

6个特早熟与早熟荔枝种质果实挥发性化合物的鉴定及香气特征分析

蒋依辉, 向旭, 钟云, 朱慧莉, 刘伟, 肖志丹

(广东省农业科学院果树研究所·农业农村部亚热带果树生物技术与遗传资源利用重点实验室·广东省热带亚热带果树研究重点实验室, 广州 510640)

摘要:【目的】探究特早熟与早熟荔枝果实挥发性成分特征及差异,为荔枝栽培、育种、加工等提供参考依据。【方法】基于顶空固相微萃取(HS-SPEM)与气相色谱质谱(GC-MS)联用技术,系统地分析了6个特早熟与早熟荔枝种质成熟果实的挥发性化合物,并运用多元统计方法比较了这两类种质挥发性组分的差异。【结果】共鉴定出103种挥发性组分,10种为共有的化合物,34种为各种质的特有化合物,以单萜类、醇类、醛酮类、酯类及倍半萜为主要成分,其中特早熟种质的挥发性物质种类以醇类、醛酮类及酯类为主,早熟种质挥发性物质则以萜类(单萜及倍半萜)及醇类为主。运用OPLS-DA方法获得上述特早熟-早熟组间的差异代谢物39个,其中下调的化合物包括异戊醇、正辛醇、异戊醛、反-2-辛烯醛、乙酸乙酯、3-甲基-3-丁烯醇乙酸酯、乙酸苄酯、戊酸苄酯、苯甲酸异戊酯、 α -萜荜油烯、 α -古巴烯、异戊酸、十四烷,上调的化合物包括 α -蒎烯、月桂烯、 α -松油烯、邻伞花烃、(+)-柠檬烯、罗勒烯、(E)-B-罗勒烯、 γ -萜品烯、萜品油烯、别罗勒烯、对-薄荷-1,5,8-三烯、芳樟醇、 β -香茅醇甲醚、对伞花烃-8-醇、蒎烯-10-醇、 α -松油醇、橙花醇甲醚、香茅醇、异香叶醇、 β -柠檬醛、香叶醇、乙酸香叶酯、(E)- β -金合欢烯、1,3-环己二烯、 α -姜黄烯、 α -姜烯,这些差异代谢产物结合各种质特有的化合物可作为区分上述特早熟-早熟种质的特征性挥发性化合物。结合香气活度值(OAV)筛选出对6个特早熟和早熟荔枝种质香气具有贡献的化合物35种,以香叶醇的OAV值最高;发现1-辛烯-3-醇、乙醛、正己醛、壬醛、左旋玫瑰醚、香叶醇、青叶醛为6个特早熟、早熟荔枝种质所共有的香气化合物,其中左旋玫瑰醚、异戊醇、乙酸乙酯、壬醛及1-辛烯-3-醇是特早熟种质三月红、香蜜早和大新荔共有的特征香气成分,而月桂烯、香叶醇、壬醛、邻伞花烃及1-辛烯-3-醇是早熟种质水东、妃子笑、白糖罂共有的特征香气成分。通过香气特征分析发现特早熟种质香型以果香为主,花香、青植香为辅,早熟种质香型以花香为主,果香、青植香为辅。【结论】综上所述,特早熟及早熟荔枝种质挥发性代谢物具有丰富的多样性,不同熟性及不同种质荔枝果实间的挥发性成分及香气成分存在显著差异,挥发性化合物可作为鉴定不同荔枝种质的指标之一。

关键词:荔枝;特早熟;早熟;挥发性物质;香气特征

中图分类号:S667.1

文献标志码:A

文章编号:1009-9980(2023)09-1915-17

Identification of volatile compounds and analysis of aroma characteristics in litchi fruits of 6 special-early maturing and early maturing germplasms

JIANG Nonghui, XIANG Xu, ZHONG Yun, ZHU Huili, LIU Wei, XIAO Zhidan

(Institute of Fruit Tree Research, Guangdong Academy of Agricultural Sciences/Key Laboratory of South Subtropical Fruit Biology and Genetic Resource Utilization, Ministry of Agriculture Rural Affairs/Guangdong Province Key Laboratory of Tropical and Subtropical Fruit Tree Research, Guangzhou 510640, Guangdong, China)

Abstract: 【Objective】Litchi germplasm resources are very important for litchi breeding, scientific research, and production. Compared with mid and late maturing germplasms, special-early maturing and early maturing litchi germplasm have smaller proportion of planting area and as smaller less number of

收稿日期:2023-04-07 接受日期:2023-05-29

基金项目:荔枝产业技术体系创新团队建设项目(2023KJ107);广东省基础与应用基础研究基金项目(2020A1515010356);广东省农村科技特派员驻镇帮镇扶村项目(KTP20210307);广州市农村科技特派员项目(20212100044)

作者简介:蒋依辉,女,副研究员,研究方向:果树栽培育种与功能成分评价研究。Tel:18620630848,E-mail:jiangnonghui2002@163.com

varieties due to their sour and astringent taste. However, due to the early maturity trait, they still have a significant place in the market. Volatile substances affect the flavor quality of fruits. Terpenes are extremely important volatile substances, among them monoterpenes and sesquiterpene have special smell and widely exist in plants. The volatile components are important sources of litchi flavor and resistance. However, there have been a few reports on special-early maturing, early maturing germplasm and wild germplasm of litchi. The purpose of this experiment was to explore the characteristics and differences of volatile components in the fruits of special-early maturing and early maturing litchi, and to provide a reference basis for litchi cultivation, breeding, and processing. **【Methods】** 6 accessions of litchi germplasm were selected and divided into special-early maturing group and early maturing group, namely Xiangmizao, Sanyuehong and Daxinli were in the special-early maturing group, and Feizixiao, Shuidong and Baitangyin in the early maturing group. The volatile compounds in mature fruits were systematically analyzed using headspace solid-phase microextraction (HS-SPEM) combined with gas chromatography-mass spectrometry (GC-MS). Principal component analysis (PCA) and orthogonal partial least squares discriminant analysis (OPLS-DA) were used to predict the stability and reliability of the model. The multivariate statistical analysis was used to screen differential metabolites; Hierarchical clustering analysis was used to analyze the metabolites of each group, and the difference of volatile components between the special-early maturing and early maturing germplasm was compared. **【Results】** A total of 103 volatile components were identified, of them the monoterpenes, alcohols, aldehyde ketones and sesquiterpene were the main components. The alcohols, aldehyde ketones and lipids were the main volatile components of the special-early germplasm, while the terpenoids (monoterpenes and sesquiterpene) and alcohols were the main volatile components of the early germplasm; Feizixiao and Shuidong had the highest cumulative content of volatile compounds, while Baitangyin, Sanyuehong, Xiangmizao, and Daxinli had lower content. It was discovered that 10 volatile components were common compounds (ethanol, 1-octen-3-ol, acetaldehyde, hexanal, ethanol, 1-octen-3-ol, acetaldehyde, hexanal, trans-2-Hexen, 1-nonanal, linalool, citronellol, geraniol, (-)-rose oxide) for all the germplasms and 34 compounds were unique compounds to each of the germplasms. Using the OPLS-DA method, 39 differential metabolites were obtained between the special-early maturing group and the early maturing group, among them the downregulated compounds included 3-Methyl-1-butanol, 1-Octanol, Isovaleraldehyde, (E)-2-Octenal, Ethyl Acetate, 3-methylbut-3-enyl acetate, Benzyl acetate, Benzyl valerate, Isoamyl benzoate, α -Cubebene, α -Copaene, Isovaleric acid, Tetradecane, the upregulated compounds included α -Pinene, Myrcene, α -Terpinene, o-Cymene, (+)-Dipentene, Ocimene, β -trans-Ocimene, γ -Terpinen, Terpinolene, Allocimene B, *p*-Mentha-1, 5, 8-triene, Linalool, β -Citronellol methyl ether, 2-(4-Methylphenyl) propan-2-ol, Pinane-10-ol, α -Terpineol, Nerol methyl ether, Citronellol, iso-Geraniol, β -Citral, Geraniol, Geranyl acetate, (E)-beta-Farnesene, ar-Curcumen, α -curcumen, α -Zingiberene. These differential metabolites combined with specific compounds of different germplasms could be employed as characteristic volatile compounds to distinguish the special-early maturing and early maturing germplasm. Based on the aroma activity value (OAV), 35 compounds contributing to the aroma of 6 litchi germplasm were screened, including 5 alcohols, 9 aldehydes, 3 lipids, 6 monoterpenes, 10 monoterpene oxides, and 2 sulfides. The main compounds were monoterpenes and aldehydes with geraniol having the highest OAV value; 18 key aroma components also obtained: geraniol, dimethyl trisulfide, myrcene, 3-methyl-1-butanol, iso-Geraniol, 1-octen-3-ol, (-)-rose oxide, ethyl acetate, hexanal, 1-hexanol, citronellol, 1-nonanal, isovaleraldehyde, o-cymene, acetaldehyde, phenethyl alcohol, dimethyl disulfide, and linalool, but there were significant differences among different germplasms. 1-octen-3-ol,

acetaldehyde, hexanal, 1-Nonanal, (-)-rose oxide, iso-Geraniol and trans-2-hexen were the common aroma compounds in the 6 lychee germplasms, while (-)-rose oxid, 3-Methyl-1-butanol, ethyl acetate, 1-nonanal, and 1-octen-3-ol were key aroma components common in the 3 special-early maturing lychee germplasms, and myrcene, geraniol, 1-nonanal, o-cymene and 1-octen-3-ol were key aroma components common in the 3 early maturing lychee germplasms. Through analysis of aroma characteristics, it was found that six litchi germplasms mainly contained 10 aroma types: floral, fruity, green plant, citrus, woody, and green fruit. In addition, some germplasms also had a small amount of vanilla, cream, nut, and sulfur-containing vegetable flavors; The aroma of the special-early maturing germplasm was mainly fruity, supplemented by floral and green plant aromas. The aroma of the early maturing germplasms was mainly floral type, supplemented by fruity and green plant aromas. 【Conclusion】 In summary, the volatile metabolites of the special-early maturing and early maturing litchi germplasms had rich diversity. There were significant differences in the volatile and aroma components in litchi fruits with different maturity, and volatile compounds could be used as indicators for identifying different litchi germplasms.

