

9个燕山板栗品种成熟时果实主要香气物质分析

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摘要:【目的】以9个燕山板栗品种为材料,分析燕山板栗在成熟时的果实香气构成特点及品种间差异,探索影响板栗香气的主要挥发性物质,为育种和贮藏研究提供理论依据。【方法】使用顶空固相微萃取结合气质联用技术(HS-SPME/GC-MS)对板栗果实的香气成分进行了测定,并结合主成分分析法(PCA)对检测结果进行分析。【结果】9个品种共检测到36种化合物,其中酚类物质7种,醇类、烷烃类和酯类物质各5种,酸类4种,酚类3种,醚类和酮类物质各1种,其他物质5种,9个品种都是以醛类物质为主。确定了每个品种主要香气物质,9个燕山板栗品种的特征香气成分构成存在一定的差异。【结论】燕山板栗成熟时的特征香气物质以醛类为主,然后是醇类和酯类。癸醛是9个品种都含有的香气物质,而且相对含量均较高。9个燕山板栗品种成熟时的主要特征香气物质是癸醛、壬醛、棕榈酸甲酯和肉豆蔻酸异丙酯。

关键词:燕山板栗;成熟;主要香气物质;HS-SPME/GC-MS;PCA

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Analysis of the main aroma compounds in nine mature Yanshan Chinese chestnut varieties

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Abstract: 【Objective】 The main aroma compounds and differences in nine Yanshan Chinese chestnut varieties at maturity were analyzed in order to provide useful information for breeding and storage research of Yanshan Chinese chestnut. 【Methods】 Nine Chinese chestnut varieties were harvested at maturity from Qianxi and Zunhua county of Tangshan city, and then were stored at $(-2 \pm 1)^\circ\text{C}$. The analyses were made on the fifth day after harvest. The aroma components of chestnut fruits were determined by headspace solid phase microextraction (HS-SPME) combined with GC-MS. 2.0 g kernel was weighed accurately and were cut into 2.0 mm³ small pieces to be preheated for 18 min at 58.5 °C with headspace sampler oven before it was moved to 15 mL headspace sample bottle. Aroma ingredients were detected by Agilent 7890A GC + 5975C inert XL MSD after 50 min extraction (65 μm PDMS/ DVB fiber) with automatic injection. The samples were analyzed with a HP-5MS capillary column (30 m × 0.320 mm × 0.25 μm). The injection temperature was 230 °C (split ratio 20:1). The initial separation temperature was kept at 40 °C for 3 min, then it was increased at 10 °C · min⁻¹ to 180 °C, and was maintained for 3 min, then the temperature was increased to 200 °C at 10 °C · min⁻¹ and kept 2 min. The EI ion source temperature, interface temperature and quadrupole temperature was 230 °C, 250 °C and 150 °C separately. The ion mass scanning range was 30-480 m/z. Besides, principal component analysis (PCA) was performed with SPSS 19.0 software for data processing. 【Results】 36 volatile aroma compounds were detected in the nine varieties, including 7 aldehydes, 5 alcohols, 5 alkanes and 5 esters, 4 acids, 3 phenolics, 1 ether, 1 ketone and 5 other substances. The contents of nonyl alcohol, octanol, pentadecane, do-

