果 树 学 报 2017,34(4):435-443
Journal of Fruit Science

DOI:10.13925/j.cnki.gsxb.20160218

4个四倍体玫瑰香味鲜食葡萄品种与其亲本果实香气成分分析

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摘 要:【目的】分析4个四倍体玫瑰香味鲜食葡萄品种的芳香化合物组分,为深入了解四倍体葡萄品种提供理论依据。【方法】以4个四倍体玫瑰香味鲜食葡萄品种('早黑宝''秋黑宝''晚黑宝'和'四倍体玫瑰香')及其二倍体亲本'瑰宝''早玫瑰香''秋红''玫瑰香'成熟期果实为材料,利用顶空固相微萃取-气质联用技术对果实的芳香化合物组分进行测定,采用面积归一法对香气成分进行定量。【结果】各品种果实芳香物质成分种类和相对含量差异较大。醛类物质相对含量最高,其中2-己烯醛占34.40%~49.81%,'四倍体玫瑰香'与亲本'玫瑰香'无显著差异,'早黑宝'和'晚黑宝'均低于亲本,而'秋黑宝'介于父母本中间;己醛占16.28%~28.43%,'四倍体玫瑰香'显著高于'玫瑰香','早黑宝'与'瑰宝'无显著差异,但低于父本'早玫瑰香','秋黑宝'和'晚黑宝'均高于'瑰宝',但低于父本'秋红'或与'秋红'无显著差异。除'秋红'外,其余7个葡萄果实中均含有相对含量较高的萜烯醇(7.24%~28.60%),'四倍体玫瑰香'最高,'早玫瑰香'最低,'四倍体玫瑰香'仅比'玫瑰香'高出3.94%,'早黑宝'分别比父母本高出20.22%、2.07%,而'晚黑宝'和'秋黑宝'分别比母本低13.21%、7.87%。【结论】里那醇和香叶醇对7个玫瑰香味葡萄品种果实香气贡献最大。二倍体玫瑰香味葡萄加倍后,主要呈香物质相对含量未因染色体加倍而加倍,而与亲本玫瑰香味浓郁程度有关。8个葡萄品种果实芳香物质中的主要成分是C6醛。

关键词:四倍体葡萄;二倍体葡萄;芳香化合物

中图分类号:S663.1 **文献标志码**:A **文章编号**:1009-9980(2017)04-0435-09

Analysis of the aromatic compounds of four tetraploid muscat flavor grapes and their diploid parents

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Abstract:【Objective】In recent years, breeders and consumers pay more and more attention to tetraploid grapes because of their big berry size with less seeds and their high yields. The researchers at the Pomology Institute, Shanxi Academy of Agricultural Science bred three tetraploid grape varieties from colchicine treated hybrid seeds, including 'Zaoheibao' 'Qiuheibao' and 'Wanheibao' with a rose fragrance. While representing one of the inherent properties of grapes, there has been no research on the analysis of the aroma composition between tetraploid and diploid grapes. In order to provide a theoretical basis for further understanding of tetraploid grapes, the aromatic compounds of fruits during their ripening period, we analyzed four tetraploid table grapes with muscat flavor including 'Zaoheibao' 'Qiuheibao' 'Wanheibao' and 'Tetraploid Muscat Hamburg' as well as their diploid parents including 'Guibao' 'Zaomeiguixiang' 'Christmas Rose' and 'Muscat Hamburg'. 【Methods】The berries were collected during August-September 2013 from eight grape vines grown in the breeding vineyards of the Pomology Institute, Shanxi Academy of Agricultural Science in Taigu, China. The samples were frozen using liquid nitrogen and stored in an

收稿日期:2016-07-11 接受日期:2016-11-24

基金项目:"十二五"国家科技支撑计划"鲜食葡萄新品种选育"(2013BAD02B04-03);国家葡萄产业技术体系(CARS-30-yz-4);山西省农业科学院院攻关项目"设施无核翠宝葡萄优质高效栽培模式研究"(YGG1503)