Key words: Litchi; Special-early maturing; Early maturing; Volatile compounds; Aroma characteristics

荔枝(*Litchi chinensis* Sonn.)属典型的亚热带常绿果树,果色鲜艳、香味浓郁,富含挥发性物质。中国是荔枝原产地,栽培历史可追溯到2300多年前,目前产量和面积均居世界之首,且种质资源极为丰富^[1];荔枝种质资源是进行荔枝育种、科研和生产的重要物质基础。相对于中晚熟种质而言,特早熟及早熟荔枝种质由于口感偏酸涩而种植面积占比偏小,品种数量也较少,但因成熟期早(特早熟种质一般在4月下旬到5月中旬,早熟种质一般在5月中旬至6月上旬),能够抢占市场先机,早熟、特早熟种质仍拥有相当重要的市场地位^[2]。妃子笑、水东和白糖罌是早熟栽培种的典型代表,三月红、香蜜早是特早熟栽培种的典型代表。香蜜早与三月红成熟期接近,食用品质优于三月红,但一直以来未被发掘利用。

在植物生长发育过程中,挥发性物质扮演着极为重要的角色,因具有挥发性和芳香味而赋予植物特殊的香气,影响果实香味品质;同时在传粉、植物防御、调节植物生长发育等方面产生重要影响^[3-4],对植物进化有着重要的意义。随着我国果树产业迅猛发展,消费者更加关注果品风味品质。萜类化合物是极为重要的挥发性物质,其中的单萜类和倍半萜类物质多有特殊气味,广泛存在于植物体内,是天然来源的挥发性化合物。研究者已就荔枝品种^[5]、不同组织部位中的果皮^[6]、果核与内膜^[7]、叶片和果肉^[8-10]进行了挥发性物质组成分析,发现荔枝富含萜烯类挥发性代谢物,具有较高的营养价值,但研究材料多集中于中晚熟品种,迄今对荔枝不同种质特别

是早熟、特早熟及野生荔枝果实中挥发性物质种类、含量及构成尚缺乏系统的比较研究。故开展特早熟、早熟荔枝果实香气品质的研究,有利于更全面地了解荔枝种质果实特点并促进香气品质的开发。

笔者在本研究中采用顶空固相微萃取(HS-SPEM)、气相色谱质谱(GC-MS)联用技术,对6种早熟、特早熟荔枝种质的成熟果肉的挥发性物质进行比较分析与鉴定,以期为荔枝种质辅助鉴定、育种、栽培及生产加工提供依据。

1 材料和方法

1.1 材料

供试验材料的6个荔枝种质分别为特早熟的香蜜早、三月红和大新荔,早熟的妃子笑、水东和白糖罌。每个种质选3株,从每株树冠边缘的东、南、西、北方向各选取20个成熟(成熟度为八九成)的无损伤且大小相近的果实。样品收集后即刻运到实验室进行分析测定。表1为采集的荔枝种质样品信息。

1.2 主要仪器与试剂

7890B/7697A 气相色谱-质谱(GC-MS)联用仪(Agilent公司,USA),固相微萃取手动进样器、50/30 μm DVB/CAR/PDMS 固相纤维萃取头(Supelco公司,USA),ME204分析天平(METTLER公司,瑞士)。正构烷烃混标(C₇-C₃₀),上海Sigma-Aldrich公司。

1.3 方法

样品制备:游离挥发性化合物的提取和测定参照王志群等^[11]的方法并加以改动。每个样品分别取

表 1 荔枝种质样品信息

Table 1 Sample information of collected litchi germplasms

名称 Name	简称 Abbreviation	采收时间 Harvesting time	成熟性 Maturity	采收地点 Harvesting location
三月红 Sanyuehong	SYH	2021-04-28	特早熟 Special-early maturing	广州天河 Tianhe, Guangzhou
香蜜早 Xiangmizao	XMZ	2021-04-27	特早熟 Special-early maturing	茂名电白 Dianbai, Maoming
大新荔 Daxinli	DXL	2021-05-12	特早熟 Special-early maturing	广西大新 Daxin, Guangxi
水东 Shuidong	SD	2021-05-25	早熟 Early maturing	广州天河 Tianhe, Guangzhou
妃子笑 Feizixiao	FZX	2021-05-28	早熟 Early maturing	广州天河 Tianhe, Guangzhou
白糖罂 Baitangying	BTY	2021-06-02	早熟 Early maturing	广州天河 Tianhe, Guangzhou

大小均匀的 20 个果实,去皮后称取果肉 50 g,匀浆后取 2 g 左右果肉浆液置于 15 mL 顶空微萃取瓶,加入内标物 5 μL (正戊醇,质量浓度为 162.2 $\text{mg}\cdot\text{L}^{-1}$),饱和 NaCl 溶液 2 mL,密封后平衡 15 min。固相微萃取 (SPME): 将装有 50/30 μm DVB/CAR/PDMS 萃取头(实验前老化 5 min)的 SPME 手持器透过瓶盖的橡皮塞插入顶空微萃取瓶,于液面上空吸附 40 min,萃取温度 60 $^{\circ}\text{C}$ 。萃取完成后迅速将萃取头放入 GC-MS 前端进样口,推出萃取头进行热脱附 3 min,同时启动仪器采集数据。

GC 条件:采用 HP-5MS 毛细管色谱柱(30.00 $\text{m}\times 0.25\text{ mm}$, 0.25 μm),载气为高纯氦气(纯度 > 99.999%),进样口温度 250 $^{\circ}\text{C}$,柱流速 0.8 $\text{mL}\cdot\text{min}^{-1}$,不分流进样。程序升温:初始温度 50 $^{\circ}\text{C}$ 保持 1 min,以 3 $^{\circ}\text{C}\cdot\text{min}^{-1}$ 升至 120 $^{\circ}\text{C}$,保持 1 min,再以 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ 升至 190 $^{\circ}\text{C}$,保持 1 min,最后以 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ 升至 260 $^{\circ}\text{C}$,保持 1 min。MS 条件:电子电离源,离子源温度 230 $^{\circ}\text{C}$,电子能量 70 eV,四极杆温度 150 $^{\circ}\text{C}$,扫描质量范围(m/z)35~400。

1.4 数据处理

定性和半定量分析:根据 GC-MS 分析得到总离子流色谱图,采用 NIST 17 数据库检索(匹配度 $\geq 80\%$)结合保留指数(RI),分别对各峰所代表的挥发性物质的化学结构和名称加以确认。化合物含量概括内标法计算,含量(w)($\mu\text{g}\cdot\text{kg}^{-1}$)=(单峰面积/内标峰面积) \times 内标物含量。每样品 3 次重复。将正构烷烃 C_7 - C_{30} 在同样的顶空和气相色谱质谱条件下进样,根据 C_7 - C_{30} 正构烷烃混标物的保留时间,计算未知化合物的保留指数(RI)。

1.4.1 香气强度(odor-activity values, OAVs)与香气类型 OAV 是挥发性组分的浓度与其香气阈值的比值^[12],香气类型与挥发性成分类型划分参照 Zhang 等^[13]的方法。

1.4.2 多元统计分析方法 采用主成分分析(principal component analysis, PCA)、正交偏最小二乘判别分析(orthogonal partial least squares discriminant analysis, OPLS-DA)预测模型的稳定性和可靠性^[14]。采用多元统计分析(VIP 值)、一维统计分析(p 值)和差异倍数(FC 值)等方法进行差异代谢物筛选,以 $\text{VIP} > 1$ 、 $p < 0.05$ 、 $\log_2\text{FC} \geq 2$ 或 $\log_2\text{FC} \leq 0.5$ 的代谢物作为差异代谢物;采用层次聚类法对各组代谢产物进行聚类分析。

结果采用(平均值 \pm 标准差)表示,在 MetaboAnalyst、迈维云网络平台进行 PCA、聚类分析和 OPLS-DA 多元统计分析和绘图,采用 IBM SPSS Statistics 25 进行显著性差异分析(Duncan 检验)。

2 结果与分析

2.1 挥发性物质的定性、定量分析

通过对挥发性成分的总离子流图(图 1-A)的分析以及各峰经谱库检索定性与归类,共检测到 103 种化合物,各化合物的保留指数、香气阈值^[15]以及在不同种质中的含量等信息见表 2。以单萜类数量最多,达 40 种,包含 13 种单萜烯和 27 种单萜氧化物,占检出总数的 38.8%;其次是倍半萜类,为 21 种,占检出总数的 20.4%;醇类、醛酮类和酯类分别为 12 种、13 种和 10 种,分别占检出总数的 11.65%、12.62%及 9.70%;其他化合物检测出数较少,如硫化物 4 种、酸类 1 种、烷烃 2 种(图 1-B)。

从不同类型挥发物总含量(图 1-C)可知,单萜类化合物总含量最高,为 20.54 $\text{mg}\cdot\text{kg}^{-1}$,占总挥发物含量的 48.74%;其中单萜氧化物达 40.43%、单萜烯为 8.3%;其次是醇类,含量为 12.09 $\text{mg}\cdot\text{kg}^{-1}$,占总挥发物含量的 28.70%;然后是醛类,含量为 5.68 $\text{mg}\cdot\text{kg}^{-1}$,占总挥发物含量的 13.48%;另外,倍半萜的数量较多,不过含量仅占 2.05%。可见单萜类、醇类、醛酮

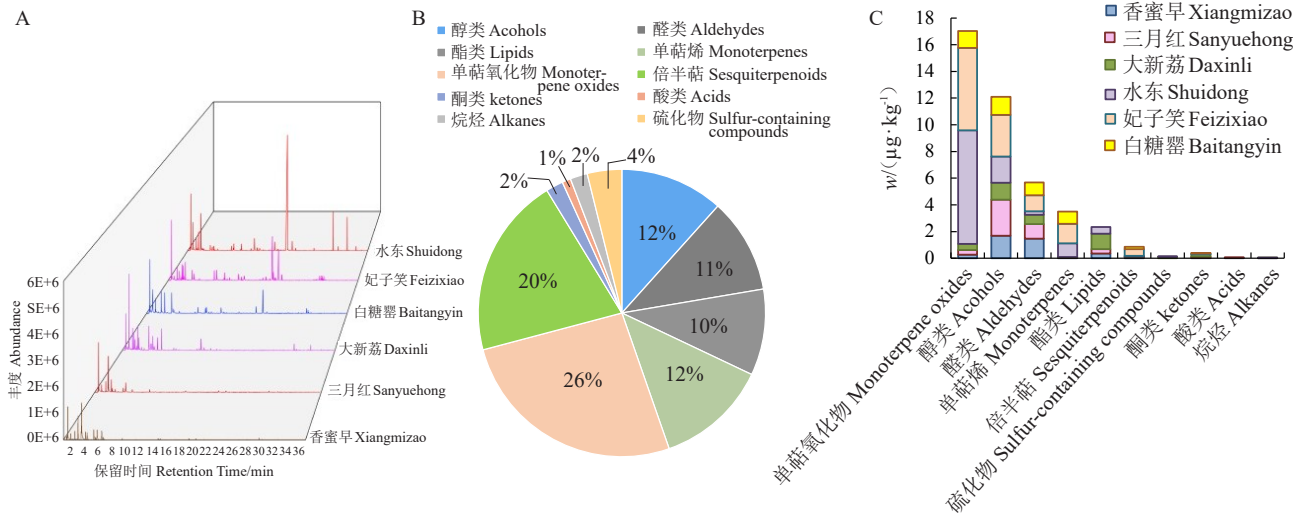


图1 6个特早熟与早熟荔枝果实挥发性成分的总离子流图(A)、总分类图(B)、各类成分含量比较图(C)

Fig. 1 Total ion flow diagram (A), general classification diagram (B) and comparison diagram of various components content (C) in litchi fruits of 6 special-early maturing and early maturing germplasm