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decane, eugenol, nonaldehyde, phenylacetaldehyde and methyl palmitate, myristic acid, ethylhexyl carbonate, palmitic acid, geranyl acetone, octane, n-pentafuran and o-dichlorobenzene were relatively higher in Yanshan Chinese chestnut. The main aroma components in different chestnut varieties and their relative contents were different. The content of phenylacetaldehyde in ‘Yanshanduanzhi’ was the highest (72.21%), followed by phenylthanol. The content of n-pentafuran in ‘Yankui’ was the highest (28.11%), followed by methyl palmitate. The content of geranyl acetone in ‘Yanli’ was the highest (24.19%), followed by nonaldehyde and decanal. Aldehydes was the primary aroma compound in ‘Yanlong’, its content was 94.19%, and the content of phenylacetaldehyde was the highest (47.08%) in ‘Yanlong’. The content of phenylacetaldehyde in ‘Yanzi’ was the highest (31.31%), followed by decanal and octane. Isopropyl myristate in ‘Yanshanzaofeng’ was the highest (29.53%), followed by palmitic acid, phenylacetaldehyde and phenylthanol. The content of n-pentafuran was the highest in ‘Zipo’ (56.44%), and the contents of isopropyl myristate, phenylacetaldehyde, decanal and azulene were 3.06%-26.96%. The content of o-dichlorobenzene in ‘Zunyu’ was the highest (29.29%), followed by pentadecane. The characteristic aroma was different among the nine varieties. The main aroma compounds of ‘Dabanhong’ were nonyl alcohol, hexyl alcohol, eugenol, nonaldehyde, decanal, 5,9,13-tetradecenal, undecanal and dodecanal. The main aroma compounds of ‘Yanshanduanzhi’ were phenylthanol, methyl palmitate, isopropyl myristate and myristic acid. The main aroma compounds of ‘Yankui’ were dodecane, 2,5-bis(1-phenyl)butyl phenol, phenylacetaldehyde and 2-methylpropionate. The main aroma compounds of ‘Yanli’ were nonyl alcohol, nonaldehyde, decanal, methoxyphenyloxime and methyl palmitate. The main aroma compounds of ‘Yanlong’ were nonaldehyde and decanal. The main aroma compounds of ‘Yanzi’ were 2,6-bis(1,1-dimethylethyl)-4-phenol, octane and ethylhexyl carbonate. The main aroma compounds of ‘Yanshanzaofeng’ were phenylthanol, 5,9,13-tetradecenal, methyl palmitate, isopropyl myristate, palmitic acid, cis-9-cetenic acid, n-pentadecanoic acid and myristic acid. The main aroma compound of ‘Zipo’ was n-pentafuran. The main aroma compounds of ‘Zunyu’ were decanal and methyl palmitate. The content of phenylacetaldehyde was higher in eight chestnut varieties except ‘Yanli’. And although the relative content of phenylacetaldehyde in ‘Yanshanduanzhi’, ‘YanLong’ and ‘Yanzi’ was 72.21%, 47.08%, 31.31%, respectively, but phenylacetaldehyde was not the main aroma compounds to the three varieties. On the contrary, the contents of methyl palmitate, isopropyl myristate, nonaldehyde, ethylhexyl carbonate and myristic acid were lower than phenylacetaldehyde, but they were the most important aroma compounds of the three varieties. Phenylacetaldehyde is only the main aroma components of aldehydes to ‘Yankui’. The relative content of decanal was lower than that of phenylacetaldehyde in 9 varieties, but it was the main contributor of aroma compounds in the 4 varieties of ‘Dabanhong’, ‘Yanlong’, ‘Yanli’ and ‘Zunyu’. Octanol, geranyl acetone and (E)-nonenal were relatively higher, but did not appear in the main aroma compounds.【Conclusion】The composition of the characteristic aroma compounds of the nine Yanshan Chinese chestnut varieties at maturity was different. The comprehensive scores of the aroma compounds in the nine Yanshan Chinese chestnut varieties were ranked as follows: ‘Danbanhong’ > ‘Yanli’ > ‘Yanshanzaofeng’ > ‘Yanzi’ > ‘Zunyu’ > ‘Zipo’ > ‘Yankui’ > ‘Yanlong’ > ‘Yanshanduanzhi’. Decanal was the aroma substance contained in all of the nine varieties, and its content was relatively higher. The main aroma compounds of the nine varieties were alcohols, esters and aldehydes. Aldehydes would play an important role in??. And it was a substance with larger amount among the characteristic aroma components. Decanal, nonaldehyde, methyl palmitate and isopropyl myristic acid were the main characteristic aroma compounds in the nine Yanshan Chinese chestnut varieties at maturity.

Key words: Yanshan Chinese chestnut; Maturity; Main aroma; HS-SPME/GC-MS; PCA

燕山板栗营养丰富,素有“干果之王”的美誉,更因其香甜糯的独特口感而备受消费者青睐^[1]。生板栗做为板栗加工的原料,成熟时各品种的香气构成不仅影响着其贮藏加工品质,也影响着该品种在产业中的发展,因此板栗香气研究逐渐受到关注^[2-3]。