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ultra-low temperature freezer. Then the aromatic compounds of the samples were determined in the College of Horticulture Science and Engineering, Shandong Agricultural University in Taian, China, using a solid phase micro-extraction (SPME) and gas chromatograghy-mass spectrometry (GC/MS). According to the mass spectrometer ion scanning map, the aromatic compounds were quantitatively analyzed by using the area normalization method, taking the average score of 3 repeated tests as the basis for the relative content of the aroma component. All collected data were analyzed using SPSS13.0 and Excel software for statistical analysis.【Results】There were significant differences in types and relative content of the aromatic components among the eight grape varieties. There were primarily seven types of aromatic components in grapes, including alcohol, aldehyde, ketone, ester, olefins, acid and others. There were one or two types of acid in 'Zaoheibao' and 'Zaomeiguixiang', respectively, while there was no acid in the other six grape varieties; in addition, there was no ester in the 'Zaoheibao'. The same aromatic components among the eight grapes were identified as twelve different types, including three types of alcohols, five types of aldehydes, two types of ketone and two types of olefin. The major aromatic compounds found in the eight grape varieties are aldehydes, with a relative content of 56.49%-81.63%, especially 2-hexene aldehyde and hexaldehyde with a green leaf flavor and fruity scent, which were the two richest compounds. The 2-hexene aldehyde was the first rich compound identified, with a relative content of 34.40%-49.81%, which was the richest in 'Qiuheibao' and 'Qiuhong' as tetraploid and diploid grapes, respectively. There were no significant differences in the relative content of 2-hexene aldehyde between 'Tetraploid Muscat Hamburg' and 'Muscat Hamburg'; but the relative content in 'Zaoheibao' and 'Wanheibao' were lower than that in their diploid parents, while that in 'Qiuheibao' was between its parents. Aldehyde was the second rich compound identified, with a relative content of 16.28%-28.43%, which was richest in 'Wanheibao' and 'Qiuhong' as tetraploid and diploid grapes, respectively. 'Tetraploid Muscat Hamburg' had a significantly higher aldehyde content than 'Muscat Hamburg' and the content in 'Zaoheibao' was lower than that in its father 'Zaomeiguixiang'; the ones in 'Qiuheibao' and 'Wanheibao' were significantly higher than that in its mother 'Guibao', yet it was lower in 'Qiuheibao' which was lower than that in its father 'Qiuhong'. Terpenoid compounds and their content are closely related to the unique fragrance of roses in Eurasian grapes, especially in the free form of monoterpene. As shown in the results, except for 'Qiuhong', the rest of the seven rose-fragrant grapes had a high relative content of terpene alcohols (7.24%-28.60%) and all contained linalool and nerol, which with an aroma of rose wood, green sweet orange fragrance flowers and roses, respectively. And except for 'Guibao' among the seven rose fragrance grapes, the rest of the six grapes contained geraniol and citronellol, which has an aroma of light sweet rose, green grass and sweet rose, respectively. The relative content of linalool and geraniol was 4.14%-25.23% in the seven grapes, of which the order from high to low in the four tetraploid grapes was: 'Zaoheibao' 'Tetraploid Muscat Hamburg' 'Wanheibao', and 'Qiuheibao', while that in the diploid grapes was 'Guibao' 'Muscat Hamburg' and 'Zaomeiguixiang'. The relative content of terpene alcohol in 'Tetraploid Muscat Hamburg' was only 3.94% higher than that in 'Muscat Hamburg', while that in 'Zaoheibao' was 2.07%, 20.21% higher than that in its parents 'Guibao' and 'Zaomeiguixiang', respectively. And it was 13.21% and 7.87% lower in 'Wanheibao' and 'Qiuheibao' than that in their parents 'Guibao'.【Conclusion】Linalool and geraniol with the fragrance of the rose wood and light sweet rose fragrance respectively played the most important role in fruit aroma of the seven grapes with a muscat flavor. According to the results, the relative content of the major fragrant substances was not doubled after doubling the chromosome of the diploid rose-fragrant grapes. The aroma rich degree of the tetraploid grape was related to the strength of the parental rose fragrance. The main fruit aromatic substance found in the eight grapes was C6 aldehyde.

Key words: Tetraploid grape; Diploid grape; Aromatic compound

多倍体是指具有3套或者3套以上完整染色体组的生物个体、居群或种。由于多倍体植株通常表现为生长旺盛、枝粗、叶厚、果大、产量高及适应性强等特点，多倍体育种日渐成为培育果树新品种的重要途径[1]。国内外应用秋水仙素诱导葡萄多倍体研究已进行多年[2-9]。2000年之后，国内育种者通过秋水仙素诱变培育出的多倍体葡萄有三倍体无核葡萄——‘无核早红’[10]、‘红标无核’[11]，四倍体葡萄——‘巨峰玫瑰’[8]、‘早黑宝’[12]、‘秋黑宝’[13]、‘晚黑宝’[14]，而四倍体葡萄由于其粒大籽少、产量高等备受育种者和消费者的青睐。

香气是葡萄果实与生俱来的属性之一[15]，因呈香物质的种类、含量和组成比例不同而呈现出不同的香型[16-18]。目前关于多倍体与二倍体葡萄香气的比较还未有报道，而研究四倍体葡萄香气特性对于推广和应用四倍体葡萄具有重要的理论意义。作为葡萄的主要香味类型之一，玫瑰香味深受消费者喜欢，是国内外葡萄的重要育种目标之一。2000年之后我国育成的四倍体葡萄均具有玫瑰香味[8, 12-14]。前人研究表明，玫瑰香味与萜类化合物有关，特别是单萜类[19]，其中的里那醇和香叶醇是主要呈香物质[20]，里那醇+香叶醇+橙花醇+香茅醇之和可能对葡萄的玫瑰香味浓郁程度起重要作用[21]。山西省农业科学院果树研究所自1989年起开展葡萄多倍体化学诱变育种研究，以具有浓郁玫瑰香味的‘瑰宝’为母本，父本分别为‘早玫瑰’和‘秋红’，成功选育出3个四倍体葡萄新品种，包括果肉具有浓郁玫瑰香味的‘早黑宝’[12]、‘晚黑宝’[14]和具有玫瑰香味的‘秋黑宝’[13]。‘四倍体玫瑰香’是我国1997年秋水仙素诱变获得的[22]，笔者以这4个四倍体玫瑰香型葡萄品种和其二倍体亲本‘玫瑰香’‘瑰宝’‘早玫瑰香’‘秋红’葡萄为试材，研究了其果实芳香化合物组分的差异，比较四倍体与二倍体葡萄香气的差异，为了解四倍体葡萄品种果实香气提供参考。