类及倍半萜是特早熟-早熟系列荔枝种质的主要挥发性组分。

分析各种质的挥发性化合物的构成,发现妃子笑与水东挥发性化合物累计含量最高,分别是 $12.51 \text{ mg} \cdot \text{kg}^{-1}$ 、 $12.32 \text{ mg} \cdot \text{kg}^{-1}$;而白糖罂、三月红、香蜜早和大新荔处于较低水平,分别为 $4.75 \text{ mg} \cdot \text{kg}^{-1}$ 、 $4.69 \text{ mg} \cdot \text{kg}^{-1}$ 、 $3.94 \text{ mg} \cdot \text{kg}^{-1}$ 、 $3.82 \text{ mg} \cdot \text{kg}^{-1}$ 。特早熟的三月红、香蜜早、大新荔以醇类含量最高,分别占总含量的 57.31%、42.74%、32.54%;其次是醛酮类和酯类,其中三月红和香蜜早的醛酮类含量分别达到总含量的 23.59%和 37.19%;大新荔的酯类含量最高,达 29.82%,还发现 4 个硫化物,其酯类、硫化物的含量高于上述栽培种。单萜氧化物和单萜烯在早熟种水东、妃子笑及白糖罂中表现突出,单萜氧化物平均含量分别为 $8.50 \text{ mg} \cdot \text{kg}^{-1}$ (68.92%)、 $6.48 \text{ mg} \cdot \text{kg}^{-1}$ (49.30%)及 $1.28 \text{ mg} \cdot \text{kg}^{-1}$ (26.99%),单萜烯平均含量分别为 $1.03 \text{ mg} \cdot \text{kg}^{-1}$ (8.37%)、 $1.45 \text{ mg} \cdot \text{kg}^{-1}$ (11.53%)及 $0.93 \text{ mg} \cdot \text{kg}^{-1}$ (19.49%);而倍半萜以妃子笑、白糖罂含量高,平均含量分别为 $0.52 \text{ mg} \cdot \text{kg}^{-1}$ 、 $0.17 \text{ mg} \cdot \text{kg}^{-1}$ 。因此醇类、醛酮类及酯类是特早熟种三月红、香蜜早与大新荔的主要挥发性化合物;单萜烯、单萜氧化物、倍半萜及醇类是早熟种水东、妃子笑与白糖罂的主要挥发性化合物。

2.2 挥发性代谢组多元统计分析

2.2.1 共有与特有的化合物筛选 通过花瓣韦恩图(图2-A)分析发现 10 种化合物为 6 个荔枝种质所共有,分别是:乙醇、1-辛烯-3-醇、乙醛、己醛、青叶醛、

壬醛、芳樟醇、香茅醇、香叶醇、左旋玫瑰醚。不同种质所特有的挥发性物质有 34 种(表 3):其中香蜜早 1 种,十二醛;三月红 1 种,苯甲酸-3-甲基-2-丁烯酯;大新荔 7 种,苯甲基-3-甲基-2-丁烯酸酯、卡达烯、二甲基三硫、2,3,5-三硫杂己烷、2,4,5,7-四硫杂辛烷、(E)-氧化芳樟醇、芳樟醇氧化物 IV;水东 6 种,2,3-丁二醇、香茅醛、香茅酸、乙酸香茅酯、 α -金合欢烯、2,3-二氢金合欢醇;妃子笑 12 种,3-甲基-3-丁烯-1-醇、紫苏醇、橙花醚、(-)-蒎萝醚、 γ -榄香烯、 β -红没药烯、顺-依兰油-4(15)-5-二烯、 γ -依兰油烯、 γ -杜松烯、 α -杜松烯、 α -去二氢菖蒲烯、依兰烯;白糖罂 7 种,对-薄荷-1,3,8-三烯、别罗勒烯、4-萜烯醇、D(+)-香芹酮、 α -律草烯、二氢姜黄烯、 β -倍半水芹烯。

2.2.2 挥发性化合物主成分分析(PCA)与聚类分析 对 6 个不同荔枝种质的 103 种挥发性代谢物进行主成分分析,PCA 图显示 PC1: 40.7%, PC2: 19.09%(图 2-B),PCA 图清晰地将各种质分开,这表明种质间的代谢谱存在明显差异。特早熟的香蜜早、三月红和大新荔分布在 PC1 的负半轴上,早熟的妃子笑、白糖罂和水东分布在 PC1 的正半轴上和 0 轴附近;而香蜜早与三月红位置较近,说明这两个种质的挥发性物质相近。

聚类热图能显示不同种质挥发性成分更细微的差异,将 103 种挥发性化合物含量绘制聚类热图,显示不同种质间存在明显的组间差异(图 2-C),样品被分为两组类别:香蜜早、三月红与大新荔聚合为一组,白糖罂、水东与妃子笑聚合为另一组。热图中从

表 2 6 个特早熟、早熟荔枝种质果实的挥发性化合物定性和定量分析
Table 2 Qualitative and quantitative analysis of volatile compounds in litchi fruits of 6 special-early maturing and early maturing germplasm

挥发性成分 Volatiles	保留 指数 RI	香气阈值 Odor Threshold	CAS	香蜜早 Xiangmizao	三月红 Sanyuehong	水东 Shuidong	妃子笑 Feizixiao	白糖罂 Baitangying	大新荔 Daxinli
				w/($\mu\text{g}\cdot\text{kg}^{-1}$)					
醇类 Alcohols									
乙醇 Ethanol	-	950	64-17-5	777.84±70.78 d	927.16±237.57 cd	1 240.82±112.46 ab	1 383.44±15.27 a	1 074.62±144.77 bc	344.90±7.52 e
3-甲基-3-丁烯-1-醇 3-Methyl-3-buten-1-ol	723	0.55	763-32-6	-	-	-	351.35±33.11 a	-	-
异戊醇 3-Methyl-1-butanol	727	0.004	123-51-3	710.24±104.39 b	954.30±211.38 a	456.01±25.62 c	-	-	308.76±35.34 d
异戊烯醇 3-Methyl-2-buten-1-ol	768	0.25	556-82-1	-	-	26.66±4.48 cd	349.08±31.31 a	7.66±7.25 c	215.23±33.23 b
2,3-丁二醇 2,3-Butanediol	791	100	513-85-9	-	-	23.10±2.43 a	-	-	-
反式-2-己烯-1-醇 trans-2-Hexen-1-ol	862	0.23	928-95-0	-	-	-	-	191.52±9.47 b	178.42±27.16 a
正己醇 1-Hexanol	863	0.005 6	111-27-3	-	411.60±86.85 a	95.15±11.67 c	326.57±18.87 b	-	128.91±12.92 c
1-辛烯-3-醇 1-Octen-3-ol	977	0.001 5	3391-86-4	101.69±30.10 c	170.02±14.86 b	112.99±14.91 c	367.58±11.40 a	41.81±4.67 d	46.67±0.94 d
苯甲醇 Benzyl alcohol	1032	2.546 2	100-51-6	-	18.40±3.69 b	12.09±1.90 c	22.41±1.27 a	-	13.14±1.41 c
正辛醇 1-Octanol	1069	0.125 8	111-87-5	13.66±1.39 b	16.24±1.50 a	-	-	-	-
苯乙醇 Phenethyl alcohol	1111	0.012	60-12-8	81.25±15.16 c	202.37±13.11 b	-	306.49±36.23 a	-	31.45±3.28 d
壬醇 1-Nonanol	1170	0.045 5	143-08-8	-	-	2.64±0.22 b	-	-	8.51±1.71 a
醛酮类 Aldehydes and ketones									
乙醛 Acetaldehyde	-	0.005	75-07-0	85.71±16.35 a	93.43±15.09 a	34.07±3.99 b	79.63±9.69 a	77.79±6.21 a	18.82±2.64 b
异戊醛 Isovaleraldehyde	649	0.001 1	590-86-3	13.60±0.73 b	30.62±3.62 a	-	-	-	-
异戊烯醛 3-Methyl-2-butenal	780	-	107-86-8	155.73±3.11 a	55.61±4.60 d	15.52±1.68 e	25.06±6.41 b	-	96.60±14.86 c
正己醛 Hexanal	800	0.005	66-25-1	422.67±60.34 b	267.44±18.38 c	31.69±3.70 d	480.77±24.51 a	406.28±32.39 b	36.09±2.01 d
青叶醛 trans-2-Hexen	847	0.088 7	6728-26-3	679.72±95.44 a	563.71±53.04 b	139.83±5.80 d	422.81±40.72 c	455.99±61.57 c	459.78±380.00 c
苯甲醛 Benzaldehyde	958	0.35	100-52-7	10.43±0.64 b	21.63±0.99 a	23.00±2.54 a	-	-	8.08±1.07 c
苯乙醛 Phenylacetaldehyde	1041	0.006 3	122-78-1	6.59±1.02 c	11.47±1.45 b	3.18±0.29 d	11.67±0.92 b	-	14.31±1.89 a
反-2-辛烯醛 (E)-2-Octenal	1056	0.003	2548-87-0	1.71±0.27 b	8.92±1.01 a	-	-	-	-
壬醛 1-Nonanal	1103	0.001 1	124-19-6	33.00±4.68 a	30.40±4.92 a	12.50±1.22 b	26.51±4.93 a	17.23±1.66 b	33.89±6.22 a
癸醛 Decanal	1205	0.003	112-31-2	46.36±3.51 b	15.05±2.44 dc	-	59.70±9.78 a	10.30±1.08 d	22.10±5.13 c
十二醛 Dodecanal	1411	0.063	112-54-9	5.55±0.57 a	-	-	-	-	-
3-羟基-2-丁酮 Acetoin	710	0.014	513-86-0	-	83.67±9.76 b	-	62.05±5.12 c	32.97±1.14 d	172.19±7.83 a
甲基庚烯酮 6-Methyl-5-hepten-2-one	986	0.068	110-93-0	19.28±1.98 a	16.91±1.34 b	-	-	13.30±1.37 c	-
酯类 Esters									
乙酸 Ethyl Acetate	612	0.005	141-78-6	217.04±55.63 c	194.52±16.29 c	337.55±13.33 b	-	-	464.35±25.80 a
乙酸异戊酯 Isoamyl acetate	874	0.088	123-92-2	56.85±0.89 c	26.08±6.29 d	120.66±11.72 b	-	-	194.07±14.70 a
2-甲基丁基乙酸酯 2-Methylbutyl acetate	876	0.005	624-41-9	-	-	3.60±0.13 b	-	-	29.43±5.48 a
3-甲基-3-丁烯醇乙酸酯 3-Methylbut-3-enyl acetate	883	-	5205-07-2	37.39±2.08 b	22.98±4.06 c	21.82±1.72 c	-	-	59.35±6.50 a
梨醇酯 Prenyl acetate	915	-	1191-16-8	12.14±2.04 b	2.89±0.27 b	7.07±0.71 b	-	-	397.67±69.63 a
乙酸苄酯 Benzyl acetate	1163	0.364	140-11-4	3.97±0.69 c	4.43±0.51 bc	4.89±0.08 b	-	-	8.49±0.46 a
戊酸苄酯 Benzyl valerate	1396	-	10361-39-4	-	6.01±0.66 a	-	-	-	2.09±0.27 b
苯甲酸异戊酯 Isoamyl benzoate	1442	0.25	94-46-2	21.59±2.95 b	59.31±6.9 a	-	-	-	3.31±0.21 c
苯甲酸 3-甲基-2-丁烯酯 3-Methyl-2-butenyl Benzoate	1451	-	5209-11-8	-	9.46±0.51 a	-	-	-	-

