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Actinidia arguta: volatile compounds in fruit and flowers

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Abstract

More than 240 compounds were detected when the volatile components of the flowers and the fruit from several *Actinidia arguta* genotypes were investigated. Around 60–70 different compounds were extracted from individual tissues of each genotype. Two different methods of volatile sampling (headspace and solvent) favoured different classes of compounds, dependent upon their volatilities and solubilities in the flower or fruit matrices. The compounds extracted from flowers largely comprised linalool derivatives including the lilac aldehydes (**12a–d**) and alcohols (**13a–d**), 2,6-dimethyl-6-hydroxyocta-2,7-dienal (**8**), 8-hydroxylinalool (**9**), sesquiterpenes, and benzene compounds that are presumed metabolites of phenylalanine and tyrosine. Extracts of fruit samples contained some monoterpenes, but were dominated by esters such as ethyl butanoate, hexanoate, 2-methylbutanoate and 2-methylpropanoate, and by the aldehydes hexanal and hex-E2-enal. A number of unidentified compounds were also detected, including 8 from flowers that are so closely related that they are either isomers of one compound or two or more closely related compounds. This is the first report of the presence of a range of linalool derivatives in *Actinidia*.

Keywords: *Actinidia arguta*; Actinidiaceae; Baby kiwifruit; Headspace; Solvent; GC–MS; Flowers; Fruit; Aroma compounds; Lilac alcohols; Lilac aldehydes; Terpenes; Esters; Aldehydes

1. Introduction

Actinidia arguta (Sieb. Et Zucc.) Planch. ex Miq. var. *arguta* is a smooth-skinned grape-sized kiwifruit native to northern China, Korea, Siberia and Japan. It is commercially available in New Zealand as well as several other fruit-producing countries. The fruit and flowers of *A. arguta* have aroma notes distinct from those of the major commercial cultivar (*A. deliciosa* [A. Chev] C.F. Liang et A.R. Ferguson var. *deliciosa* 'Hayward'). Several studies have been performed on the volatile aroma and flavour compounds of kiwifruit fruit (Bartley and Schwede, 1989; Paterson et al., 1991; Young and Paterson, 1990, 1995; Young et al., 1983, 1992), and one on the flowers (Tatsuka et al., 1990). There is a paucity of studies on *A. arguta*. In 'Hayward' fruit, 80–90 compounds have been identified, with ca. 15 shown to be important (Perera et al., 1998; Young and Paterson, 1990, 1995). In artificial systems, increased levels of hex-E2-enal and hexanal enhanced the perceived intensity of kiwifruit flavour, while increased levels of ethyl butanoate enhanced the perception of characteristic kiwifruit flavour (Gilbert et al., 1996). Terpenes are present at very low levels, if at all in headspace analyses, although some are present as glycosides which can be released by enzymatic hydrolysis (Young and Paterson, 1995).

A. arguta fruit have been described as having banana, floral, fruit candy, grassy, green, and melon odours, and blackcurrant, fruit candy, grassy, green, melon, stalky/woody and tropical flavours (unpublished data). Some *A. arguta* flowers sampled in the orchard were described as having sweet, aromatic aromas with magnolia, vanilla, tea-rose and balsam/sandalwood notes (unpublished observations), while others were described as containing strong carnation, honey or citrus-lime aromas. Fresh 'Hayward' flowers were described as tea-rose, sweet, cider, and hawthorn-like.

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This work is an investigation of the volatile compounds present in the flowers and fruit of some *A. arguta* genotypes to determine what makes them distinct from 'Hayward' kiwifruit. The data also suggest tissue specific terpene biosynthetic pathways are operating.

2. Results and discussion

2.1. Different compounds are identified with solvent or headspace extraction depending on the tissue being extracted

A feature of the data in Tables 1 and 2 is the difference between the relative amounts of compounds identified in the headspace and the solvent extracts. The more volatile, lower molecular weight, compounds were more poorly represented in the solvent extracts. This occurred even for compounds that constituted a large proportion of the aroma profile. 3-methylbutanal was present in all headspace extracts (at 20% of total in A4), but was not detected in the solvent extracts of petals of the same flowers.

The solvent extracts displayed a bias towards the higher molecular weight, non-volatile, and wax soluble fatty acid esters (oleates and linoleates) and hydrocarbons (C_{15}–C_{20}). Compounds such as 8-hydroxylinalool, 2-(4-methoxyphenyl)ethanol, 2-(4-hydroxyphenyl)ethanol and squalene were all substantial components of the solvent extract of petals but were not observed in the headspace extracts (Table 1).

