋白质等大分子物质，因其对小分子香气成分的吸附作用，也会延缓一些香气成分的水解损失[76]。

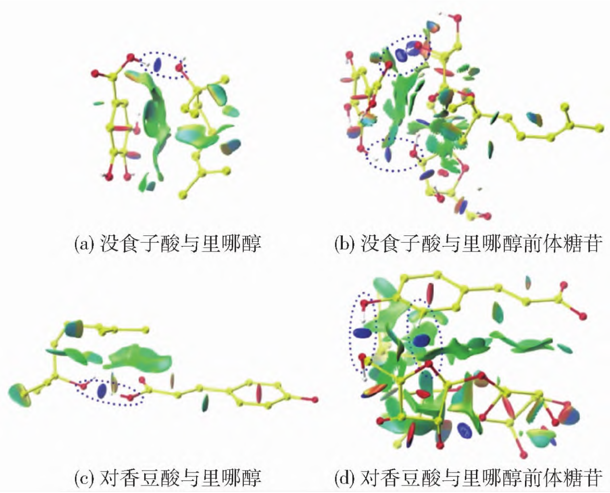


图 4　酚酸与萜烯及其糖苷的非共价相互作用

Fig. 4　Non-covalent interactions of phenolic acids with terpenes and terpene glycosides

4　总结及展望

从葡萄酒典型香气物质、香气物质检测方法、香气感知互作机理和基质效应等方面进行阐述，重点介绍了葡萄酒增香的方法与机理。但嗅觉与

香气是一个集生理学、心理学、物理学、化学等多学科为一体的复杂问题，香气物质的嗅觉形成理论还需进一步揭示。一方面，在研究香气成分的互作机制时，目前仅在理想体系下以简单混合物为研究对象阐述可能的作用，没有考虑到基质成分对香气释放的影响。另一方面，随着量子化学、分子动力学模拟等技术的发展使得深入探究香气物质与多元基质间分子层面的互作机制成为可能。此外，葡萄酒陈酿阶段的香气保护、鼻后香气及其感知相互作用、味觉与香气特征的相互作用也是未来葡萄酒风味研究的重点。

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Research Progress on Aroma Compounds in Wine

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Abstract: Aroma is an important indicator of wine sensory evaluation and also an important factor for affecting the quality style and consumer orientation of wine. Aroma compounds in wines with various styles are complex and diverse, which are affected by grape varieties, fermentation technologies, aging conditions and other factors. Maintaining varietal typicality, enhancing fermentative odorants and improving aging flavor quality of wine have always been the goals of wine flavor research, making it crucial to comprehensively analyze the formation pathway and aroma presentation mechanisms of odorants in wine. In this review, the formation patterns of varietal odorants and fermentative odorants and the regulatory mechanisms of winemaking processes on the production of wine odorants were discussed from the perspective of fermentation regulation, and the relationships between related flavor enzymes and aroma precursors with aroma compounds were introduced. Meanwhile, the forming path of aging aroma were discussed, and the influencing mechanism of different oak products and aging technologies on shaping wine aging aroma characteristics was summarized. Additionally, the detection technologies of odorants and the research methods of the synergy effect between odorants were briefly described, the effects of key odorants interaction and matrix effect on wine flavor perception were analyzed. Finally, future research directions and trends were proposed, with a view to provide theoretical basis and technical support for the establishment of flavor-oriented wine technology control methods.

Keywords: wine; aroma compounds; analysis technique; aroma synergy; matrix effects

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