表 2 (续) Table 2 (Continued)

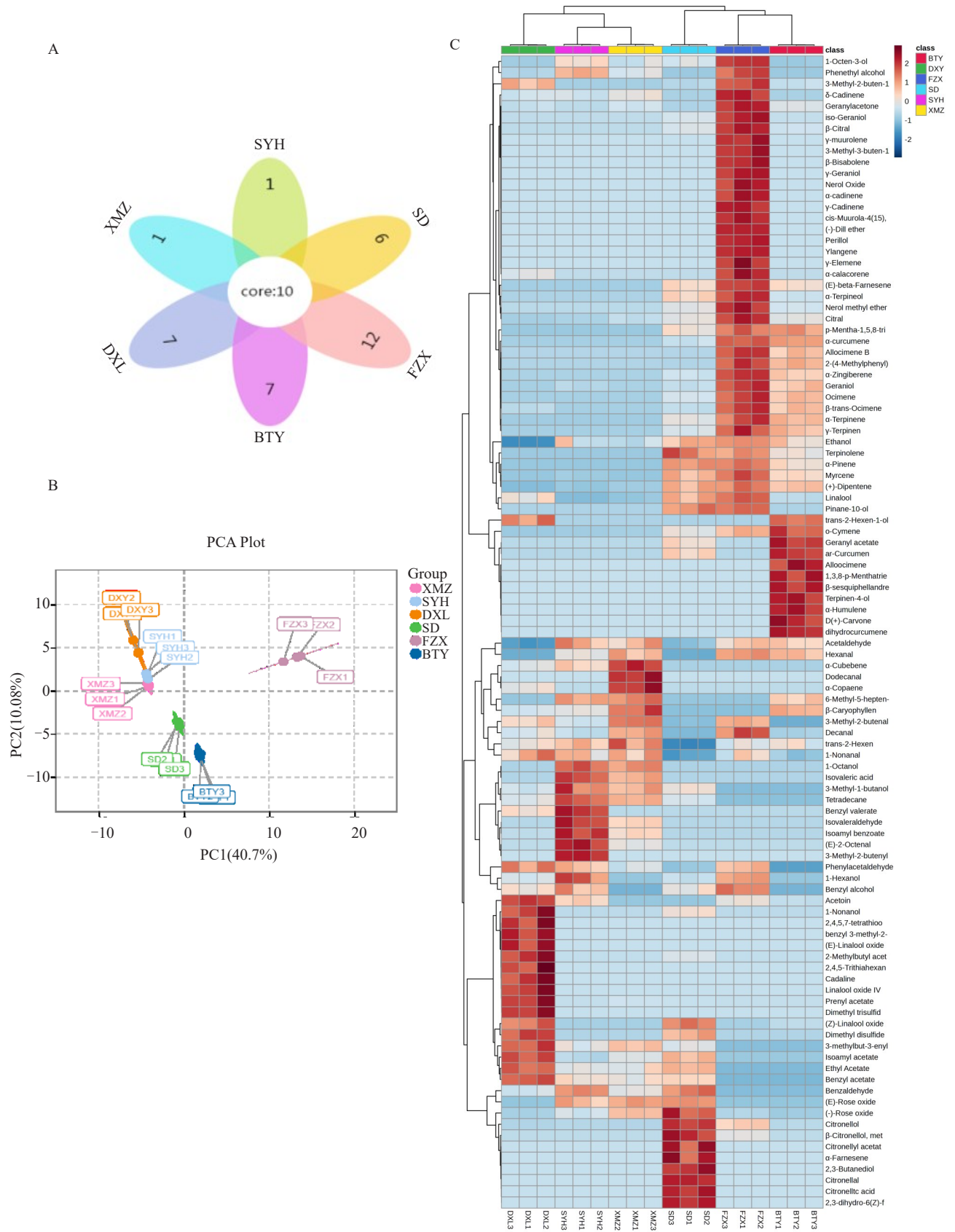
挥发性成分 Volatiles	保留 指数 RI	香气阈值 Odor Threshold	CAS	w/($\mu\text{g}\cdot\text{kg}^{-1}$) 香蜜早 Xiangmizao	三月红 Sanyuehong	水东 Shuidong	妃子笑 Feizixiao	白糖罂 Baitangying	大新荔 Daxinli
苯基-3-甲基-2-丁烯酸酯 Benzyl 3-methyl-2-butenate	1494	-	37526-89-9	-	-	-	-	-	10.94 \pm 1.40 a
单萜烯类 Monoterpenes									
α -蒎烯 α -Pinene	932	0.014	80-56-8	-	-	5.29 \pm 0.30 b	5.84 \pm 0.36 a	3.16 \pm 0.38 c	-
月桂烯 Myrcene	990	0.001 2	123-35-3	-	16.22 \pm 3.73 d	267.18 \pm 37.10 b	394.36 \pm 44.09 a	193.41 \pm 12.51 c	-
α -松油烯 α -Terpinene	1015	0.08	99-86-5	-	-	5.41 \pm 0.51 c	16.17 \pm 2.85 a	10.45 \pm 0.66 b	-
邻伞花烃 <i>O</i> -Cymene	1023	0.004	527-84-4	4.45 \pm 0.14 d	2.38 \pm 0.22 d	42.69 \pm 6.49 c	87.48 \pm 9.99 b	137.06 \pm 18.33 a	-
(+)-柠檬烯 (+)-Dipentene	1026	0.034	5989-27-5	36.17 \pm 1.15 c	21.59 \pm 4.10 c	252.56 \pm 33.10 b	315.44 \pm 35.05 a	222.22 \pm 12.83 b	-
罗勒烯 Ocimene	1037	0.034	13877-91-3	-	-	16.81 \pm 0.71 c	79.83 \pm 11.28 a	44.95 \pm 5.22 b	-
(E)-B-罗勒烯 β -trans-Ocimene	1047	0.034	3779-61-1	-	-	14.97 \pm 1.31 c	126.71 \pm 16.05 a	67.97 \pm 9.86 b	12.14 \pm 1.91 cd
γ -蒎烯 γ -Terpinen	1057	1	99-85-4	-	-	5.20 \pm 0.44 c	21.58 \pm 3.65 a	12.59 \pm 1.59 b	-
蒎烯 Terpinolene	1087	0.2	586-62-9	-	-	415.48 \pm 75.44 a	356.04 \pm 36.51 a	181.77 \pm 21.78 b	-
对-薄荷-1,3,8-三烯 1,3,8-p-Menthatriene	1109	0.015	18368-95-1	-	-	-	27.98 \pm 2.63 a	15.08 \pm 2.30 b	-
别罗勒烯 Alloocimene B	1128	-	7216-56-0	-	-	-	13.83 \pm 1.54 a	11.93 \pm 1.16 b	-
对-薄荷-1,5,8-三烯 p-Mentha-1,5,8-triene	1133	-	21195-59-5	-	-	6.67 \pm 0.96 c	-	-	-
2,6-二甲基-2,4,6-辛三烯 Alloocimene	1140	-	673-84-7	-	-	-	-	10.44 \pm 1.50 a	-
单萜氧化物类 Monoterpene oxides									
(S)-氧化芳樟醇 Z)-Linalool oxide	1071	0.1	5989-33-3	-	-	59.24 \pm 4.93 a	-	8.35 \pm 0.21 a	62.07 \pm 8.99 b
(E)-氧化芳樟醇 (E)-Linalool oxide	1086	0.19	34995-77-2	-	-	-	-	-	284.00 \pm 42.89 a
芳樟醇 Linalool	1099	0.006	78-70-6	12.63 \pm 2.97 e	4.24 \pm 0.89 e	108.08 \pm 14.95 b	146.93 \pm 9.23 a	34.65 \pm 2.42 d	67.94 \pm 13.91 c
左旋玫瑰醚 (-)-Rose oxide	1110	0.000 5	3033-23-6	67.95 \pm 1.57 b	26.57 \pm 5.31 c	118.47 \pm 20.37 a	12.15 \pm 1.17 cd	3.67 \pm 0.19 d	7.18 \pm 0.39 d
(E)-玫瑰醚 (E)-Rose oxide	1126	0.08	876-18-6	21.17 \pm 1.37 ab	18.80 \pm 3.42 b	22.63 \pm 0.44 a	-	-	-
香茅醛 Citronellal	1151	0.006	106-23-0	-	-	20.97 \pm 0.54 a	-	-	-
橙花醛 Nerol oxide	1153	-	1786-08-9	-	-	-	13.82 \pm 1.68 a	-	-
(-)-蒎烯 (-)-Dill ether	1156	2.9	70786-44-6	-	-	-	7.15 \pm 0.03 a	-	-
芳樟醇氧化物 IV Inalool oxide IV	1172	3	39028-58-5	-	-	-	-	-	-
4-蒎烯醇 Terpinen-4-ol	1175	1.2	562-74-3	-	-	-	-	-	4.81 \pm 0.80 a
β -香茅醇甲醚 β -Citronellol, methyl ether	1176	-	1000333-81-4	-	-	243.03 \pm 32.16 a	47.34 \pm 2.95 b	-	-
对伞花烃-8-醇 2-(4-Methyl-1phenyl) propan-2-ol	1182	-	1197-01-9	-	-	-	17.51 \pm 2.07 a	11.18 \pm 1.00 b	-
蒎烯-10-醇 Pinane-10-ol	1185	-	514-99-8	-	-	17.10 \pm 2.29	19.23 \pm 0.82	-	-
α -松油醇 α -Terpineol	1189	0.33	98-55-5	-	-	40.05 \pm 5.1 b	96.89 \pm 9.77 a	12.84 \pm 1.20 c	-
橙花醇甲醚 Nerol methyl ether	1202	-	1000352-64-1	-	-	24.99 \pm 2.27 b	133.20 \pm 14.64 a	15.22 \pm 0.70 b	-
7-甲基-3-亚甲基-6-辛烯-1-醇 γ -Geraniol	1218	-	13066-51-8	-	-	-	88.48 \pm 7.30 a	-	-
香茅醇 Citronellol	1228	0.062	106-22-9	98.88 \pm 9.65 c	176.28 \pm 26.18 c	7 434.17 \pm 404.09 a	3 190.05 \pm 331.62 b	249.38 \pm 24.74 c	19.08 \pm 4.34 c
异香叶醇 Iso-Geraniol	1233	0.001 1	5944-20-7	-	-	30.50 \pm 4.12 b	316.47 \pm 33.59 a	5.46 \pm 1.04 c	-
β -柠檬醛 β -Citral	1240	0.053	106-26-3	-	-	12.28 \pm 1.73 b	92.54 \pm 7.23 a	6.88 \pm 0.80 b	-
D(+)-香芹酮 D(+)-Carvone	1242	0.16	2244-16-8	-	-	-	-	6.80 \pm 0.89 a	-
香叶醇 Geraniol	1255	0.001 1	106-24-1	39.89 \pm 4.59 cd	107.63 \pm 27.13 cd	194.36 \pm 20.93 c	1 665.67 \pm 181.24 a	831.86 \pm 134.35 b	8.18 \pm 0.87 d
柠檬醛 Citral	1270	0.04	5392-40-5	26.54 \pm 4.35 c	8.60 \pm 0.41 cd	64.83 \pm 5.85 b	247.59 \pm 24.77 a	61.36 \pm 5.48 b	-