相较于水果^[4-8]、茶^[9-11]等食品的风味物质分析,国内对板栗的香气研究略少。叶兴乾等^[12]、崔亚辉等^[13]对炒板栗和烤板栗的香气成分比较分析发现,2-戊基呋喃、4-羟基-2-丁酮、3-甲基-1-丁醇和苯甲醛是主要特征性挥发物。板栗切片膨化后,挥发性成分复杂,其中醛类最多,分析认为己醛、壬醛、羟基丙酮和雪松醇对膨化的板栗风味贡献较大^[14],其中的雪松醇主要体现杉木芳香,这种物质在其他关于板栗的香气研究中报道很少。对即食板栗仁进行超高压杀菌处理后,其风味物质构成发生改变,产生苯乙烯、棕榈酸等新的物质,而异戊醛、5-羟甲基糠醛等原有的特征性香气物质消失^[15]。郭豪宁等^[16]研究认为5-羟甲基糠醛、2-羟基- γ -丁内酯和2,5-二甲基-4-羟基-3(2H)-呋喃酮是峰甘板栗中的特征性风味物质。魏宾等^[17-18]采用ATD-GC/MC方法检测板栗花中挥发性香气,发现酯类和醇类是构成板栗花香气的主要成分。王琳等^[19]、高洁等^[20]分析认为板栗发酵酒的挥发性香气以酯类物质为主,其次是醇类化合物。梁建兰等^[2]研究发现板栗果仁在干燥粉碎后,主要香气成分发生显著变化的是1-羟基-2-丙酮、糠醛、乙酸等物质。迄今为止,板栗的香气研究主要集中在板栗不同熟制方式和加工产品等方面,关于板栗品种和采后香气品质的研究鲜见报道。

中国拥有优秀的板栗种质资源,但长期以来板栗果实品质育种目标多集中在丰产、甜糯和抗性等方面^[21-27],由于对资源的香气特征不明确,长期忽视香味品质性状,资源优势未得到充分利用。本研究采用顶空固相萃取结合气质联用技术(HS-SPME/GC-MS)对成熟时的‘燕山早丰’‘大板红’‘燕山短枝’‘燕奎’‘遵玉’‘紫珀’‘燕龙’‘燕紫’‘燕丽’9个燕山板栗品种进行香气成分检测,用主成分法分析香气构成,以期对板栗育种和优化贮藏技术提供科学的指导,同时为后续板栗长期贮藏期间香气代谢研究奠定基础。

1 材料和方法

1.1 材料

2017年9月于河北省唐山市迁西县和遵化市采收充分成熟的9个燕山板栗品种(‘燕山早丰’‘大板红’‘燕山短枝’‘燕奎’‘遵玉’‘紫珀’‘燕紫’‘燕龙’‘燕丽’),于 $-2^{\circ}\text{C}\pm 1^{\circ}\text{C}$ 保存,各品种分别在采收后第5天进行HS-SPME/GC-MS检测。每个样品重复分析3次。

1.2 方法

1.2.1 样品处理方法 将去壳后的生栗仁切成 2.0 mm^3 左右的小块,准确称取 2.0 g 于 15 mL 顶空样品瓶内,置 58.5°C 的顶空进样器加热炉内预热 18 min ,之后萃取 50 min ($65\text{ }\mu\text{m}$ PDMS/DVB 萃取头)并自动进样开始GC-MS检测。

1.2.2 检测条件 气质联用仪:Agilent 7890A GC + 5975C inert XL MSD,自动进样器为Sampler 80。

色谱条件:HP-5MS 石英毛细柱($30.0\text{ m}\times 320\text{ }\mu\text{m}\times 0.25\text{ }\mu\text{m}$),载气为He(99.999%),流量 $1.0\text{ mL}\cdot\text{min}^{-1}$,分流比20:1,进样口温度 230°C ,分离起始温度 40°C ,保持 3 min ,以 $10^{\circ}\text{C}\cdot\text{min}^{-1}$ 升至 180°C ,保持 3 min ,再以 $10^{\circ}\text{C}\cdot\text{min}^{-1}$ 升至 200°C ,保持 2 min 。

质谱条件:EI离子源,电子能量 70 eV ,离子源温度 230°C ,接口温度 250°C ,四极杆温度 150°C , $30\sim 480\text{ m/z}$ 范围内进行质量扫描。各组分质谱数据经NIST 11 谱库检索及查阅相关资料来确定香气成分。

1.2.3 数据分析方法 运用面积归一化法计算得各香气成分的相对含量^[2,28]。

用SPSS 19.0 软件进行主成分分析。首先根据特征值和累积贡献率确定主成分数,然后对变量进行标准化处理得到各成分的得分系数,由此可以列出每个主成分的函数,函数表达式为 $f_n=a_1\cdot\chi_1+a_2\cdot\chi_2+\dots+a_n\cdot\chi_n$ (其中 a 为系数, χ 为香气化合物, n 为主成分数);将标准化值代入函数表达式可以计算出每个样品的主成分得分,得分最高者为该样品的最佳因子,最佳因子结合香气成分检测结果可以逐一确定各品种的主要香气化合物。