1　材料和方法

1.1　材料

试验时间为2013年8—10月，葡萄果实材料采自山西省农业科学院果树研究所葡萄育种园，葡萄品种8个，分别为‘早黑宝’‘秋黑宝’‘晚黑宝’‘四倍体玫瑰香’‘玫瑰香’‘瑰宝’‘早玫瑰香’‘秋红’，架式均为立架，5 a以上树龄。于各品种成熟期（可溶性固形物含量超过18%），分别从5株葡萄树上采集1个果穗，放冰盒内带回实验室，然后从每个果穗穗尖部、穗中部和穗基部上随机采集20粒成熟度一致的浆果（同时考虑到果穗的阳面和阴面），3次重复，液氮冷冻果粒放-80 ℃冰箱。香气测定在山东省泰安市山东农业大学园艺科学与工程学院进行。

1.2　方法

参照Sánchez-Palomo等[23]的方法，利用顶空固相微萃取-气质联用（HS-SPME-GC-MS）方法测定葡萄果实芳香物质含量，略有改动，参照谭伟等[21]的方法。

1.3　数据处理

对香气物质的定性是根据质谱全离子扫描（Scan）的图谱，结合NIST08和WILEY7比对结果及参考相关文献；定量分析采用面积归一化法，取3次重复平均值作为香气物质的相对含量。应用SPSS13.0和Excel软件进行统计分析。

2　结果与分析

2.1　4个四倍体玫瑰香味葡萄品种及其二倍体亲本果实香气成分种类分析

由表1可以看出，8个葡萄品种果实中香气成分

表1　4个四倍体玫瑰香味葡萄品种和其二倍体亲本香气成分种类（单位：种）

Table 1　Species of aromatic compositions detected in four tetraploid grapes and their parents（Units: species）

品种 Varieties	醇 Alcohol	醛 Aldehyde	酮 Ketone	酯 Ester	酸 Acid	烯烃 Alkenes	其他 Others	总计 Total
四倍体玫瑰香 Tetraploid Muscat Hamburg	16	11	2	3		5	3	40
早黑宝 Zaoheibao	15	11	2		1	3	9	41
秋黑宝 Qiuheibao	16	8	3	2		4	5	38
晚黑宝 Wanheibao	18	11	2	3		4	5	43
玫瑰香 Muscat Hamburg	18	13	2	2		4	5	44
瑰宝 Guibao	12	9	2	1		4		28
早玫瑰香 Zaomeiguixiang	13	10	3	4	2	7	6	45
秋红 Christmas Rose	11	9	2	4		2	3	31

主要有7类，为醇、醛、酮、酯、烯烃、酸和其他，其中醇类物质种类最多，其次为醛类，仅四倍体‘早黑宝’和其二倍体父本‘早玫瑰香’葡萄果实中检测到酸类，而‘早黑宝’和二倍体母本‘瑰宝’中分别未检测到酯类和其他类。8个葡萄品种香气成分中共有的物质有3种醇类、5种醛类、2种酮类和2种烯烃类。与二倍体亲本‘玫瑰香’相比，‘四倍体玫瑰香’中醇和醛的种类减少，酯和烯烃的种类增加。‘早黑宝’中醇和醛的种类多于二倍体亲本‘瑰宝’和‘早玫瑰香’，烯烃的种类减少。‘秋黑宝’和‘晚黑宝’中醇的种类多于二倍体亲本‘瑰宝’和‘秋红’，烯烃的种类均比父本多2种，前者醛的种类比亲本少，酮的种类比亲本多1种，酯则比母本多1种，比父本少2种；后者醛的种类比亲本多2种，酯则比母本多2种，比父本少1种。

由表2可以看出，8个葡萄品种果实中主要的香气成分是醛类，相对含量占56.49%~81.63%。4个四倍体葡萄品种中以‘秋黑宝’最高，‘早黑宝’最低；4个二倍体亲本中以‘秋红’最高，‘玫瑰香’最低。相对含量居第二位的是醇类，占14.23%~39.54%，4个四倍体品种中以‘早黑宝’最高，‘秋黑宝’最低，4个二倍体亲本中以二倍体‘玫瑰香’最高，‘秋红’最低。酮类物质相对含量占1.17%~2.26%，以‘早玫瑰香’中最高，‘四倍体玫瑰香’最低。烯烃类物质相对含量占0.53%~11.90%，‘早玫瑰香’中最高，‘秋红’最低。酯类物质相对含量均低于1.0%，占0~0.79%，