表 2 (续) Table 2 (Continued)

挥发性成分 Volatiles	保留 指数 RI	香气阈值 Odor Threshold	CAS	香蜜早 Xiangmizao	三月红 Sanyuehong	水东 Shuidong	妃子笑 Feizixiao	白糖罂 Baitangying	大新荔 Daxinli
				w/($\mu\text{g}\cdot\text{kg}^{-1}$)					
紫苏醇 Perillol	1297	1.1	536-59-4	-	-	-	7.35±0.25 a	-	-
香茅酸 Citronellc acid	1315	-	502-47-6	-	-	12.01±0.85 a	-	-	-
乙酸香茅酯 Citronellyl acetate	1361	1	150-84-5	-	-	90.52±18.07 a	-	-	-
乙酸香叶酯 Geranyl acetate	1388	0.15	105-87-3	-	-	1.98±0.37 b	-	5.66±0.58 a	-
(E)-香叶基丙酮 Geranylacetone	1458	0.06	3796-70-1	9.88±1.29 bc	4.65±0.66 d	-	75.73±5.76 a	14.41±1.03 b	6.71±1.67 cd
倍半萜 Sesquiterpenoids									
α -萹澄茄油烯 α -Cubebene	1356	-	17699-14-8	5.73±0.53 a	2.48±0.47 b	-	-	-	1.29±0.26 c
依兰烯 Ylangene	1377	-	14912-44-8	-	-	-	15.82±0.48 a	-	-
α -古巴烯 α -Copaene	1381	-	3856-25-5	16.47±2.41 a	5.18±0.77 b	-	-	-	3.71±0.86 b
β -石竹烯 β -Caryophyllen	1424	0.064	87-44-5	23.30±3.30 a	9.45±0.50 c	-	-	17.02±1.04 b	7.15±0.78 c
γ -榄香烯 γ -Elemene	1439	-	29873-99-2	-	-	-	26.65±3.90 a	-	-
二氢姜黄烯 Dihydrocurumene	1452	-	1461-02-5	-	-	-	-	4.23±0.22 a	-
α -律草烯 α -Humulene	1460	0.16	6753-98-6	-	-	-	-	8.65±0.7 a	-
(E)- β -金合欢烯 (E)-beta-Farnesene	1462	0.087	18794-84-8	-	-	4.36±0.40 b	9.66±0.31 a	4.18±0.31 b	-
顺-依兰油-4(15)-5-二烯 cis-Murola-4(15),5-diene	1469	-	157477-72-0	-	-	-	14.44±0.91 a	-	-
γ -依兰油烯 γ -Muurole	1482	-	30021-74-0	-	-	-	35.70±3.22 a	-	-
1,3-环己二烯 ar-Curcumen	1484	-	451-55-8	-	-	2.94±0.45 b	-	6.72±0.50 a	-
α -姜黄烯 α -Curcumene	1487	-	644-30-4	-	-	16.40±2.54 c	97.53±3.56 a	73.88±1.61 b	-
α -姜烯 α -Zingiberene	1498	-	495-60-3	-	-	15.04±1.91 c	10.30±7.36 a	47.11±3.92 b	-
α -金合欢烯 α -Farnesene	1510	0.087	502-61-4	-	-	6.44±1.36 a	-	-	-
β -红没药烯 β -Bisabolene	1512	-	495-61-4	-	-	-	89.08±6.73 a	-	-
γ -杜松烯 γ -Cadinene	1520	-	39029-41-9	-	-	-	28.92±1.75 a	-	-
β -倍半水芹烯 β -Sesquiphellandrene	1529	-	20307-83-9	-	-	-	-	11.32±1.05 a	-
δ -杜松烯 δ -Cadinene	1530	-	483-76-1	20.80±2.77 b	11.90±3.54 c	-	77.06±6.16 a	-	12.51±2.36 c
α -杜松烯 α -Cadinene	1544	-	24406-05-1	-	-	-	13.44±1.47 a	-	-
α -去二氢萹蒲烯 α -Calacorene	1550	-	21391-99-1	-	-	-	8.99±1.28 a	-	1.45±0.31 b
2,3-二氢金合欢醇 2,3-Dihydro-6(Z)-farnesol	1696	-	51411-24-6	-	-	9.33±0.45 a	-	-	-
硫化物 Sulfur-containing compounds									
二甲基二硫 Dimethyl disulfide	741	0.001 1	624-92-0	-	-	11.16±1.51 b	-	-	16.92±1.76 a
二甲基三硫 Dimethyl trisulfide	966	0.000 1	3658-80-8	-	-	-	-	-	23.59±3.18 a
2,3,5-三硫杂己烷 2,3,5-Trithiahexane	1123	-	42474-44-2	-	-	-	-	-	63.07±15.36 a
2,4,5,7-四硫杂辛烷 2,4,5,7-Tetrathiooctane	1517	-	85544-38-3	-	-	-	-	-	8.16±1.54 a
其他 Others									
异戊酸 Isovaleric acid	832	0.49	503-74-2	31.23±3.25 b	46.62±4.14 a	-	-	-	-
十四烷 Tetradecane	1400	1	629-59-4	7.20±0.23 b	10.02±0.83 a	3.30±0.19 c	-	-	3.70±0.43 c
卡达烯 Cadalene	1687	-	483-78-3	-	-	-	-	-	1.86±0.56 a

注：“-”表示该物质未检出或未检测到阈值。

Note: “-” indicates that the substance has not been detected or the threshold has not been retrieved.



从深褐色到深蓝色的颜色序列表明化合物含量从高到低。

The color sequence from dark brown to dark blue indicates that the abundance of compounds is from high to low.

图 2 6个特早熟与早熟荔枝种质果实挥发性化合物的花瓣韦恩图(A)、PCA 评分图(B)、聚类热图(C)

Fig. 2 Petal Venn plot (A), PCA score plot (B) and cluster heat map (C) of volatile compounds in the fruits of six special-early maturing and early maturing litchi germplasm

表 3 特早熟 vs 早熟荔枝种质差异代谢物及不同种质特征的挥发性化合物

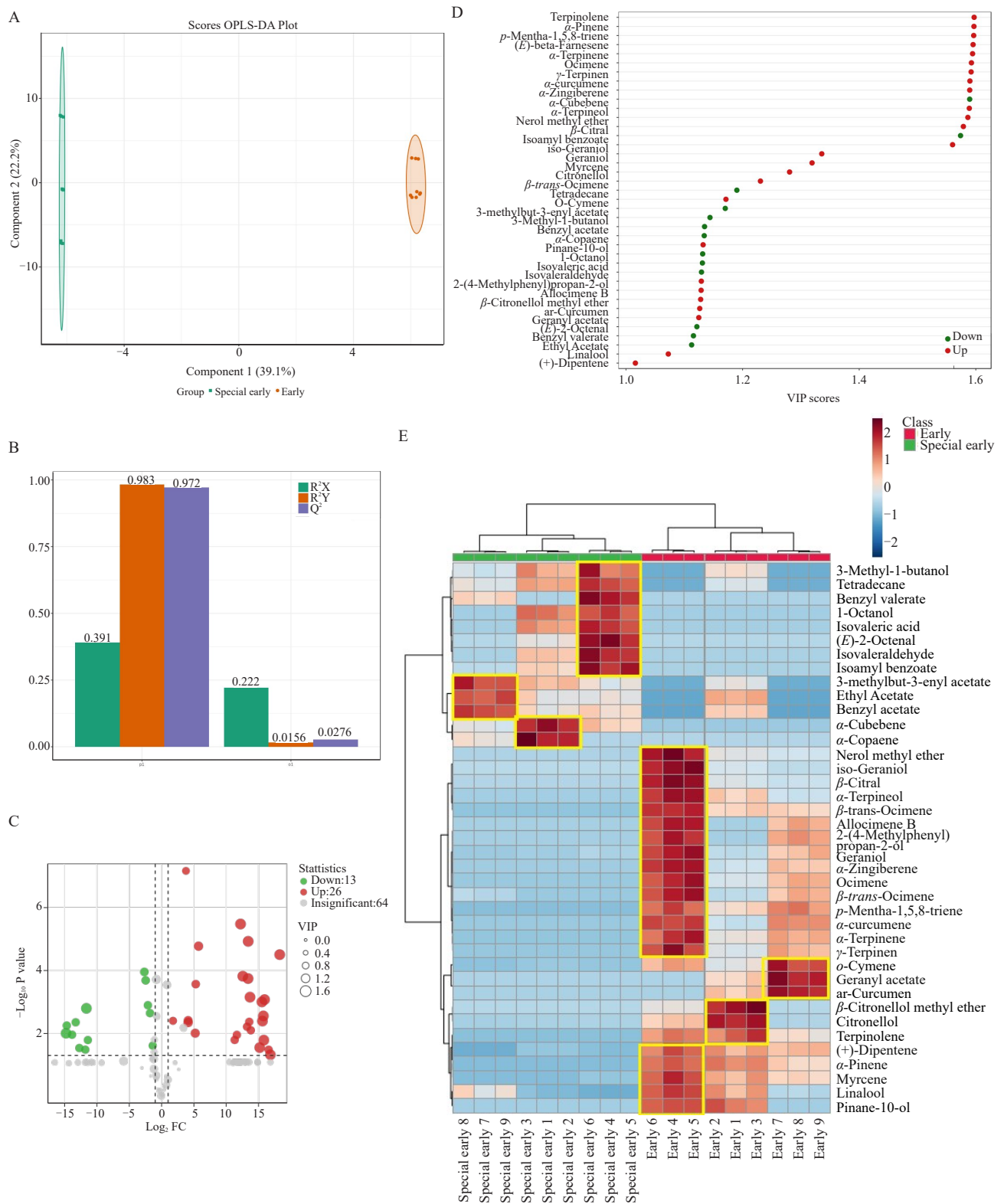
Table 3 Differential metabolites in special-early maturing vs early maturing litchi germplasm and characteristic volatiles of different germplasms