The compounds collected by the two sampling methods also reflected their relative solubilities in the sample matrix. While 2- and 3-methylbutanal were detected in the headspace of many of the flower samples and not in the solvent extract, these compounds were not seen in the headspace of the fruit samples but were detected in the solvent extracts (Tables 1 and 2). Because of the polar nature of these aldehydes their air/water (fruit) partition coefficients might be lower than their air/wax (flowers) partition coefficients. Headspace sampling identified which compounds contributed to the aroma of these flowers and fruits. Solvent extraction identified the less-volatile or more matrix-soluble flavour or aroma compounds and possible biosynthetic precursors of some of the volatile compounds.

2.2. Flowers

Sixty to seventy compounds were identified from flowers sampled during petal expansion (Table 1). These could be separated into a number of major groups; the major contributors being terpenes and benzene compounds. A number of linalool derivatives have been recorded for the first time in *Actinidia*, and they were significant components of some extracts. A group of eight unidentified (possibly terpenoid) compounds were also isolated using solvent extraction only. Their mass spectra indicate they may comprise one or more groups of diastereoisomers.

2.2.1. Linalool derivatives

The main groups of compounds in the flowers were four diastereoisomers each of lilac aldehyde (**12a–d**) and lilac alcohol (**13a–d**), which were present in nearly all of the solvent and headspace extracts (Table 1). There are eight possible isomers (four pairs of enantiomers) of each of these compounds, but only four can be resolved on the GC columns used in this study. The amount of lilac alcohol in each sample ranged from 11% (A1) to 57.5% (A7) of the compounds extracted by solvent, with an average value of 32%. The lilac aldehyde content ranged from 0.16% (A1) to 4.7% (A3) of the compounds present, with an average content of 1.4%. Alcohol levels were generally lower in the headspace (12–16%) than in the solvent extracts, while aldehyde levels were higher in the headspace (4–14%).

The lilac compounds have not been reported in previous headspace or solvent extraction studies of 'Hayward' flowers (Tatsuka et al., 1990) or fruit (Bartley and Schwede, 1989; Jordan et al., 2002; Takeoka et al., 1986; Young and Paterson, 1990), and we have also not found them in a range of *A. deliciosa* flowers or fruit, including 'Hayward' (unpublished data). Lilac alcohol (**13**) is proposed to arise via reduction of lilac aldehyde (**12**), which may be biosynthetic derivatives (Fig. 1) of geranyl diphosphate (**1**) via linalyl diphosphate (**2**) and linalool (**3**) (Pichersky et al., 1994; Tollsten and Bergstrom, 1993). Only small concentrations (<1%) of linalool were found in six of the solvent extracts, but linalool was a major component in the headspace of three out of the four headspace extracts (up to 27%, Table 1). Linalool was a minor constituent of an SDE extract of 'Hayward' flowers, but was absent from the headspace extract (Tatsuka et al., 1990).

2,6-dimethyl-6-hydroxyocta-2,7-dienal (**8**) is an intermediate in the chemical synthesis of lilac aldehyde [Fig. 1, (**12**)] from linalool (**3**) (Wilkins et al., 1993), and was identified in three of the *A. arguta* solvent extracts at concentrations of around 10%. It was not observed in the headspace. The first reported natural source of this compound was in a solvent extract of apricot flowers (Watanabe et al., 1974). Two other compounds in apricot flowers that were identified in the *A. arguta* extracts were the Z- and E- isomers of 8-hydroxylinalool[1]

[1] The mass spectral library identifies this compound as 1-hydroxylinalool. However, this is an unrealistic structure and is most likely a mis-naming of 8-hydroxylinalool (**9**). In the present work, the $LiAlH_4$ reduction of 2,6-dimethyl-6-hydroxy-2,7-octadienal (**8**) produced two compounds that the mass spectral library identified as 1-hydroxylinalool. Reduction of this aldehyde would be expected to produce 8-hydroxylinalool (2,6-dimethyl-2,7-octadien-1,6-diol).

Table 1
A. arguta flowers—percentage of each compound as a fraction of the total compounds detected in each sample. Headspace extracts were not carried out for A2, 3, 5, 6, and 7 (all female)