表2 4个四倍体玫瑰香味葡萄品种和其二倍体亲本香气成分种类的相对含量

Table 2 Relative content of aromatic compositions detected in four tetraploid grapes and their parents %

品种 Varieties	醇 Alcohol	醛 Aldehyde	酮 Ketone	酯 Ester	酸 Acid	烯烃 Alkenes	总计 Total
四倍体玫瑰香 Tetraploid Muscat Hamburg	37.32	58.95	1.17	0.48		1.58	99.50
早黑宝 Zaoheibao	39.54	56.49	1.83		0.04	0.83	98.73
秋黑宝 Qiuheibao	26.37	69.18	1.44	0.28		2.34	99.61
晚黑宝 Wanheibao	30.30	64.88	1.44	0.55		2.41	99.58
玫瑰香 Muscat Hamburg	38.39	56.75	1.85	0.71		1.87	99.57
瑰宝 Guibao	37.25	59.64	1.49	0.05		1.57	100.00
早玫瑰香 Zaomeiguixiang	23.39	59.63	2.26	0.79	0.60	11.90	98.57
秋红 Christmas Rose	14.23	81.63	1.99	0.32		0.53	98.70

最高的为‘早玫瑰香’。4个四倍体葡萄品种之间香气成分相对含量有差异，且与亲本二倍体之间也有差异。

2.2 4个四倍体玫瑰香味葡萄品种及其二倍体亲本果实香气成分含量分析

2.2.1 *醛类物质* 4个四倍体玫瑰香味葡萄品种及4个二倍体葡萄品种果实中主要的芳香物质均是醛类，其中主要是2-己烯醛和己醛，均具有绿叶清香和果香（表3）。2-己烯醛相对含量最高，占34.40%~49.81%，四倍体中‘秋黑宝’最高，二倍体亲本中‘秋红’最高，其次是‘瑰宝’，‘玫瑰香’最低；‘四倍体玫瑰香’与二倍体亲本‘玫瑰香’中2-己烯醛相对含量无显著差异，‘早黑宝’和‘晚黑宝’中2-己烯醛相对含量均低于二倍体亲本，‘秋黑宝’中高于二倍体母本‘瑰宝’，低于二倍体父本‘秋红’。

己醛相对含量为16.28%~28.43%，四倍体和二倍体亲本中最高的分别是‘晚黑宝’‘秋红’，最低的分别是‘早黑宝’‘瑰宝’。‘四倍体玫瑰香’己醛相对含量显著高于亲本二倍体‘玫瑰香’；‘早黑宝’中相对含量与二倍体母本‘瑰宝’无显著差异，但低于二倍体父本‘早玫瑰香’；‘秋黑宝’和‘晚黑宝’中相对含量均高于二倍体母本‘瑰宝’，后者与二倍体父本‘秋红’无显著差异，而前者低于‘秋红’。

相对含量居于第三位的是3-己烯醛，占0.25%~1.58%，‘四倍体玫瑰香’中相对含量低于‘玫瑰香’；‘早黑宝’中相对含量低于二倍体母本‘瑰宝’，而高于父本‘早玫瑰香’；‘秋黑宝’和‘晚黑宝’中的均低于二倍体父本‘秋红’。其余醛类相对含量均低于1.0%。

2.2.2 *醇类物质* 第二大类芳香物质醇类，在4个四倍体葡萄品种之间和4个二倍体亲本之间种类和相对含量均有差异（表3）。除‘秋红’未检测到萜烯醇外，其余7个品种果实香气中均检测到相对含量较高的萜烯醇。四倍体中以‘四倍体玫瑰香’含量最高，为28.60%；其次为‘早黑宝’‘晚黑宝’；二倍体‘玫瑰香’和‘瑰宝’萜烯醇相对含量差异不显著，但

表3　4个四倍体玫瑰香味葡萄品种和其二倍体亲本香气成分的相对含量

Table 3　Relative content of aromatic compositions detected in four tetraploid grapes and their parents