熟性 Maturity	种质 Germplasms	不同种质特有的化合物 Specific compounds of different germplasm	不同种质高丰度的差异代谢物 Differential metabolites with high abundance in different germplasms	39个差异代谢物(特早熟 vs 早熟) 39 differential metabolites (Special-early maturing vs Early maturing)
特早熟 Special-early maturing	香蜜早 Xiangmizao	十二醛 Dodecanal	异戊烯醛、 α -萜澄茄油烯 3-Methyl-2-butenal, α -Cubebene	下调的化合物: 异戊醇、正辛醇、异戊醛、反-2-辛烯醛、乙酸乙酯、3-甲基-3-丁烯醇乙酸酯、乙酸苄酯、戊酸苄酯、苯甲酸异戊酯、 α -萜澄茄油烯、 α -古巴烯、异戊醛、十四烷 Down-regulated compound: 3-Methyl-1-butanol, 1-Octanol, Isovaleraldehyde, (E)-2-Octenal, Ethyl Acetate, 3-methylbut-3-enyl acetate, Benzyl acetate, Benzyl valerate, Isoamyl benzoate, α -Cubebene, α -Copaene, Isovaleric acid, Tetradecane
	三月红 Sanyuehong	苯甲酸-3-甲基-2-丁烯酯 3-Methyl-2-butenyl Benzoate	异戊醇、十四烷、正辛醇、异戊酸、反-2-辛烯醛、异戊醛、苯甲酸异戊酯、戊酸苄酯 3-Methyl-1-butanol, Tetradecane, 1-Octanol, Isovaleric acid, (E)-2-Octenal, Isovaleraldehyde, Isoamyl benzoate, Benzyl valerate	
早熟 Early maturing	大新荔 Daxinli	苯甲基-3-甲基-2-丁烯酸酯、卡达烯、二甲基三硫、2,3,5-三硫杂己烷、2,4,5,7-四硫杂辛烷、(E)-氧化芳樟醇、芳樟醇氧化物 benzyl 3-methyl-2-butenate, Cadalene, Dimethyl trisulfide, 2,3,5-Trithiahexane, 2,4,5,7-tetrathiooctane, (E)-Linalool oxide, Linalool oxide IV	3-甲基-3-丁烯醇乙酸酯、乙酸乙酯、乙酸苄酯 3-methylbut-3-enyl, Ethyl Acetate, Benzyl acetate	上调的化合物: α -蒎烯、月桂烯、 α -松油烯、邻伞花烃、(+)-柠檬烯、罗勒烯、(E)-B-罗勒烯、 γ -萜品烯、萜品油烯、别罗勒烯、对-薄荷-1,5,8-三烯、芳樟醇、 β -香茅醇甲醚、对伞花烃-8-醇、蒎烯-10-醇、 α -松油醇、橙花醇甲醚、香茅醇、异香叶醇、 β -柠檬醛、香叶醇、乙酸香叶酯、(E)- β -金合欢烯、1,3-环己二烯、 α -姜黄烯、 α -姜烯 Up-regulated compound: α -Pinene, Myrcene, α -Terpinene, o-Cymene, (+)-Dipentene, Ocimene, β -trans-Ocimene, γ -Terpinen, Terpinolene, Allocimene B, p-Mentha-1,5,8-triene, Linalool, β -Citronellol methyl ether, 2-(4-Methylphenyl)propan-2-ol, Pinane-10-ol, α -Terpineol, Nerol methyl ether, Citronellol, iso-Geraniol, β -Citral, Geraniol, Geranyl acetate, (E)-beta-Farnesene, ar-Curcumen, α -curcumene, α -Zingiberene
	水东 Shuidong	2,3-丁二醇、香茅醛、香茅酸、乙酸香茅酯、 α -金合欢烯、2,3-二氢金合欢醇 2,3-Butanediol, Citronellal, Citronellol, Citronellyl acetate, α -Farnesene, 2,3-dihydro-6(Z)-farnesol	β -香茅醇甲醚、香茅醇、1,3-环己二烯 β -Citronellol methyl ether, Citronellol, ar-Curcumen	
	妃子笑 Feizixiao	3-甲基-3-丁烯-1-醇、紫苏醇、橙花醚、(-)-蒎烯、 γ -榄香烯、 β -红没药烯、顺-依兰油-4(15)-5-二烯、 γ -依兰油烯、 γ -杜松烯、 α -杜松烯、 α -去二氢菖蒲烯、依兰烯 3-Methyl-3-buten-1-ol, Perillol, Nerol Oxide, (-)-Dill ether, γ -Elemene, β -Bisabolene, cis-Murola-4(15),5-diene, γ -muurolene, γ -Cadinene, α -cadinene, α -calacorene, Ylangene	橙花醇甲醚、异香叶醇、 β -柠檬醛、 α -松油醇、(E)-B-罗勒烯、别罗勒烯、对伞花烃-8-醇、香叶醇、 α -姜烯、罗勒烯、(E)-B-罗勒烯、对-薄荷-1,5,8-三烯、 α -姜黄烯、 α -松油烯、 γ -萜品烯、(+)-柠檬烯、 α -蒎烯、月桂烯、芳樟醇 Nerol methyl ether, iso-Geraniol, β -Citral, α -Terpineol, β -trans-Ocimene, Allocimene B, 2-(4-Methylphenyl)propan-2-ol, Geraniol, α -Zingiberene, Ocimene, β -trans-Ocimene, p-Mentha-1,5,8-triene, α -curcumene, α -Terpinene, γ -Terpinen, (+)-Dipentene, α -Pinene, Myrcene, Linalool	
白糖罂 Baitangying	对-薄荷-1,3,8-三烯、别罗勒烯、4-萜烯醇、D(+)-香芹酮、 α -律草烯、二氢姜黄烯、 β -倍半水芹烯 1,3,8-p-Menthatriene, Allocimene B, Terpinen-4-ol, D(+)-Carvone, α -humulene, dihydrocurcumene, β -sesquiphellandrene	邻伞花烃、乙酸香叶酯、1,3-环己二烯 o-Cymene, Geranyl acetate, ar-Curcumen		

深红褐色到深蓝色,可清楚地看出各个样品挥发性物质的含量高低。

2.2.3 特早熟与早熟荔枝种质果实挥发性化合物差异比较 以香蜜早、三月红与大新荔为特早熟组,妃子笑、白糖罂与水东为早熟组,进行OPLS-DA多元统计分析。OPLS-DA模型验证显示R2X=0.391, R2Y=0.983, Q2>0.9(图3-B),说明模型具有重要意义。OPLS-DA得分图(图3-A)的横坐标方向显示组间差异明显;选取VIP≥1、p<0.05的差异代谢物绘制火山图(图3-C),发现特早熟 vs 早熟共有39个差异代谢物(表3)。VIP得分图(图3-D)展示了

VIP≥1的化合物及其上调、下调情况。其中26个化合物显著上调[α -蒎烯、月桂烯、 α -松油烯、邻伞花烃、(+)-柠檬烯、罗勒烯、(E)-B-罗勒烯、 γ -萜品烯、萜品油烯、别罗勒烯、对-薄荷-1,5,8-三烯、芳樟醇、 β -香茅醇甲醚、对伞花烃-8-醇、蒎烯-10-醇、 α -松油醇、橙花醇甲醚、香茅醇、异香叶醇、 β -柠檬醛、香叶醇、乙酸香叶酯、(E)- β -金合欢烯、1,3-环己二烯、 α -姜黄烯、 α -姜烯],包含单萜类化合物占22种,倍半萜4种,说明这类化合物在早熟荔枝种质中的含量是显著高于特早熟的;13个化合物显著下调(异戊醇、正辛醇、异戊醛、反-2-辛烯醛、乙酸乙酯、3-甲基-3-丁烯醇乙酸



A. OPLS-DA 得分图; B. OPLS-DA 模型验证图; C. 火山图; D. VIP 得分图; E. 差异代谢物聚类热图; 黄色框内化合物为丰度较高的差异挥发物代谢物, 样品 Special early 1~3 为 XMZ, Special early 4~6 为 SYH, Special early 7~9 为 DXY, Early 1~3 为 SD, Early 4~6 为 FZX, Early 7~9 为 BTY.

A. OPLS-DA score chart; B. OPLS-DA model validation chart; C. volcano chart; D. VIP score chart; E. Differential metabolite cluster heat map; The compounds in the yellow wireframe are differential metabolites with high abundance. In the sample, Special early 1~3 is XMZ, Special early 4~6 is SYH, Special early 7~9 is DXY; Early 1~3 is SD, Early 4~6 is FZX, and Early 7~9 is BTY.

图3 特早熟与早熟种质挥发性化合物差异比较

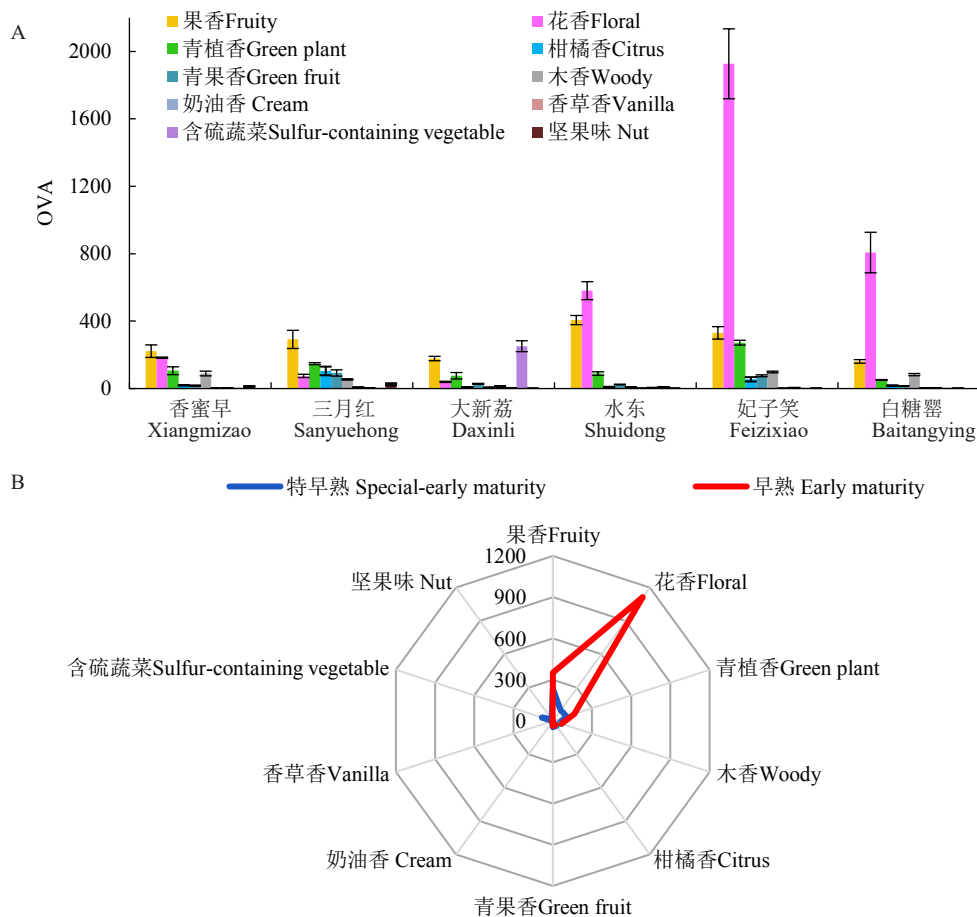
Fig. 3 Comparison of volatile substances between special-early maturing and early maturing germplasm