2 结果与分析

2.1 9个燕山板栗品种成熟时香气成分种类比较分析

表1显示,9个燕山板栗品种共检测到36种香气物质,其中‘大板红’14种,‘燕山短枝’4种,‘燕奎’9种,‘燕丽’和‘燕紫’各8种,‘燕龙’和‘紫珀’各

表 1 9 个燕山板栗品种香气成分检测结果

Table 1 Detection results of the aroma compounds in nine varieties of Yanshan Chinese chestnut

化合物种类 Compound classification	化合物 Compound	化合物相对含量 Compound relative content/%								
		大板红 Da banhong	燕山短枝 Yanshan Duanzhi	燕奎 Yankui	燕丽 Yanli	燕龙 Yanlong	燕紫 Yanzi	燕山早丰 Yanshan Zaofeng	紫珀 Zipo	遵玉 Zunyu
醇类 Alcohols	壬醇 Nonyl alcohol	10.71	-	-	14.63	-	11.04	-	-	-
	苯乙醇 Phenyl ethanol	5.69	15.87	-	-	5.82	-	13.23	-	-
	辛醇 Octanol	5.90	-	-	13.69	-	-	1.99	-	-
	癸醇 Decyl alcohol	-	-	-	2.77	-	-	-	-	-
	正己醇 Hexyl alcohol	5.90	-	-	-	-	-	-	-	-
小计 Subtotal		22.30	15.87	-	31.09	5.82	11.04	15.22	-	-
烷烃类 Alkanes	十六烷 Cetane	-	-	-	-	-	-	1.44	-	8.21
	十四烷 Tetradecane	-	-	-	-	-	-	-	-	6.34
	十二烷 Dodecane	-	-	10.11	-	-	-	-	-	1.44
	十五烷 Pentadecane	-	-	-	-	-	-	-	-	26.36
	二十六烷 Hexacosane	-	-	-	-	-	-	-	-	5.66
小计 Subtotal		-	-	10.11	-	-	-	1.44	-	48.01
酚类 Phenolic	2,6-二(1,1-二甲ethyl)-4-苯酚 2,6-bis(1,1-dimethylethyl)-4-phenol	-	-	-	-	-	1.55	-	-	-
	丁香酚 Eugenol	11.78	-	-	-	-	-	-	-	-
	2,5-二叔丁基酚 2,5-bitertiary butyl phenol	-	-	4.74	-	-	-	-	-	-
	小计 Subtotal		11.78	-	4.74	-	-	1.55	-	-
醛类 Aldehydes	苯乙醛 Phenylacetaldehyde	10.68	72.21	16.26	-	47.08	31.31	13.24	26.96	7.79
	壬醛 Nonaldehyde	15.32	-	-	20.86	9.31	-	-	-	-
	癸醛 Decanal	31.80	5.82	7.36	17.02	6.13	16.03	3.36	5.97	1.78
	(E)-壬烯醛(E)-Nonenal	-	-	-	-	31.67	-	-	-	-
	5,9,13-十四碳三烯醛 5,9,13-tetradecenal	2.39	-	-	-	-	-	1.90	-	-
	十一醛 Undecanal	1.54	-	-	-	-	-	-	-	-
	十二醛 Dodecanal	1.88	-	-	-	-	-	-	-	-
小计 Subtotal		63.61	78.03	23.62	37.88	94.19	47.34	18.50	32.93	9.57
酯类 Esters	棕榈酸甲酯 Methyl palmitate	0.56	-	11.83	2.07	-	4.69	1.40	-	0.72
	邻苯二甲酸二丁酯 Dibutyl phthalate	-	-	-	-	-	-	-	-	8.35
	肉豆蔻酸异丙酯 Isopropyl myristate	2.94	6.11	-	-	-	-	29.53	3.06	-
	碳酸异辛酯 Ethyl-hexyl carbonate	-	-	-	-	-	13.53	-	-	-
	2-甲基丙酸酯 2-methylpropionate	-	-	4.62	-	-	-	-	-	-
小计 Subtotal		3.50	6.11	16.45	2.07	-	18.22	30.93	3.06	9.07
酸类 Acids	棕榈酸 Palmitic acid	-	-	-	-	-	-	15.40	-	-
	顺式-9-十六碳烯酸 Cis-9-cetenic acid	-	-	-	-	-	-	5.26	-	-
	正十五酸 n-Pentadecanoic acid	-	-	-	-	-	-	2.45	-	-
	肉豆蔻酸 Myristic acid	1.32	-	-	-	-	-	7.37	-	-
小计 Subtotal		1.32	-	-	-	-	-	30.48	-	-
酮类 Ketones	香叶基丙酮 Geranyl acetone	-	-	-	24.19	-	8.94	3.45	-	-
小计 Subtotal		-	-	-	24.19	-	8.94	3.45	-	-
醚类 Ethers	正辛基醚 Octane	-	-	6.06	-	-	12.91	-	-	4.53
小计 Subtotal		-	-	6.06	-	-	12.91	-	-	4.53
其他 Others	甘菊蓝 Azulene	-	-	10.92	-	-	-	-	7.57	-
	甲氧基苯基-肟 Methoxyphenyl-oxime	0.55	-	-	4.77	-	-	-	-	-
	邻二氯苯 o-Dichlorobenzene	-	-	-	-	-	-	-	-	29.29
	萘 Naphthalene	-	-	-	-	-	-	-	-	0.97
	正戊基呋喃 n-pentafuran	-	-	28.11	-	-	-	-	-	56.44
小计 Subtotal		0.55	-	39.03	4.77	-	-	-	64.01	30.26