化合物种类 Compound categories	化合物名称 Compounds	相对含量 Relative content/%							
		四倍体玫瑰香 Tetraploid Muscat Hamburg	早黑宝 Zaoheibao	秋黑宝 Qiuheibao	晚黑宝 Wanheibao	玫瑰香 Muscat Hamburg	瑰宝 Guibao	早玫瑰香 Zaomei guixiang	秋红 Christmas Rose
醇类 Alcohol	乙醇 Ethanol	7.16 f	8.21 d	10.83 b	7.89 e	11.22 b	9.88 c	13.64 a	10.92 b
	α-甲基-α-(4-甲基-3-戊烯基)环氧乙烷甲醇 α-Methyl-α-[4-methyl-3-pentenyl] oxiranemethanol	0.58 c	0.10 f	1.30 a	0.28 e	0.36 d	0.72 b		
	1-辛烯-3-醇 1-Octen-3-ol	0.05 d	0.14 a	0.04 d	0.09 c	0.08 c	0.04 d		0.11 b
	1-庚醇 1-Heptanol	0.15 c	0.56 a	0.16 c	0.18 c	0.25 b	0.22 b		0.26 b
	1-辛醇 1-Octanol	0.07 ab	0.09 a	0.07 ab	0.09 a	0.10 a	0.07 ab	0.07 ab	0.06 b
	2,2,6-三甲基-6-乙烯基四氢-2H-呋喃-3-醇 2H-Pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl-	0.16 c	0.13 c	0.51 a	0.08 d	0.22 b	0.08 d		
	1-己醇 1-Hexanol	0.33 e	2.22 a	0.53 d	2.62 a	0.66c	0.38 e	0.95 b	0.92 b
	2-乙基己醇 1-Hexanol, 2-ethyl-	0.02 b			0.04 ab			0.03 b	0.06 a
	7-甲基-3-甲烯基-6-辛烯-1-醇 7-Methyl-3-methylene-6-octen-1-ol	0.09 a	0.03 b		0.08 a	0.07 a		0.04 b	
	反式-2-己烯-1-醇 Trans-2-Hexen-1-ol	0.11 c						1.42 a	1.18 b
	叶醇 Cis-3-Hexen-1-ol		0.29 b	0.04 c	0.31 b	0.06 c			0.44 a
	顺-2-己烯-1-醇 Cis-2-Hexen-1-ol		0.31 c	0.68 b	1.04 a	0.52 b	0.35 c		
	2-丙基-1-戊醇 2-Propyl-1-pentanol			0.03 a					
	1-壬醇 1-Nonanol				0.04 a				
	苯乙醇 Phenylethyl Alcohol				0.04 b	0.04 b			0.09 a
	6-甲基-5-庚烯-2-醇 6-methylhept-5-en-2-ol					0.15 a			
	2,5-二甲基-2-乙烯基-4-己烯-1-醇 2,5-Dimethyl-2-vinyl-4-hexen-1-ol						0.12 a		
	4-乙基环己醇 4-Ethylcyclohexanol								0.09 a
	2-乙烯基-2,5-二甲基-4-己烯-1醇 2,5-Dimethyl-2-vinyl-4-hexen-1-ol								0.10 a
萜烯醇 Terprnols	里那醇 Linalol	20.35 b	18.20 c	10.23 e	1.90 f	16.61 d	25.20 a	0.16 g	
	脱氢芳樟醇 Hotrienol	0.10 a		0.15 a		0.13 a	0.09 a		
	橙花醇 Cis-Geraniol	2.36 b	0.69 d	0.62 d	3.99 a	1.94 c	0.03 e	2.21 b	
	异香叶醇 Isogeraniol	0.12 b	0.04 c		0.19 a	0.08 b		0.01 c	
	香叶醇 *Trans*-Geraniol	4.09 cd	7.03 b	0.96 e	11.06 a	4.49 c		3.98 d	
	香茅醇 β-Citronellol	1.58 a	1.50 a	0.07 d	0.38 c	1.41 a		0.81 b	
	松油醇 α-Terpineol			0.15 a			0.07 b	0.03 c	
	4-萜烯醇 4-Terpineol							0.04 a	
醛 Aldehyde	己醛 Hexanol	21.23 b	16.28 d	21.97 b	27.33 a	18.89 c	16.91 d	18.49 c	28.43 a
	3-己烯醛 3-Hexenal	0.98 c	0.52 e	1.15 b	0.90 c	0.80 d	1.05 b	0.25 f	1.58 a
	2-己烯醛 (E)-2-Hexenal	35.27 e	38.12 d	44.65 b	34.40 e	34.95 e	40.32 c	39.83 c	49.81 a
	辛醛 Octanal	0.10 e	0.12 de		0.15 bc	0.17 b	0.13 cd	0.12 de	0.21 a
	壬醛 Nonanal	0.28 b	0.27 b	0.21 c	0.33 ab	0.43 a	0.27 b	0.29 b	0.30 b
	山梨醛 Sorbaldehyde	0.51 c		0.70 b	0.63 b	0.66 b	0.61 b		0.92 a
	癸醛 Decanal	0.23 b		0.16 c	0.18 c	0.34 a	0.24 b	0.22 b	0.21 b
	2-壬烯醛 2-Nonenal, (E)-	0.12 b	0.17 a	0.07 c	0.09 c	0.15 a	0.11 b	0.10 b	0.07 c
	柠檬醛 Citral	0.04 c	0.09 b		0.19 a	0.06 c		0.07 c	
	反式柠檬醛 *Trans*-Citral	0.15 c	0.16 c	0.27 b	0.60 a	0.22 b		0.26 b	
	反式2,6-壬二醛 *Trans*-2-trans-6-Nonadienal	0.04 a				0.04 a			