酯、乙酸苄酯、戊酸苄酯、苯甲酸异戊酯、 α -萜澄茄油烯、 α -古巴烯、异戊酸、十四烷),包含醇类化合物2种,醛类化合物2种,酯类化合物5种,倍半萜2种,表明该类化合物在早熟荔枝种质中的含量是显著低于特早熟的。从差异代谢物聚类热图中可以清晰地分辨出各种质中丰度较高的差异挥发性代谢物(图3-E、表3),这些特有的化合物与高丰度的差异代谢物可以作为各种质特征性挥发性化合物。

2.3 不同荔枝种质果实的香气特征分析

香气成分对食品香气体系的贡献不仅仅取决于浓度,更是与其自身阈值密切相关^[16],利用香气活度值OVA可以分析挥发性物质对荔枝果实香气的贡献程度。为明确不同熟性及不同荔枝种质果实香型特征,依照各种香气物质在感官特征方面所表现出的芳香系列进行分类,并以同类香型的香气成分OAV总和代表每个香型的总强度,分别构建了不同

荔枝种质香气特征图和早熟-特早熟荔枝香气特征雷达图(图4)。从图4-A中可以看出,6个荔枝种质主要包含10种香型:花香(占总OVA值的50.98%)、果香(22.43%)、青植香(10.46%)、柑橘香(3.01%)、木香(4.81%)、青果香(3.57%),此外个别种质还有少量的香草香、奶油香、坚果香及含硫蔬菜味。花香和果香对早熟-特早熟荔枝香气的贡献最大。其中特早熟种香蜜早、三月红、大新荔的香气类型以果香为主,花香为辅,平均花香/果香比值分别为0.83、0.26、0.22;早熟种水东、妃子笑、白糖罂的香气类型以花香为主,平均花香/果香比值分别为1.43、5.83、5.01。早熟种的花香/果香比值显著高于特早熟种($p < 0.01$),妃子笑中除了含有最丰富的花香和果香以外,还有较丰富的青植香、青果香和木香,香气种类和含量最丰富;大新荔尽管果香、花香极淡,但却具有较浓的含硫蔬菜味、奶油香。特早熟组的总



A. 不同荔枝种质果实香气特征柱状图; B. 特早熟-早熟荔枝香气特征雷达图。

A. Histogram of aroma characteristics of different germplasm of litchi; B. Radar map of aroma characteristics of Special-early maturing and Early maturing litchi.

图4 6个特早熟早熟荔枝种质果实香气特征比较

Fig. 4 Comparison of aroma characteristics in litchi fruits of 6 special-early maturing and early maturing germplasms

OVA 值仅为早熟组的 40.7%, 这表明早熟种质的香气活度更高。从图 4-B 中可以看出, 特早熟组荔枝种质以果香为主, 花香、青植香为辅, 兼具少量橘香、青果香、木香、坚果香、蒜香及奶油香的一类香型, 而早熟组荔枝种质则以花香为主, 果香、青植香为辅, 兼具少量木香、青果香、橘香、香草香的一类香型。

OVA \geq 1 的挥发性组分通常对整体风味具有贡献, 且数值越大其香气的贡献越大^[12], 结合文献报道的香气成分的阈值和属性描述^[15,17-19], 计算 6 个不同种质荔枝香气成分的 OAV 值。结果显示有 35 种化合物的 OVA \geq 1 (表 4), 这些化合物被认为是 6 个特早熟-早熟种质的香气化合物, 包括 5 种醇类、9 种醛类、3 种酯类、6 种单萜烯、10 种单萜氧化物、2 种硫化

物, 以单萜和醛类为主, 其中香叶醇的香气活度值最高(平均 OVA 为 431.5)。以 OAV \geq 10 的挥发性成分为关键香气成分^[19], 获得关键香气成分 18 种: 香叶醇、二甲基三硫、月桂烯、异戊醇、异香叶醇、1-辛烯-3-醇、左旋玫瑰醚、乙酸乙酯、正己醛、正己醇、香茅醇、壬醛、异戊醛、邻伞花烃、乙醛、苯乙醇、二甲基二硫、芳樟醇, 但不同种质间存在较大差异(表 5)。1-辛烯-3-醇、乙醛、正己醛、壬醛、左旋玫瑰醚、香叶醇、青叶醛为 6 个特早熟-早熟荔枝种质所共有的香气化合物, 其中左旋玫瑰醚、异戊醇、乙酸乙酯、壬醛、1-辛烯-3-醇是 3 个特早熟种质共有的关键香气成分, 月桂烯、香叶醇、壬醛、邻伞花烃、1-辛烯-3-醇是 3 个早熟种质共有的关键香气成分。

表 4 6 个特早熟早熟荔枝果实中特征香气成分的 OVA 值及香气特征

Table 4 OVA value and aroma characteristics of characteristic aroma components in litchi fruits of 6 special-early maturing and early maturing litchi germplasms

类别 Classification	化合物 Compound	香气特征 Aroma character	香气 阈值 Odor Thresh- old	OVA 值 OVA value						
				香蜜早 Xiang- mizao	三月红 Sanyue- hong	大新荔 Daxinli	水东 Shui- dong	妃子笑 Feizi- xiao	白糖罂 Baitang- ying	平均 值 Mean
醇类 Alcohols	异戊醇 3-Methyl-1-butanol	果味、香蕉 Fruity, banana	0.004 0	177.6	238.6	77.2	114.0	-	-	151.8
	异戊烯醇 3-Methyl-2-buten-1-ol	果味、绿色 Fruity, green	0.250 0	-	-	-	-	1.4	-	1.4
	正己醇 1-Hexanol	果味、绿色、苹果皮和油性 Fruity, green, apple-skin and oily	0.005 6	-	73.5	23.0	17.0	58.3	-	43.0
	1-辛烯-3-醇 2-1-Octen-3-ol	蘑菇、泥土味、真菌味、绿色、油性、 植物味、鲜味和咸味 Mushroom, earthy, fungal, green, oily, vegetative, umami sensation and savory brothy	0.001 5	67.8	113.4	31.1	75.3	245.1	27.9	93.4
醛酮类 Aldehydes and ketones	苯乙醇 Phenethylalcohol	花香、甜味、玫瑰味 Floral, sweet, rosey	0.012 0	6.8	16.9	2.6	-	25.5	-	13.0
	乙醛 Acetaldehyde	辛辣、新鲜、醛类、清爽、绿色 Pungent, fresh, aldehydic, refreshing and green	0.005 0	17.1	18.7	3.8	6.8	15.9	15.6	13.0
	异戊醛 Isovaleraldehyde	果味、干绿色、巧克力、坚果、叶、可可 Fruity, dry green, chocolate, nutty, leafy and cocoa	0.001 1	12.4	27.8	-	-	-	-	20.1
	正己醛 Hexanal	木质、植物、苹果、草、柑橘和橙子 Woody, vegetative, apple, grassy, citrus and orange	0.005 0	84.5	53.5	7.2	6.3	96.2	81.3	54.8
	青叶醛 trans-2-Hexen	新鲜绿色、叶、果味带有浓郁的 植物气息 Fresh green, leafy, fruity with rich vegetative nuances	0.088 7	7.7	6.4	5.2	1.6	4.8	5.1	5.1
	苯乙醛 Phenylacetaldehyde	绿色、甜、花、风信子、三叶草蜂蜜 Green, sweet, floral, hyacinth, clover honey	0.006 3	1.1	1.8	2.3	-	1.9	-	1.8
	反-2-辛烯醛 (E)-2-Octenal	新鲜黄瓜、草本、香蕉、蜡质、绿叶 Fresh cucumber, fatty, green herbal, banana, waxy, green leaf	0.003 0	-	3.0	-	-	-	-	3.0

表 4 (续) Table 4 (Continued)

	壬醛 1-Nonanal	蜡质、醛糖、玫瑰、鲜橙皮、脂肪皮 Waxy, aldehydic, rose, fresh orris orange peel, fatty peely	0.001 1	30.0	27.6	30.8	11.4	24.1	15.7	23.3
	癸醛 Decanal	柑橘花香、柑橘和橘子皮 Citrus floral, citrus and orange peel with a slight green melon nuance	0.003 0	15.5	5.0	7.4	-	19.9	3.4	10.2
	3-羟基-2-丁酮 Acetoin	甜奶油、奶 Sweet cream, milk	0.014 0	-	6.0	12.3	-	4.4	2.4	6.3
酯类 Esters	乙酸乙酯 Ethyl Acetate	空灵的水果味、甜美的草绿色 Ethereal fruity, sweet weedy green	0.005 0	43.4	38.9	92.9	67.5	-	-	60.7
	乙酸异戊酯 Isoamyl acetate	甜美的水果味、香蕉般绿色和 成熟的细微差别 Sweet fruity, banana-iike with a green ripe nuance	0.088 0	0.65	0.30	2.21	1.37	-	-	1.13
	2-甲基丁基乙酸酯 2-Methylbutyl acetate	甜、香蕉、果味 Sweet, banana, fruity	0.005 0	-	-	5.9	-	-	-	5.9
单萜烯 Monoter- penes	月桂烯 Myrcene	木质、植物、柑橘、水果味, 带有 热带芒果和轻微的绿叶薄荷味 Woody, vegetative, citrus, fruity with a tropical mango and slight leafy minty nuances	0.001 2	-	13.5	-	222.7	328.6	161.2	181.5
	邻伞花烃 <i>O</i> -Cymene	-	0.004 0	1.1	-	-	10.7	21.9	34.3	17.0
	(+)-柠檬烯 (+)-Dipentene	柑橘、橙、鲜甜 Citrus, orange, fresh sweet	0.034 0	1.1	-	-	7.4	9.3	6.5	6.1
	罗勒烯 Ocimene	柑橘、绿色、木质 Citrus, green, woody	0.034 0	-	-	-	-	2.4	1.3	1.8
	(<i>E</i>)- β -罗勒烯 β -trans-Ocimene	甜草药 Sweet herbal	0.034 0	-	-	-	-	3.7	2.0	2.9
	萜品油烯 Terpinolene	油性木质、柠檬/酸橙、热带草本 植物 Oily woody, lemon/lime, tropical herbal	0.200 0	-	-	-	2.1	1.8	-	1.9
单萜氧 化物 Monoter- pene oxides	(<i>E</i>)-氧化芳樟醇 (<i>E</i>)-Linalool oxide	花香 Floral	0.190 0	-	-	1.5	-	-	-	1.5
	芳樟醇 Linalool	柑橘、橙、柠檬、花香、蜡质、木本 Citrus, orange, lemon, floral, waxy, aldehydic and woody	0.006 0	2.1	-	11.3	18.0	24.5	5.8	12.3
	左旋玫瑰醚 (-)-Rose oxide	甜花香、金属、荔枝、玫瑰 Sweet floral, metallic, lychee, rose	0.000 5	135.9	53.1	14.4	236.9	24.3	7.3	78.7
	香茅醛 Citronellal	花香、绿色、玫瑰色、柑橘、柠檬 Floral, green, rose, citrus and lemons	0.006 0	-	-	-	3.5	-	-	3.5
	香茅醇 Citronellol	花卉、蜡质、玫瑰花蕾、柑橘 Floral, waxy, rose bud, citrus	0.062 0	1.6	2.8	-	119.9	51.5	4.0	36.0
	异香叶醇 β -trans-Ocimene	-	0.001 1	-	-	-	27.7	287.7	5.0	106.8
	β -柠檬醛 β -Citral	柠檬 Lemon	0.053 0	-	-	-	-	1.8	-	1.8
	香叶醇 Geraniol	甜美的花香、水果、玫瑰、蜡状、柑橘味 Sweet floral, fruity, rose, waxy, citrus	0.001 1	36.3	97.8	7.4	176.7	1514.2	756.2	431.5
	柠檬醛 Citral	甜柠檬 Sweet lemon citral	0.040 0	-	-	-	1.6	6.2	1.5	3.1
	(<i>E</i>)-香叶基丙酮 Geranylacetone	花香、水果、绿色、梨、香蕉、依兰 Floral, fruity, green, pear, banana, ylang	0.060 0	-	-	-	-	1.3	-	1.3
	二甲基三硫 Dimethyl trisulfide	硫磺味的熟洋葱 Sulfurous cooked onion savory meaty	0.000 1	-	-	235.9	-	-	-	235.9
合计 Total			642.43	798.62	589.74	1 138.66	2 776.47	1 136.44		

注:大部分物质香气特征查自 <http://www.thegoodscentscompany.com/index.html>,“-”表示该物质未检出或未查询到。

Note: Most of the characteristic aroma components were searched from <http://www.thegoodscentscompany.com/index.html>, ‘-’ indicates that the substance has not been detected or found.