注：“-”表示未检出。

Note: “-” means undetected.

5种,‘燕山早丰’13种,‘遵玉’11种。醛类是所有供试板栗品种中都含有的一类物质,且‘大板红’‘燕山短枝’‘燕丽’‘燕龙’和‘燕紫’5个品种的醛类物质在挥发性成分中含量最高,为37.88%~94.49%;癸醛是唯一在9个品种中都含有的香气化合物,含量为1.78%~31.80%;除燕丽外,8个板栗品种均含有苯乙醛,含量为7.79%~47.08%。各品种检测的化合物种类不同,分布在醇、醛、酸、酯、醚、酚、烷烃和酮醚等物质中,其中醇类、酯类和醛类是9个燕山板栗品种主要的香气化合物种类。

2.2 9个燕山板栗品种香气成分相对含量比较分析

根据化合物的相对含量,壬醇、辛醇、十五烷、十二烷、丁香酚、苯乙醛、壬醛、棕榈酸甲酯、肉豆蔻酸、碳酸异辛酯、棕榈酸、香叶基丙酮、正辛基醚、正戊基呋喃和邻二氯苯这15种成分是板栗中含量比较高的香气化合物,但不同品种的主要香气化合物类别及其相对含量有差异。‘大板红’‘燕丽’和‘燕紫’均有壬醇,且燕丽与大板红和燕紫中壬醇含量差异显著($p < 0.05$)。‘大板红’‘燕山短枝’‘燕龙’和‘燕山早丰’均有苯乙醇,燕山短枝和‘燕山早丰’与‘大板红’和‘燕龙’间差异显著($p < 0.05$),短枝与其余3个品种相比差异极显著($p < 0.01$)。‘大板红’中癸醛含量最高(31.80%),其次是壬醛和丁香酚。‘燕山短枝’中苯乙醛含量最高(72.21%),其次是苯乙醇。‘燕奎’中正戊基呋喃含量最高(28.11%),其次是棕榈酸甲酯。‘燕丽’中香叶基丙酮含量最高(24.19%),其次是壬醛和癸醛。‘燕龙’中4种醛类物质含量占到94.19%,其中苯乙醛含量最高,达47.076%,壬醛、(E)-壬烯醛、癸醛含量在5.8%~32.0%,另一种物质苯乙醇含量为5.82%。燕紫中苯乙醛含量最高(31.31%),其次是癸醛和正辛基醚。‘燕山早丰’中肉豆蔻酸异丙酯含量最高(29.53%),其次是棕榈酸、苯乙醛和苯乙醇。‘紫珀’中正戊基呋喃含量最高,达56.44%,肉豆蔻酸异丙酯、苯乙醛、癸醛和甘菊蓝含量在3.06%~27.0%。‘遵玉’中邻二氯苯含量最高(29.285%),其次是十五烷。

2.3 9个燕山板栗品种香气成分的主成分分析

对测得的9个燕山板栗品种香气成分进行主成分分析,通过主成分特征值及贡献率表(表2)可知,前7个特征根都大于1,累积方差贡献率达97.696%,说明它们可以一起解释原始变量的绝大部分信息,因此选取前7个主成分的数据作为9个品