表3(续) Table 3(continued)

化合物种类 Compound categories	化合物名称 Compounds	相对含量 Relative content/%							
		四倍体玫瑰香 Tetraploid Muscat Hamburg	早黑宝 Zaoheibao	秋黑宝 Qiuheibao	晚黑宝 Wanheibao	玫瑰香 Muscat Hamburg	瑰宝 Guibao	早玫瑰香 Zaomei guixiang	秋红 Christmas Rose
	4-甲基-4-戊烯醛 4-Pentenal, 4-methyl-		0.23 a						
	庚烯醛 Cis-Hept-2-enal		0.10 a		0.08 a	0.04 b			0.10 a
	(2E)-8-氧代-2-壬烯醛 (2E)-8-Oxo-2-nonenal		0.43 a						
酮 Ketone	2-辛酮 2-Octanone	0.94 d	1.52 b	0.90 d	1.18 c	1.51 b	1.26 c	1.80 a	1.76 a
	甲基庚烯酮 5-Hepten-2-one, 6-methyl-	0.23 cd	0.31 b	0.21 d	0.26 c	0.34 b	0.23 cd	0.42 a	0.23 cd
	双氢-2,2,6-三甲基-四氢-2H-吡喃-3-酮 Double hydrogen-2,2,6-trimethyl-4H-2H- pyran-3-ketone			0.33 a					
	2-羟基-2-环戊烯-1-酮 2-Hydroxycyclopent-2-en-1-one							0.04 a	
酯 Ester	癸酸乙酯 Decanoic acid, ethyl ester	0.04 b		0.07 a	0.09 a	0.07 a	0.05 b		0.10 a
	香叶酸甲酯 Methyl geranate$_2$	0.43 b			0.32 b	0.64 a			
	己二酸-2,3-二甲基二甲基酯 Hexanedioic acid, 2,3-dimethyl-, dimethyl ester	0.01 a							
	辛酸乙酯 Octanoic acid, ethyl ester			0.21 a	0.14 b				0.17 ab
	甲酸庚酯 Formic acid, heptyl ester							0.50 a	
	丙酮酸甲酯 Pyruvic acid, methyl ester							0.09 a	
	乙酸香叶酯 Acetic acid, geraniol ester							0.16 a	
	三甲基乙酸苯酯 Pivalic acid, phenyl ester							0.04 a	
	亚硫酸丁烯酯 4-Methyl-1,3,2-dioxathiane 2-oxide								0.01 a
	水杨酸甲酯 Methyl salicylate								0.04 a
酸 Acid	己酸 Hexanoic acid		0.04 b					0.12 a	
	乙酸 Acetic acid							0.48 a	
烯烃 Alkenes	月桂烯 β-Myrcene	0.67 b	0.25 d	1.01 a	1.10 a	0.70 b	0.62 b	0.44 c	0.13 e
	右旋柠檬烯 D-Limonene	0.53 c	0.45 cd	0.84 a	0.86 a	0.73 b	0.68 b	0.75 b	0.40 d
	反式罗勒烯 β-trans-Ocimene	0.09 b		0.16 a	0.13 a		0.08 b		
	罗勒烯β-Ocimene	0.22 b		0.33 a	0.31 a	0.24 b	0.19 c		
	β-法呢烯 (Z)- β-Farnesene	0.07 b						9.77 a	
	2-甲基-1, 5-己二烯 2-Methyl-1,5-hexadiene		0.13 a						
	1-甲烯基-1H-苯并环丙烯 1-Methylene-1H-indene				0.01 a				
	3-乙基环己烯 3-Ethylcyclohexene					0.20 a			
	α-法呢烯 α-Farnesene							0.42 a	
	α-人参烯 (-)-α-Panasinsen							0.19 a	
	1,5-庚二烯 1,5-Heptadiene, (E)-							0.18 a	
	2-乙基环己烯 Cyclohexene, 3-ethyl-							0.15 a	
总计 Total		99.53	98.73	99.61	99.58	99.57	100	98.57	98.70

注:同行数字后不同小写字母表示不同葡萄果实在 $P < 0.05$ 差异显著。

Note: Different small letters indicate significant difference in the same line at $P < 0.05$ among different grapes.