	Solvent extract (headspace extract)								
	Male		Female						
Component	A8	A9	A1	A4	A2	A3	A5	A6	A7
Terpenes									
camphor	–	–	–	0(0.02)	–	–	–	–	–
β-caryophyllene	–	–	0(1.56)	–	–	–	–	–	–
2,6-dimethyl-6-hydroxyocta-2,7-dienal	9.42(0)	9.84(0)	–	8.72(0)	–	–	–	–	–
2,6-dimethylocta-3,7-diene-2,6-diol	–	–	–	–	–	–	–	–	0.3
eucalyptol	–	–	0(0.31)	0(0.10)	–	–	–	–	–
E,E-α-farnesene	–	–	–	–	–	0.89	–	–	–
Z,E-farnesol	0.15(0)	–	–	0.30(0)	–	–	–	–	–
E,E-farnesyl acetate	–	–	–	–	–	1.41	–	–	–
geranylacetone	0.22(0.55)	0(0.65)	0(0.37)	0(0.16)	1.23	0.65	0.76	0.74	0.4
germacrene D	–	–	0(0.48)	–	–	–	–	–	–
hexahydrofarnesylacetone	–	–	–	–	–	0.87	–	–	–
E-8-hydroxylinalool	21.87(0)	8.65(0)	–	7.22(0)	36.2	–	13.24	15.2	0.7
Z-8-hydroxylinalool	0.91(0)	–	–	0.30(0)	2.51	–	0.65	1.7	–
lilac alcohol a (**13a**)[b]	15.85(7.6)	20.9(10.4)	8.3(11.3)	21.4(1.51)	10.64	23.8	16.24	7.02	26
lilac alcohol b (**13b**)	2.55(2.03)	3.28(3.18)	1.04(0)	5.72(0.72)	3.46	9.1	4.52	6.68	7.6
lilac alcohol c (**13c**)	3.21(0.25)	2.39(0.66)	1.21(0.97)	4.5(0.06)	6.32	10.63	6.17	7.84	10.4
lilac alcohol d (**13d**)	3.10(2.02)	0.89(1.97)	0.52(4.0)	4.81(0.62)	3.51	4.08	3.48	4.29	5.4
lilac alcohol formate 1	0(0.78)	–	–	–	–	–	–	–	–
lilac alcohol formate 2	0(0.10)	–	–	–	–	–	–	–	–
lilac aldehyde 1 (**12a**)[b]	0.59(2.88)	1.09(7.31)	0.06(1.69)	0.68(1.65)	1.91	0.24	0.57	0.9	0.3
lilac aldehyde 2 (**12b**)	0.11(2.69)	0.18(0)	0(0.65)	0.11(1.34)	0.62	0.08	0.19	0.15	0.1
lilac aldehyde 3 (**12c**)	0.10(2.15)	0.15(5.19)	0.09(1.18)	0.13(1.29)	1.21	0.08	0.16	0.3	0.1
lilac aldehyde 4 (**12d**)	0.19(1.02)	0.27(1.62)	0(0.47)	0.27(0.77)	0.96	0.08	0.25	0.4	0.1
limonene	–	–	–	–	–	0.01	–	–	–
linalool	0.33(24.1)	0(27.14)	0(0.93)	0.08(10.6)	1.05	–	0.08	0.16	0.07
cis-linalool oxide	0(0.07)	–	–	0(0.07)	–	–	–	–	–
trans-linalool oxide	0(0.25)	–	–	–	–	–	–	–	–
6-methylhept-5-en-2-one	0.15(0.86)	0.20(0.61)	0(0.17)	0.2(0.15)	0.36	0.17	0.16	0.16	0.1
β-myrcene	0(0.19)	0(0.25)	–	0(0.14)	–	–	–	–	–
ocimene	0(0.18)	0(0.30)	0(0.26)	0(0.11)	–	–	–	–	–
E-β-ocimene	0(0.63)	0(2.53)	–	0(1.68)	–	–	–	–	–
phytol	0.15(0)	–	–	–	3.43	13.69	6.74	7.01	–
α-pinene	–	–	0(0.28)	0(0.04)	–	–	–	–	–
β-pinene	–	–	0(0.14)	–	–	–	–	–	–
sabinene	–	–	0(0.61)	–	–	–	–	–	–
squalene	5.62(0)	6.56(0)	11.80(0)	14.59(0)	4.92	–	9.8	14.8	8.5
terpinolene	–	0(0.28)	–	–	–	–	–	–	–
3,7,11,15-tetramethyl hexadeca-6,10,14-trienol	–	–	–	–	1.27	–	–	–	–
Benzenoid compounds									
benzaldehyde	–	0(0.11)	–	0(0.08)	–	–	–	–	–
benzene	0(0.27)	0(0.84)	0(1.91)	0(0.80)	–	–	–	–	–
benzyl alcohol	8.30(0.10)	–	–	–	–	0.16	1.11	–	–
benzyl benzoate	–	–	–	–	–	–	1.74	–	–
ethylbenzaldehyde	0(0.26)	–	–	–	–	–	–	–	–
2-(4-hydroxyphenyl)ethanol	1.42(0)	4.79(0)	11.37(0)	2.71(0)	–	–	2.85	–	–
methoxybenzene	–	–	0(0.12)	0(0.08)	–	–	–	–	–
2-(4-methoxyphenyl)ethanol	13.40(0)	12.56(0)	31.09(0)	2.62(0)	5.47	–	18.27	13.2	0.12
methyl 4-methoxybenzoate	–	–	–	–	–	–	–	–	0.2
methyl salicylate	–	–	–	–	0.1	–	–	–	0.16
naphthalene	–	–	0(2.91)	–	–	–	–	–	–
phenol	–	–	0(0.11)	–	–	–	–	–	–
2-phenylethanal	–	–	–	–	–	–	0.13	–	–
2-phenylethanol	3.26(13.4)	8.18(10.5)	8.58(17.2)	11.5(6.25)	3.81	10.5	4.48	5.42	15.3
2-phenylethyl acetate	0(0.30)	–	–	0(0.10)	–	–	–	–	–
trimethylbenzene	–	–	0(0.33)	–	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