种数据分析的有效成分。

表2 9个燕山板栗品种香气成分的特征值和累计贡献率
Table 2 Cumulative contribution rates and initial eigenvalues of the aroma components in nine varieties of Yanshan Chinese chestnut

主成分 Principal component	特征值 Eigenvalue	贡献率 Percent of variable/%	累计贡献率 Cumulative percent of variable/%
1	8.408	23.357	23.357
2	6.800	18.889	42.245
3	6.658	18.495	60.740
4	4.942	13.728	74.468
5	3.806	10.572	85.040
6	3.264	9.067	94.107
7	1.292	3.589	97.696
8	0.830	2.304	100.000

对7个主成分中的各个变量进行标准化处理后得到成分得分系数矩阵(表3),竖读矩阵,可列出7个主成分的得分函数,函数表达式为 $f_n = a_1 \times \chi_1 + a_2 \times \chi_2 + \dots + a_n \times \chi_n$ (其中a为表3中所示系数, χ 为香气化合物, $n=1,2,3,4,5,6,7$)。将9个燕山板栗品种香气成分的标准化值代入各函数,即得9个品种的主成分得分(表4)。表4所示 $f_1 \sim f_7$ 中数值最大的即为该品种最佳因子,并结合表1可确定各品种主要香气化合物,即:

‘大板红’最佳因子为第1公共因子,则大板红主要香气化合物为:壬醇、正己醇、丁香酚、壬醛、癸醛、5,9,13-十四碳三烯醛、十一醛、十二醛。

‘燕山短枝’最佳因子为第2公共因子,则燕山短枝主要香气化合物为:苯乙醇、棕榈酸甲酯、肉豆蔻酸异丙酯、肉豆蔻酸。

‘燕奎’最佳因子为第5公共因子,则燕奎主要香气化合物为:十二烷、2,5-二叔丁基酚、苯乙醛、2-甲基丙酸酯。

‘燕丽’最佳因子为第3公共因子,则燕丽主要香气化合物为:壬醇、壬醛、癸醛、甲氧基苯基-呋、棕榈酸甲酯。

‘燕龙’最佳因子为第1公共因子,则燕龙主要香气化合物为壬醛和癸醛。

‘燕紫’最佳因子为第6公共因子,则燕紫主要香气化合物为:2,6-二(1,1-二甲基乙基)-4-苯酚、正辛基醚、碳酸异辛酯。

‘燕山早丰’最佳因子为第2公共因子,则燕山早丰主要香气化合物为:苯乙醇、5,9,13-十四碳三

表3 主成分得分系数矩阵

Table 3 Scoring coefficient matrix of principal components

化合物 Compound	主成分 Component						
	1	2	3	4	5	6	7
壬醇 Nonanol	0.068	-0.035	0.098	-0.039	0.012	0.119	-0.010
苯乙醇 Phenylthanol	0.031	0.095	-0.058	0.002	-0.067	-0.062	0.232
辛醇 Octanol	0.042	-0.019	0.062	-0.147	0.100	-0.036	0.015
癸醇 Decyl alcohol	0.039	-0.034	0.072	-0.138	0.089	-0.047	0.015
正己醇 Hexyl alcohol	0.060	0.030	0.065	0.144	0.030	0.012	-0.001
十六烷 Pentadecane	-0.099	0.053	0.054	0.005	0.051	0.026	0.022
十四烷 Tetradecane	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
十二烷 Dodecane	-0.015	-0.085	-0.069	0.054	0.142	0.012	0.208
十五烷 Pentadecane	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
二十六烷 Hexacosane	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
香叶基丙酮 Geranyl acetone	0.042	-0.034	0.063	-0.152	0.053	0.056	0.002
萘 naphthalene	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
2,6-二(1,1-二甲基乙基)-4-苯酚 2,6-bis(1,1-dimethylethyl)-4-phenol	0.004	-0.043	0.005	-0.022	-0.126	0.250	-0.035
丁香酚 Eugenol	0.060	0.030	0.065	0.144	0.030	0.012	-0.001
2,5-二叔丁基酚 2,5-bitertiary butyl phenol	-0.015	-0.085	-0.069	0.054	0.142	0.012	0.208
邻二氯苯 <i>o</i> -Dichlorobenzene	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
正辛基醚 Octane	-0.037	-0.067	-0.004	0.008	-0.044	0.248	0.067
苯乙醛 Phenylacetaldehyde	-0.001	-0.007	-0.059	0.013	-0.207	-0.090	0.153
壬醛 Nonaldehyde	0.072	-0.011	0.098	-0.031	0.053	-0.083	0.143
甘菊蓝 Azulene	-0.016	-0.087	-0.078	0.053	0.108	-0.046	-0.242
癸醛 Decanal	0.083	-0.020	0.082	0.074	0.012	0.072	0.000
(<i>E</i>)-壬烯醛 (<i>E</i>)-Nonenal	0.002	-0.001	-0.011	-0.007	-0.110	-0.130	0.344
5,9,13-十四碳三烯醛 5,9,13-tetradecenal	0.061	0.096	0.007	0.086	0.076	0.061	-0.001
十一醛 Undecanal	0.060	0.030	0.065	0.144	0.030	0.012	-0.001
十二醛 Dodecanal	0.060	0.030	0.065	0.144	0.030	0.012	-0.001
2-甲基丙酸酯 2-methylpropionate	-0.015	-0.085	-0.069	0.054	0.142	0.012	0.208
正戊基呋喃 <i>n</i> -pentafuran	-0.012	-0.059	-0.060	0.035	0.042	-0.082	-0.562
甲氧基苯基-脒 Methoxyphenyl-oxime	0.046	-0.031	0.080	-0.123	0.093	-0.046	0.015
棕榈酸甲酯 Methyl palmitate	-0.008	-0.094	-0.057	0.023	0.123	0.116	0.202
邻苯二甲酸二丁酯 Dibutyl phthalate	-0.101	0.034	0.066	0.014	0.038	0.012	0.022
肉豆蔻酸异丙酯 Isopropyl myristate	0.023	0.114	-0.075	-0.038	0.055	0.051	-0.043
碳酸异辛酯 Ethyl-hexyl carbonate	0.004	-0.043	0.005	-0.022	-0.126	0.250	-0.035
棕榈酸 Palmitic acid	0.017	0.108	-0.071	-0.051	0.076	0.077	0.001
顺-9-十六碳烯酸 Cis-9-cetenic acid	0.017	0.108	-0.071	-0.051	0.076	0.077	0.001
正十五酸 <i>n</i> -Pentadecanoic acid	0.017	0.108	-0.071	-0.051	0.076	0.077	0.001
肉豆蔻酸 Myristic acid	0.028	0.114	-0.060	-0.026	0.082	0.080	0.000

表4 主成分得分表

Table 4 Score table of principal components

品种 Variety	f ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇	F	排名 Ranking
大板红 Dabanhong	6.173	0.564	5.298	4.654	-0.067	1.671	5.009	3.54	1
燕山短枝 Yanshanduanzhi	-0.03	1.581	-5.161	1.169	-15.604	-6.752	1.466	-2.74	9
燕奎 Yankui	-0.528	-4.879	-4.935	3.493	3.568	-0.633	-9.111	-1.48	7
燕丽 Yanli	5.784	-2.601	7.709	-6.568	5.081	1.988	3.621	2.25	2
燕龙 Yanlong	1.375	-0.033	-2.049	0.567	-13.051	-9.046	0.778	-2.18	8
燕紫 Yanzi	1.971	-3.184	0.869	-0.523	-7.574	7.664	5.983	0.05	4
燕山早丰 Yanshanzaofeng	2.145	7.772	-5.219	-2.659	1.168	2.541	4.198	1.21	3
紫珀 Zipo	-0.259	-3.948	-5.307	2.771	-2.153	-6.817	29.558	-1.05	6
遵玉 Zunyu	-8.620	2.591	5.151	1.332	1.490	1.770	3.515	0.01	5

烯醛、棕榈酸甲酯、肉豆蔻酸异丙酯、棕榈酸、顺式-9-十六碳烯酸、正十五酸、肉豆蔻酸。

‘紫珀’最佳因子为第7公共因子,则紫珀主要香气化合物为正戊基呋喃。

‘遵玉’最佳因子为第3公共因子,则遵玉主要香气化合物为癸醛和棕榈酸甲酯。

根据各主成分的贡献率和得分可知主成分综合评价指数(表4), $F=f_1 \times 0.24 + f_2 \times 0.19 + f_3 \times 0.18 + f_4 \times 0.14 + f_5 \times 0.15 + f_6 \times 0.91 + f_7 \times 0.36$ 。综合排名第一为‘大板红’,最后为‘燕山短枝’。