显著高于‘早玫瑰香’。

4个四倍体玫瑰香味葡萄中均检出的单萜类有:里那醇、橙花醇、香叶醇和香茅醇,分别具有玫瑰木香气、青甜橙花和玫瑰花香气、淡甜玫瑰花香气、青草味和玫瑰花香;里那醇以‘四倍体玫瑰香’含量最高,为20.35%,分别是‘早黑宝’‘秋黑宝’和‘晚黑宝’的1.12、1.99、10.71倍;橙花醇以‘晚黑宝’中含量最高,其次为‘四倍体玫瑰香’,‘早黑宝’和‘秋黑宝’中差异不显著;香叶醇含量由高到低依次为‘晚黑宝’‘早黑宝’‘四倍体玫瑰香’‘秋黑宝’;‘早黑宝’和‘四倍体玫瑰香’中香茅醇含量显著高于‘晚黑宝’‘秋黑宝’。‘四倍体玫瑰香’和‘秋黑宝’中均检出有脱氢芳樟醇,含量无显著差异;除‘秋黑宝’外,其余3个四倍体中均检出异香叶醇。

除‘秋红’外,其余3个具有浓郁玫瑰香味的二倍体葡萄品种果实香气均检出里那醇和橙花醇,另外,‘玫瑰香’和‘瑰宝’均检出脱氢芳樟醇,‘玫瑰香’和‘早玫瑰香’均检出香叶醇、异香叶醇和香茅醇,‘瑰宝’和‘早玫瑰香’均检出松油醇。

‘四倍体玫瑰香’与二倍体亲本‘玫瑰香’检出的萜烯醇类种类一样,但相对含量有差异,前者里那醇和橙花醇比后者分别高出3.74%和0.42%。四倍体‘早黑宝’比二倍体母本‘瑰宝’多检出3种萜烯醇,未检出‘瑰宝’中的脱氢芳樟醇和松油醇,检出的里那醇相对含量比‘瑰宝’低7.0%,而橙花醇相对含量显著高于‘瑰宝’;‘早黑宝’未检出二倍体父本‘早玫瑰香’中的松油醇和4-萜烯醇,检出的里那醇、香叶醇和香茅醇相对含量比‘早玫瑰香’高出18.04%、3.05%和0.69%,而橙花醇显著低于‘早玫瑰香’。‘秋黑宝’比二倍体母本‘瑰宝’多检出2种萜烯醇,其中共同检出的里那醇显著低于‘瑰宝’,橙花醇和松油醇则显著高于‘瑰宝’。‘晚黑宝’比二倍体母本‘瑰宝’多检出3种萜烯醇,未检出脱氢芳樟醇和松油醇,其中共同检出的里那醇显著低于‘瑰宝’,橙花醇则显著高于‘瑰宝’。

2.2.3　*酮类物质*　8个葡萄品种果实中均检出2-辛酮和甲基庚烯酮。2-辛酮相对含量为0.90%~1.80%,有花香和草香香气,并伴有木樨草的香气,‘四倍体玫瑰香’中相对含量低于‘玫瑰香’;‘早黑宝’中相对含量高于二倍体母本‘瑰宝’,而低于父本‘早玫瑰香’;‘秋黑宝’和‘晚黑宝’中的均低于二倍体亲本。甲基庚烯酮相对含量低于0.45%,具有柠檬草和乙酸异丁酯般的香气,四倍体品种间、二倍体品种间及四倍体和二倍体亲本间差异较小。

2.2.4　*酯类物质*　酯类物质相对含量为0~0.79%,较低(表3)。‘早黑宝’中未检出酯类物质。除‘早玫瑰香’外,其余6个品种均检出有癸酸乙酯,具有果香、葡萄味,但相对含量为0.10%或低于0.10%。‘四倍体玫瑰香’‘玫瑰香’‘晚黑宝’中均检出有香叶酸甲酯;‘秋黑宝’‘晚黑宝’和其二倍体父本‘秋红’中检出辛酸乙酯,具有果香、甜橙味。‘四倍体玫瑰香’‘早玫瑰香’和‘秋红’中检出的特有酯类分别为1、4、2种。

2.2.5　*烯烃类物质*　烯烃类物质对葡萄香气也具有重要的影响。8个葡萄品种果实中均检出月桂烯和右旋柠檬烯(表3),分别具有香脂气味、柠檬香气,其中‘晚黑宝’中相对含量最高,其次是‘秋黑宝’,两者均高于二倍体亲本‘瑰宝’和‘秋红’;‘四倍体玫瑰香’的右旋柠檬烯相对含量显著低于亲本二倍体‘玫瑰香’;‘早黑宝’中相对含量均显著低于亲本。‘四倍体玫瑰香’比‘玫瑰香’检出的烯烃多2种,未检出1种;‘早黑宝’检出二倍体亲本中未有的烯烃1种,未检出母本和父本中的烯烃分别为2、5种;‘晚黑宝’和‘秋黑宝’中检出了相对含量均高于母本‘瑰宝’的反式罗勒烯和罗勒烯。

2.2.6　*酸类物质*　仅四倍体‘早黑宝’和二倍体母本‘早玫瑰香’中检出微量的己酸,相对含量分别为0.04%、0.12%,后者还检出0.48%的乙酸,其具有烧烤味、煮水果味、甜味、蜂蜜味、药味等多样的风味(表3)。