	Solvent extract (headspace extract)								
	Male		Female						
Component	A8	A9	A1	A4	A2	A3	A5	A6	A7
Esters									
ethyl acetate	0(0.05)	–	–	0(0.04)	–	–	–	–	–
ethyl hexanoate	–	–	–	–	0.03	–	–	–	–
hex-Z3-enyl acetate	–	–	–	0(0.32)	–	–	–	–	–
methyl acetate	–	–	–	0(1.20)	–	–	–	–	–
3-methylbutyl acetate	–	–	–	0(0.18)	–	–	–	–	–
Aldehydes									
acetaldehyde	–	0(0.64)	–	0(0.28)	–	–	–	–	–
decanal	0(0.87)	0(1.77)	0(0.13)	0(1.74)	–	–	0.06	–	–
heptanal	0.15(0)	0.40(0)	1.16(0)	0.8(0.21)	0.65	0.48	0.23	0.32	0.4
hexanal	–	–	0(0.32)	–	0.03	0.03	0.04	0.05	0.04
2-methylbutanal	0(0.52)	0(1.11)	0(1.15)	0(1.83)	–	–	–	–	–
3-methylbutanal	0(4.25)	0(2.65)	0(5.83)	0(20.49)	–	–	–	–	–
3-methylbut-2-enal	0(0.01)	–	–	–	–	–	–	–	–
2-methylpropanal	–	–	–	0(0.18)	–	–	–	–	–
nonanal	0(1.07)	6.18(1.4)	15.5(0.8)	10.1(2.1)	2.18	2.72	2.4	1.52	4.7
octanal	–	0(0.45)	0(0.05)	0(0.18)	–	0.04	–	–	0.04
undecanal	–	–	–	–	–	–	–	–	0.08
Ketones									
acetone	0(0.41)	–	0(1.40)	–	–	–	–	–	–
butan-2-one	0(1.83)	0(1.19)	0(2.47)	0(2.20)	–	–	–	–	–
butane-2,3-dione	0(0.10)	–	–	–	–	–	–	–	–
3-hydroxybutan-2-one	0(0.61)	–	–	0(0.99)	–	–	–	–	–
7,8-dihydro-β-ionone	–	–	–	0(0.04)	–	–	–	–	–
β-ionone	–	–	–	0(0.08)	–	–	–	–	–
jasmone	–	0(0.33)	–	–	–	–	–	–	–
2-methylpentan-3-one	–	0(0.19)	–	0(0.07)	–	–	–	–	–
4-methylpentan-2-one	–	0(0.09)	–	0(0.05)	–	–	–	–	–
octan-3-one	–	0(0.56)	–	0(0.15)	–	–	–	–	–
pentadecan-2-one	–	0(0.07)	–	–	–	–	–	–	–
Alcohols									
ethanol	0(0.45)	0(0.54)	0(0.65)	0(13.78)	–	–	–	–	–
butanol	0(0.56)	–	–	0(0.12)	–	–	–	–	–
butan-2-ol	–	0(1.04)	–	0(0.70)	–	–	–	–	–
2-ethylhexanol	–	–	–	0(0.08)	–	–	–	–	–
hexadecanol	–	–	0.52(0)	–	–	–	–	–	–
hexanol	0(0.12)	–	0(0.27)	–	–	–	–	–	–
hex-Z3-enol	–	–	0(0.06)	–	–	–	–	–	–
methanol	0(0.25)	0(0.39)	0(0.62)	0(0.41)	–	–	–	–	–
1-methoxypropan-2-ol	–	–	0(2.36)	0(0.12)	–	–	–	–	–
2-methylbutanol	–	0(4.7)	0(11.4)	0(20.2)	–	–	–	–	–
3-methylbutanol	0.44(20.8)	–	–	–	0.1	0.21	0.12	0.16	0.04
3-methylbut-2-enol	0(0.41)	–	–	–	–	–	–	–	–
3-methylbut-3-enol	0(0.54)	–	–	–	–	–	–	–	–
2-methylbut-3-en-2-ol	0(0.23)	0(0.48)	0(0.50)	0(0.49)	–	–	–	–	–
2-methylpropanol	0(0.53)	0(0.17)	0(0.17)	–	0.03	0.04	0.03	0.06	0.04
nonanol	0(0.19)	0(0.27)	–	0(0.59)	–	–	–	–	–
pentanol	0(0.01)	–	–	–	–	–	–	–	–
pentan-2-ol	–	–	–	–	0.02	5.82	–	–	–
pentan-3-ol	–	0(0.09)	0(0.80)	–	–	–	–	–	–
penten-3-ol	0(0.13)	0(0.27)	0(0.49)	0(0.33)	–	–	–	–	–
propanol	0(0.55)	–	–	–	–	–	–	–	–
octanol	–	–	–	–	–	0.05	0.04	–	0.09
octan-4-ol	–	–	–	–	–	–	–	–	0.03
oct-1-en-3-ol	0(0.86)	–	–	0(1.24)	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