表5 6个特早熟早熟荔枝种质果实的关键香气成分

种质 Germplasms	香蜜早 Xiangmizao	三月红 Sanyuehong	大新荔 Daxinli	水东 Shuidong	妃子笑 Feizixiao	白糖罂 Baitangying
关键香气成分 Key aroma components (OVA≥10)	香叶醇、乙醛、壬醛、癸醛、异戊醛、1-辛烯-3-醇、正己醛、左旋玫瑰醚、乙酸乙酯、异戊醇 Geraniol, Acetaldehyde, 1-Nonanal, Decanal, Isovaleraldehyde, 1-Octen-3-ol, Hexanal, (-)-Rose oxide, Ethyl acetate, 3-Methyl-1-butanol	香叶醇、月桂烯、苯乙醇、乙醛、壬醛、异戊醛、乙酸乙酯、左旋玫瑰醚、正己醛、正己醇、1-辛烯-3-醇、异戊醇 Geraniol, Myrcene, Phenethyl alcohol, Acetaldehyde, 1-Nonanal, Isovaleraldehyde, Ethyl acetate, (-)-Rose oxide, Hexanal, Hexanol, 1-Octen-3-ol, 3-Methyl-1-butanol	芳樟醇、3-羟基-2-丁酮、左旋玫瑰醚、二甲基二硫、正己醇、壬醛、1-辛烯-3-醇、异戊醇、乙酸乙酯、二甲基三硫 Linalool, Acetoin, (-)-Rose oxide, Dimethyl disulfide, 1-Hexanol, 1-Nonanal, 1-Octen-3-ol, 3-Methyl-1-butanol, Ethyl acetate, Dimethyl trisulfide	香叶醇、异戊醇、左旋玫瑰醚、月桂烯、香茅醇、1-辛烯-3-醇、乙酸乙酯、异香叶醇、芳樟醇、正己醇、壬醛、邻伞花烺、二甲基二硫 Geraniol, 3-Methyl-1-butanol, (-)-Rose oxide, Myrcene, Citronellol, 1-Octen-3-ol, Ethyl acetate, iso-Geraniol, Linalool, 1-Hexanol, 1-Nonanal, O-Cymene, Dimethyl disulfide	香叶醇、月桂烯、异香叶醇、1-辛烯-3-醇、正己醛、正己醇、香茅醇、苯乙醇、芳樟醇、左旋玫瑰醚、壬醛、邻伞花烺、癸醛、乙醛 Geraniol, Myrcene, iso-Geraniol, 1-Octen-3-ol, Hexanal, 1-Hexanol, Citronellol, Phenethyl alcohol, Linalool, (-)-Rose oxide, 1-Nonanal, O-Cymene, Decanal, Acetaldehyde	香叶醇、月桂烯、正己醛、邻伞花烺、1-辛烯-3-醇、壬醛、乙醛 Geraniol, Myrcene, Hexanal, O-Cymene, 1-Octen-3-ol, 1-Nonanal, Acetaldehyde

3 讨论

3.1 不同荔枝种质果肉挥发性代谢产物特征

不同种属的荔枝挥发性物质在种类和含量方面有很大的差异^[5], Johnston等^[20]最早利用GC-MS在荔枝果肉中检测出48种挥发性风味化合物, Toulemonde等^[21]从荔枝果肉中鉴定出89种挥发性化合物, 多数研究者认为荔枝果肉的挥发性组分以萜烯类、醇类、酯类、醛类为主并影响果实的风味^[20-22]。笔者在本研究中同样发现特早熟-早熟系列荔枝果肉中含有大量的单萜类、倍半萜类、醇类及醛类, 其数量极为丰富, 为荔枝果肉中主要的挥发性成分, 以单萜氧化物占据多数, 倍半萜的数量虽然丰富, 但含量并不高。值得一提的是, 野生种质大新荔的含硫化物远高于其他几个栽培种, 而这在以往的文献中未见报道。硫化物通常具有杀菌驱虫作用, 在葱蒜等高抗病虫的植物中大量存在^[23], 这可能与野生荔枝种质具有较强的抗病虫性有直接关系, 其在荔枝种质中的作用机制有待进一步研究。

3.2 早熟与特早熟荔枝种质挥发性代谢物差异

以往的研究主要集中于中晚熟栽培种质的挥发性组分^[24-25], 而对特早熟、早熟荔枝种质的挥发性组分特点未见报道。笔者在本研究中发现, 醇类、醛酮类及酯类是特早熟种质三月红、香蜜早与大新荔的主要挥发性组分; 单萜烯、单萜氧化物、倍半萜及醇类是早熟种质水东、妃子笑与白糖罂的主要挥发性组分。早熟组的累计挥发性化合物含量与数量总体高于特早熟组, 这与早熟荔枝果实香气的表现更浓

郁相一致。

通过挥发性代谢产物PCA图及聚类热图, 可将不同荔枝种质明显地区分出来, 并依据熟性聚成两大类, 这说明熟性相同种质的挥发性代谢产物具较高相似性但不尽相同。另外, 差异代谢物聚类热图可清楚地显示出各个种质样品中丰度较高的挥发性差异代谢物, 说明这些差异代谢物可作为区分6个特早熟、早熟荔枝种质的特征指标。

3.3 不同荔枝种质挥发性物质的香气特征

香气活度值概念的提出为解决挥发性成分对体系香气贡献度问题提供了重要的科学依据和技术手段^[12]。笔者通过每个芳香类型的累计OAV值构建的香气特征图, 发现特早熟早熟荔枝种质主要包含以花香、果香、青植香、柑橘香、木香、青果香为主的10种香型, 花香和果香对特早熟-早熟荔枝香气的贡献最大, 但特早熟与早熟种质的花香/果香比值存在较大的差异。

Wu等^[26]认为, 玫瑰醚、1-辛烯-3-醇、芳樟醇、香叶醛和香叶醇是晚熟荔枝怀枝果实的主要香气成分, 唐忠盛^[27]等分析筛选出荔枝汁的10种特征香气物质: 顺式-玫瑰醚、香茅醇、香叶醇、苯乙醇、芳樟醇、柠檬烯、1-辛烯-3-醇、辛酸、辛酸乙酯、乙酸异戊酯。本研究表明, 35种化合物对早熟系列荔枝果实的香气贡献较大, 1-辛烯-3-醇、乙醛、正己醛、青叶醛、壬醛、左旋玫瑰醚、香叶醇是6个特早熟-早熟荔枝种质共有的香气化合物, 也是这类荔枝的主体香气成分, 其中香叶醇的香气活度最大。

笔者研究发现, 香气强度较高的萜类化合物以

单萜为主,尽管倍半萜数量众多,但由于倍半萜的阈值能被检索到的极少,少数能检索到的却香气阈值较高,使得倍半萜香气活度值缺失或较低,这说明倍半萜类并非是荔枝果实的主要香气来源。不过,部分倍半萜具有特殊的气味使得其发挥着某些独特的作用,比如可通过吸引和趋避起到植物信息素的作用^[28-29]。本试验中早熟的水东、妃子笑与白糖罂是易受蒂蛀虫危害的种质,均含较多的倍半萜类化合物,其中水东特有的 α -金合欢烯、2,3-二氢金合欢醇及含量较高的1,3-环己二烯、(E)- β -金合欢烯,妃子笑特有的 β -红没药烯、 γ -杜松烯、 α -杜松烯,以及白糖罂特有的二氢姜黄烯、 β -倍半水芹烯,在特早熟的三月红、香蜜早中却未检出,这些倍半萜类物质可能对蒂蛀虫具有吸引作用。倍半萜类的独特作用有待后续验证。

4 结 论

笔者在本试验中系统地研究了6个特早熟-早熟荔枝种质挥发性代谢物组成和含量的全面信息,共鉴定出103种挥发性组分,10种为共有的化合物、34种为各种质的特有化合物,以单萜类、醇类、醛酮类、酯类及倍半萜为主要成分,其中的特早熟种质挥发性物质种类以醇类、醛酮类及酯类为主,早熟种质挥发性物质则以萜类(单萜及倍半萜)及醇类为主。运用OPLS-DA方法获得上述特早熟-早熟组间的差异代谢物39个,并结合各种质特有的化合物获得区分上述特早熟-早熟种质的特征性挥发性化合物。结合香气活度值筛选出对6个特早熟-早熟荔枝种质香气具有贡献的化合物35种,以香叶醇最高;发现1-辛烯-3-醇、乙醛、正己醛、壬醛、左旋玫瑰醚、香叶醇、青叶醛为6个特早熟-早熟荔枝种质所共有的香气化合物,其中左旋玫瑰醚、异戊醇、乙酸乙酯、壬醛及1-辛烯-3-醇是特早熟种质三月红、香蜜早和大新荔共有的关键香气成分,而月桂烯、香叶醇、壬醛、邻伞花烃及1-辛烯-3-醇是早熟种质水东、妃子笑与白糖罂共有的关键香气成分。通过香气特征分析,发现特早熟种质香型以果香为主,花香、青植香为辅;早熟种质香型以花香为主,果香、青植香为辅。结果表明早熟、特早熟荔枝种质挥发性代谢物具有丰富的多样性,且后者的挥发性物质及香气物质更为丰富;不同熟性及不同荔枝种质果实间的挥发性成分存在显著差异,鉴于试验种质为特早熟、早熟荔枝种质的典型代表,部分挥发性化合物应可作为鉴定该类荔枝种质

的指标。本试验结果可为荔枝栽培、育种、加工等提供参考依据。

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