3　讨　论

萜类物质及其含量与欧亚葡萄特有的玫瑰香味密切相关,含量最丰富的是存在于果皮中的单萜[19],游离态形式的单萜对葡萄果实香气贡献最大。本研究中,4个四倍体葡萄品种中‘四倍体玫瑰香’‘早黑宝’和‘晚黑宝’果肉均具有浓郁的玫瑰香味,4个二倍体亲本中‘玫瑰香’‘瑰宝’和‘早玫瑰香’也具有浓郁的玫瑰香味;四倍体‘秋黑宝’具玫瑰香味,二倍体亲本‘秋红’稍有玫瑰香味。8个品种中仅‘秋红’未检出萜烯醇类香气成分,其余7个品种均检出的单萜醇类有里那醇和橙花醇,除‘瑰宝’外,其余6个葡萄品种中还均检出香叶醇和香茅醇。这4种萜烯醇中,香味最浓的里那醇和香叶醇,是玫瑰香味中的主

要呈香物质，橙花醇和香茅醇起到辅助的作用[20]，这其中里那醇对玫瑰香葡萄果实香气贡献又最大[15]。笔者之前研究了4个无核鲜食葡萄及其亲本的果实香气，结果表明具有玫瑰香味的品种中里那醇+香叶醇+橙花醇+香茅醇之和较高，与玫瑰香味浓郁程度一致；无香味的品种萜烯醇类相对含量极低或无[21]。本研究结果与之基本一致，除‘秋红’外，7个玫瑰香味葡萄果实中，里那醇+香叶醇+橙花醇+香茅醇占7.25%~28.61%，四倍体葡萄中由高到低依次为：‘四倍体玫瑰香’‘早黑宝’‘晚黑宝’‘秋黑宝’；二倍体亲本以‘瑰宝’最高，其次为‘玫瑰香’，‘早玫瑰香’最低。“里那醇+香叶醇”占4.14%~25.23%，四倍体葡萄中由高到低依次为：‘早黑宝’‘四倍体玫瑰香’‘晚黑宝’‘秋黑宝’，二倍体亲本以‘瑰宝’最高，其次为‘玫瑰香’，‘早玫瑰香’最低。

在非玫瑰香型葡萄果实中，己醛、己醇、2-己烯醛等C6化合物的相对含量超过70%[24]，而商佳胤等[25]研究结果中，‘玫瑰香’葡萄果实中低于50%。本研究中，除‘秋红’C6化合物的相对含量为83.28%外，其余7个玫瑰香味葡萄果实香气成分中C6化合物的相对含量为56.69%~69.72%，未超过70%，但高于50%，这可能是由于香气因品种[18,26-27]、产地[28-29]、栽培[25,30-31]等不同所产生的差异。在所有的C6化合物中，2-己烯醛和己醛相对含量较高，占53.84%~78.24%，均具有绿叶清香和果香，其中前者在果实芳香化合物中相对含量最高，占到了34.40%~49.81%，说明8个葡萄品种果实芳香物质中最主要的成分是C6醛。

多倍体葡萄深受育种家的重视，首先是二倍体加倍成四倍体后果粒增大。罗耀武等[22]人工诱变获得的‘四倍体玫瑰香’，果粒显著增大，且保持了二倍体‘玫瑰香’原有的色、香、味，这仅是口感上，关于其香气成分的变化未有报道。本文研究结果表明，‘四倍体玫瑰香’和‘玫瑰香’种类和含量均有差异，前者独有的成分有5种，后者独有的成分有6种，但是两者独有成分的相对含量均较低；而对玫瑰香葡萄果实香气贡献较大的萜烯醇类，‘四倍体玫瑰香’中的相对含量仅比‘玫瑰香’高3.22%，说明‘玫瑰香’染色体加倍后，‘四倍体玫瑰香’葡萄果实主要呈香物质相对含量未因染色体加倍而加倍。另外3个四倍体玫瑰香味葡萄中，‘早黑宝’萜烯醇类含量高于亲本‘瑰宝’和‘早玫瑰香’，而‘晚黑宝’和‘秋黑宝’萜烯醇类含量低于亲本‘瑰宝’，高于‘秋红’。Wu等[32]和Liu等[33]的研究表明，萜类物质在不同的二倍体杂交组合群体中表现出不一样的分离规律，笔者前期的统计研究也表明香味浓的与香味浓的杂交组合后代有香味的比例较大[34]。本研究中的3个四倍体葡萄均由二倍体葡萄杂交后染色体再加倍得到，‘早黑宝’的较浓玫瑰香味可能与父母本均具有浓郁的玫瑰香味有关，而‘晚黑宝’和‘秋黑宝’的玫瑰香味程度可能与母本具有浓郁玫瑰香味，而父本玫瑰香味较淡有关。

4 结 论

7个玫瑰香味葡萄果实中，里那醇+香叶醇含量较高，是玫瑰香味的主要呈香物质，与玫瑰香味浓郁程度基本一致；二倍体葡萄加倍后，四倍体葡萄果实主要呈香物质相对含量未因染色体加倍而加倍，玫瑰香味浓郁程度与亲本玫瑰香味浓郁程度有关；果实中C6醛是8个葡萄品种果实芳香物质中最主要的成分。

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