	Solvent extract (headspace extract)								
	Male		Female						
Component	A8	A9	A1	A4	A2	A3	A5	A6	A7
Acids									
acetic acid	–	0(1.44)	0(2.87)	–	–	0.22	0.09	0.17	0.1
dodecanoic acid	–	–	–	–	1.05	–	0.62	0.43	–
heptanoic acid	–	–	–	–	0.44	0.27	0.13	0.17	0.4
hexanoic acid	–	–	–	–	0.11	0.17	0.07	0.17	0.2
3-methylbutanoic acid	–	–	–	–	–	0.36	0.14	0.08	0.5
nonanoic acid	–	–	–	–	2.33	–	1.56	2.6	–
octanoic acid	–	–	–	–	0.11	0.1	0.07	0.02	0.2
Hydrocarbons									
eicosane	–	–	–	–	–	1.05	0.42	–	0.3
heptacosane	–	–	–	0.75(0)	–	–	–	–	–
heptadecane	–	–	–	–	–	0.34	–	–	–
hexacosane	–	–	1.39(0)	–	–	2.75	–	–	–
hexadecane	–	–	–	–	0.09	–	–	–	–
hexa-1,4-diene	–	0(0.41)	–	–	–	–	–	–	–
hexa-Z2,Z4-diene	–	–	0(6.28)	–	–	–	–	–	–
3-methylcyclopentene	0(0.26)	–	–	–	–	–	–	–	–
3-methylpenta-1,3-diene	0(0.24)	–	–	–	–	–	–	–	–
nonacosane	–	–	–	0.23(0)	–	–	–	–	–
nonadecane	–	–	–	–	–	0.48	0.24	–	–
nonane	–	0(0.11)	–	–	–	2.09	–	–	–
octane	–	0(1.10)	–	0(0.01)	–	–	–	–	–
pentacosane	0.30(0)	0.60(0)	2.60(0)	1.65(0)	–	0.4	–	–	0.6
pentadecane	0(0.29)	–	–	–	–	–	0.06	–	–
tricosane	–	–	–	–	2.59	–	1.37	1.26	2.4
Sulphur compounds									
bis(1-methylethyl)disulphide	–	–	–	–	0.03	0.05	–	0.07	0.06
carbon disulphide	0(0.01)	–	0(0.07)	0(0.05)	–	–	–	–	–
dimethyl disulphide	–	–	0(0.88)	–	–	–	–	–	–
Nitrogen compounds									
butanenitrile	0(0.48)	–	–	0(0.80)	–	–	–	–	–
methenamine	–	0(0.64)	–	–	–	–	–	–	–
2-methylbutanenitrile	–	0(0.81)	0(0.32)	0(0.15)	–	–	–	–	–
Furans									
tetrahydrofuran	–	0(0.09)	–	–	–	–	–	–	–
Unidentified compounds[a]									
unknown 6	–	–	0(0.31)	–	–	–	–	–	–
unknown 7	–	–	0(0.37)	–	–	–	–	–	–
unknown 25	–	0(0.32)	–	–	–	–	–	–	–
unknown 27	–	0(1.28)	–	–	–	–	–	–	–
unknown 33	0(0.65)	–	0(11.5)	0(0.23)	–	–	–	–	–
unknown 34	–	–	0(0.02)	–	–	–	–	–	–
unknown 47	0(0.08)	–	–	–	–	–	–	–	–
unknown 59	–	0(1.78)	–	–	–	–	–	–	–
unknown 93	3.21(0)	–	–	–	–	–	–	–	–
unknown 95	0.30(0)	–	–	–	–	–	–	–	–
unknown 100	0.61(0)	–	–	–	–	–	–	–	–
unknown 106	2.89(0)	5.22(0)	2.60(0)	0.30(0)	–	–	–	–	–
unknown 156	0.15(0)	2.09(0)	0.17(0)	0.08(0)	–	0.19	0.2	1.59	0.2
unknown 157	0.91(0)	5.22(0)	1.73(0)	0.23(0)	–	1.22	–	4.49	–
unknown 158	0.03(0)	0.07(0)	0.09(0)	0.03(0)	–	1.79	0.1	0.28	1.8
unknown 159	0.08(0)	0.30(0)	0.09(0)	0.08(0)	–	–	–	–	–
unknown 204	–	–	–	–	–	0.47	–	–	1.1