3 讨论

果实的特征香气成分对其风味和品质起着主要作用,不同种类的果实,其挥发性物质的组成不同,特征香气成分差异很大。 γ -癸内酯、丁酸甲酯、丁酸乙酯、己酸甲酯、2,5-二甲基-4-甲氧基-3(2H)呋喃酮、沉香醇、(E)-2-己烯醛是草莓的主要特征香气物质^[5]。在130种菠萝蜜香气成分中以酯类物质为主,异戊醇是9个品系都具有的特征香气成分^[6]。以C6-C12偶数碳原子的 γ 和 δ 内酯形式存在的内酯类物质是桃果实香味影响最大的特征香气成分^[29]。本研究中,检测到的特征香气物质有3种醇、7种醛、4种酯、4种酸、2种酚。‘紫珀’的特征香气物质为正戊基呋喃,主要体现果香及类似蔬菜青香的香韵。癸醛是9个品种都含有的香气成分,癸醛、壬醛、棕榈酸甲酯和肉豆蔻酸异丙酯是燕山板栗重要的特征性香气物质。

果实的香气品质受香气化合物含量和各化合物组成比例等多方面的影响^[30]。在桃果实检测到的挥发性成分中, γ -己内酯在内酯类香气物质中含量最高,但对香气形成的作用小;而检测到的酮类物质含量较低,但对桃香气品质的影响较大^[29]。‘燕山短枝’‘燕龙’和‘燕紫’中苯乙醛相对含量最高(分别为72.207%、47.076%、31.314%),但对这3个品种香气做出主要贡献的化合物中不含苯乙醛,而棕榈酸甲酯、肉豆蔻酸异丙酯、壬醛、碳酸异辛酯、肉豆蔻酸等含量较苯乙醛低的物质却成为这些品种主要香气化合物之一。另外,9个品种均检测到了癸醛,相对含量较苯乙醛低,但癸醛是‘大板红’‘燕龙’‘燕丽’和‘遵玉’4个品种的特征香气主要贡献者,体现柑橘类香气,其它5个品种的特征香气中不含有癸醛。辛醇、香叶基酮和(E)-壬烯醛相对含量较高,但并没有出

现在主要的特征性香气物质中;苯乙醛是8个品种均含有且相对含量较高的香气物质,但只出现在‘燕奎’的特征香气成分中,这些物质在板栗香气中的作用还有待进一步分析。

风味物质化学构成不稳定,很容易受到外界环境影响^[31]。报道称燕山板栗的香气化合物主要由醛类、酯类、醇类、酮类和酸类构成,但生板栗和不同加工方式的熟板栗表现出来的香型差别大^[3,12,13]。炒板栗和烤板栗以焦甜香味为主,煮板栗以甜香为主,少了焦香味,生板栗则以清雅的花香和果香为主。‘大板红’‘燕龙’‘燕丽’和‘遵玉’主要表现为醛类物质的香型,并以清甜的玫瑰花、绿茶、柑橘和甜橙的混合香型为主。‘燕山早丰’和‘燕山短枝’为醇、酸、酯、醛的混合香型,香气较淡。‘燕奎’主要香气化合物中含苯乙醛,有玉簪花的香气。梁建兰等^[2]对板栗粉碎前后香气成分进行检测,发现‘大板红’在干燥粉碎过程中消失了3-糠醛等8种香气成分,相对于新鲜的生板栗又产生了27种香气物质,其中酮类12种,醛类4种,酯和醇各2种。不同的产地和栽培管理措施也影响着果实中香气物质构成^[32]。有报道认为5-羟甲基糠醛是‘燕龙’板栗的特征性香气物质^[33],本研究中的燕龙等9个样品均未检出。关于每个燕山板栗品种炒煮前后的香气变化及采收后贮藏过程中挥发性物质变化情况需进一步系统深入的研究。

4 结论

9个燕山板栗品种成熟时的主要香气物质构成差异较大,根据各主成分的综合评价指数,‘大板红’排名第一,最后为‘燕山短枝’。9个品种的香气物质都以醇类、酯类和醛类为主,醛类物质的作用相对更为突出,是特征香气成分中数量最多的一种物质,其中癸醛是9个品种都含有的香气物质,而且相对含量较高。通过主成分分析,癸醛、壬醛、棕榈酸甲酯、肉豆蔻酸异丙酯是9个燕山板栗品种成熟时重要的特征性香气物质。

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