(*continued on next page*)

Table 1 (*continued*)

Component	Solvent extract (headspace extract)								
	Male		Female						
	A8	A9	A1	A4	A2	A3	A5	A6	A7
unknown 205	–	–	–	–	–	1.51	–	–	10.4
unknown 206	–	–	–	–	–	0.56	–	–	0.5
unknown 207	–	–	–	–	–	0.19	–	–	0.2
unknown 227	–	–	–	–	1.23	–	0.75	0.55	–

[a] The numbering of these unknown compounds is based upon that in our in-house database of compounds in *Actinidia* species and their genotypes. Retention Indices and mass spectral data are listed in Section 4.6.

[b] The configurations of the lilac aldehydes and alcohols is discussed in the last two paragraphs of Section 4.4.

[2,6-dimethylocta-2,7-diene-1,6-diol, (**9**)]. This compound is the reduction product of the above aldehyde (**8**). It was present in the *A. arguta* solvent extracts at concentrations of up to 36%, but it too was not detected in the headspace. Both (**8**) and (**9**) have not been previously reported in 'Hayward' flowers (Tatsuka et al., 1990) and we have not found them in a range of *A. deliciosa* flowers or fruit (unpublished data).

Two headspace samples contained the furanoid form of *trans*- and *cis*-linalool oxide (**6**) at $<0.25\%$ of the headspace (Table 1). Linalool oxide is structurally similar to lilac alcohol (**13**), differing only in the placement of the hydroxyl group on the adjacent carbon atom (Fig. 1). Linalool oxide is thought to be formed from linalool via 6,7-epoxylinalool (**4**) (Pichersky et al., 1994). The other linalool-derived compounds were two

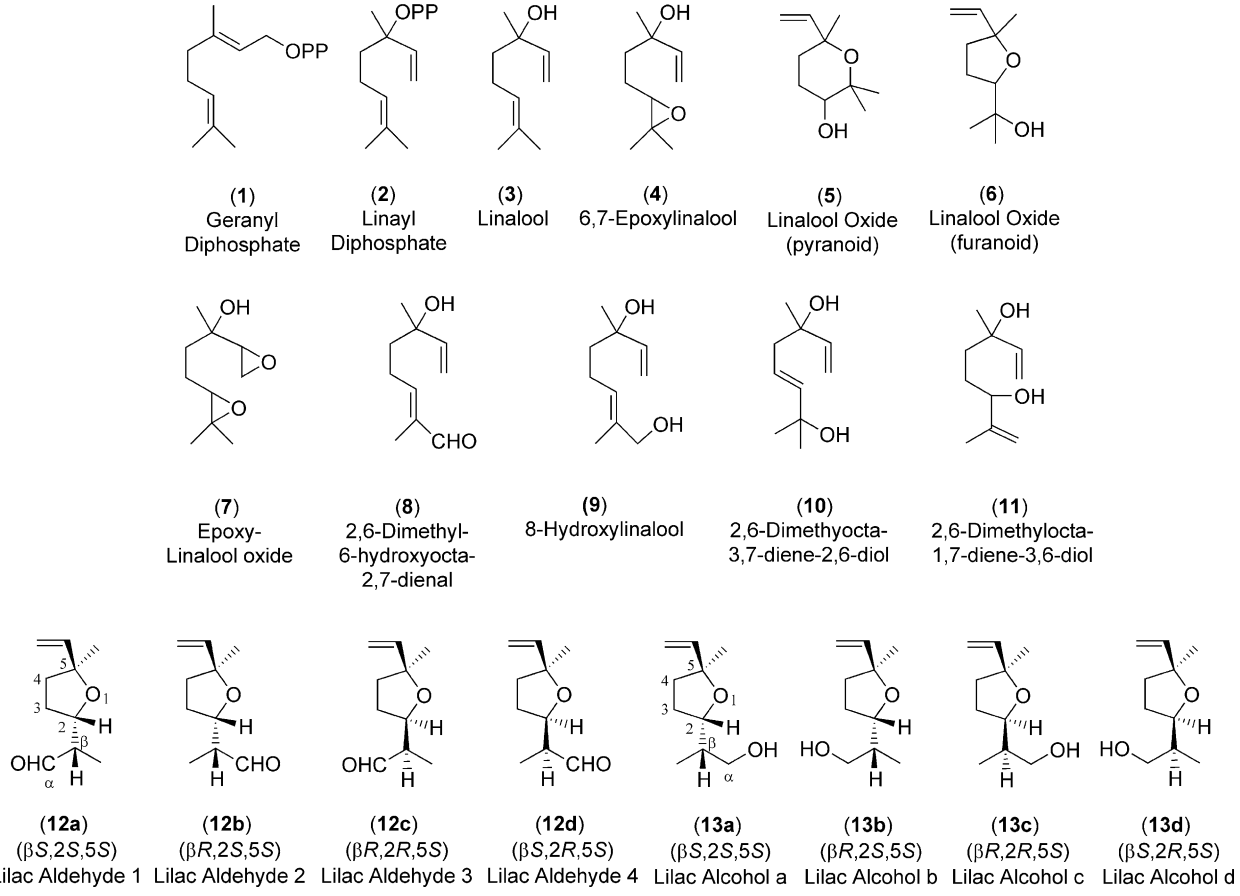

Fig. 1. Structures of compounds identified and of some biosynthetic intermediates. Only one enantiomer of each lilac alcohol and lilac aldehyde diastereoisomer is shown. Assignment of the configurations of the lilac aldehydes and alcohols is discussed in the last two paragraphs of Section 4.4.

Table 2
A. arguta fruit—percentage of each compound as a component of the total compounds detected in each sample

	Solvent extract (headspace extract)				
Component	A1	A3	A5	A6	A7
Terpenes					
camphene	–	–	–	0(0.01)	–
camphor	7.30(0)	10.8(0)	8.52(0)	36.6(0)	–
2-carene	0.21(0)	–	–	–	–
cis-carveol	0.18(0)	–	–	–	–
carvone	0.28(0)	–	–	–	–
p-cymene	–	–	–	0(1.19)	–
endo-5,5,6-trimethylnorbornan-2-one	0.41(0)	0.75(0)	0.93(0)	2.24(0)	–
eucalyptol	0.37(0)	–	0(0.03)	10.9(3.3)	–
limonene	0.02(0)	0.6(0.04)	0.1(0.12)	1.4(1.4)	(0.04)
linalool	0.25(0)	2.2(0.06)	–	–	–
p-mentha-1,3,8-triene	–	–	–	–	(0.08)
p-menth-1-en-4-ol	–	–	–	1.03(0.6)	–
menthol	0.82(0)	–	1.16(0)	2.50(0)	–
6-methylhept-5-en-2-one	0.07(0)	0.09(0)	–	–	(0.02)
1-methyl-4-(1-methylethenyl)benzene	–	–	0(0.37)	0(0.77)	–
1-methyl-4-(1-methylethyl)-cyclohex-2-enol	–	–	–	0.36(0)	–
β-myrcene	–	0(0.04)	0(1.40)	0(1.31)	(0.06)
E-β-ocimene	–	0(0.52)	0(0.04)	0(0.10)	–
Z-β-ocimene	–	0(0.96)	–	–	–
β-phellandrene	–	–	–	0(0.20)	–
α-pinene	0.1(0.12)	0(0.02)	0.27(0)	0(1.42)	–
β-pinene	0(0.72)	–	0.1(0.03)	0(0.72)	–
sabinene	–	–	–	1.61(0)	–
squalene	0.22(0)	0.29(0)	–	–	–
α-terpinene	–	0(0.01)	–	0(0.47)	–
β-terpinene	–	0(0.07)	–	0(0.88)	–
γ-terpinene	–	–	–	1.5(1.07)	–
α-terpineol	1.21(0)	–	–	0.6(0.11)	(1.29)
terpinolene	0(0.06)	4.04(0.2)	0.4(1.21)	0.86(3.3)	–
Benzenoid compounds					
benzyl alcohol	0.70(0)	0.88(0)	–	1.31(0)	–
benzyl benzoate	0.74(0)	–	–	–	–
dimethylbenzaldehyde	0(0.07)	–	–	–	–
1,2-dimethylbenzene	0(0.09)	0(0.01)	–	–	–
ethylbenzaldehyde	–	0(0.04)	–	–	–
ethyl benzoate	5.4(0.04)	6.1(0.12)	0(0.58)	0(0.60)	–
2-(4-hydroxyphenyl)ethanol	–	0.88(0)	–	–	–
methyl benzoate	2.33(0)	0(0.03)	1.04(0.4)	0(0.19)	–
styrene	0.16(0)	–	–	0.27(0)	–
Esters					
butyl acetate	–	–	0(0.01)	–	
dimethyl carbonate	–	0(0.02)	–	–	–
ethyl but-E2-enoate	0.06(0)	0(0.03)	–	–	(0.06)
ethyl acetate	0(0.44)	0(1.93)	0(12.35)	0(0.56)	(0.97)
ethyl butanoate	7.6(2.25)	0(22.5)	0(40.1)	0(23.1)	(65.8)
ethyl decanoate	–	1.2(0.01)	–	0(0.04)	(0.23)
ethyl heptanoate	–	0.17(0)	–	–	–
ethyl hexadecanoate	4.89(0)	–	7.63(0)	–	–
ethyl hexadec-9-enoate	3.51(0)	–	–	–	–
ethyl hexanoate	2.43(0)	29.8(2.0)	0(0.96)	0(0.72)	(1.36)
ethyl hexa-2,4-dienoate	–	0(0.09)	–	–	–
ethyl hex-2-enoate	–	0.2(0.05)	–	–	–
ethyl hex-3-enoate	–	0(0.02)	–	–	–
ethyl linoleate	5.63(0)	0.74(0)	–	0.40(0)	–
ethyl linolenate	7.97(0)	–	4.33(0)	–	–
ethyl 2-methylbutanoate	–	0(6.52)	–	–	–
ethyl 3-methylbutanoate	–	–	–	0(0.01)	–

(*continued on next page*)

Table 2 (*continued*)

Component	Solvent extract (headspace extract)				
	A1	A3	A5	A6	A7
ethyl 2-methylpropanoate	–	0(24.6)	–	–	–
ethyl octanoate	3.80(0)	14.5(0.04)	–	–	–
ethyl oct-Z4-enoate	–	0.85(0)	–	–	–
ethyl oleate	1.05(0)	–	–	–	–
ethyl pentanoate	0.12(0)	0(0.04)	0(0.11)	1.5(0.03)	(0.10)
ethyl propanoate	–	0(0.01)	0(0.79)	0(0.05)	(0.01)
hexadecyl acetate	–	–	–	3.51(0)	–
methyl acetate	–	0(0.02)	0(0.04)	–	(0.01)
methyl butanoate	–	0(0.30)	0(0.78)	0(0.67)	(1.60)
1-methylethyl tetradecanoate	4.04(0.09)	4.23(0)	–	3.23(0)	–
methyl hexadecanoate	8.39(0)	–	16.3(0)	–	–
methyl linoleate	6.70(0)	4.07(0)	19.9(0)	–	–
methyl linolenate	0.65(0)	–	–	–	–
methyl octadecanoate	0.85(0)	0.45(0)	5.4(0)	–	–
methyl oleate	3.99(0)	3.62(0)	17.3(0)	–	–
methyl prop-2-enoate	–	0(0.09)	–	–	–
propyl butanoate	–	–	–	–	(0.002)
Aldehydes					
acetaldehyde	0(1.80)	0(0.04)	–	0(0.05)	(0.04)
decanal	0.50(0)	0.57(0.01)	–	0.29(0)	–
hepta-E2,E4-dienal	0.12(0)	–	–	1.24(0)	–
heptanal	–	0(0.01)	–	–	–
hept-Z2-enal	0.17(0)	–	–	0.86(0)	–
hexanal	1.1(22.5)	0.14(0.26)	0.3(0.13)	1.9(1.30)	(0.35)
hex-E2-enal	1.13(58)	0(2.89)	0.96(1.1)	3.8(5.87)	(3.03)
hex-Z2-enal	0(0.76)	0(0.06)	–	0(0.28)	(0.05)
hex-E3-enal	0(0.08)	–	–	–	–
hex-Z3-enal	0(0.29)	–	–	0(0.02)	–
3-methylbutanal	0.06(0)	–	0.04(0)	–	–
2-methylpentenal	–	0(0.02)	–	–	–
nona-E2,Z6-dienal	0.13(0)	–	–	–	–
nonanal	–	1.00(0)	–	0.4(0.03)	–
non-E2-enal	0.12(0)	–	–	–	–
octanal	0.19(0)	–	–	–	(0.24)
oct-E2-enal	0.06(0)	–	–	–	–
propanal	0(0.09)	–	–	–	–
Ketones					
acetone	0(0.06)	0(0.01)	0(0.02)	0(0.07)	(0.04)
butan-2-one	–	0(0.35)	–	–	(0.64)
cyclopentanone	–	0(0.01)	–	–	–
3-hydroxybutan-2-one	0(0.13)	–	–	–	–
4-hydroxy-4-methylpentan-2-one	0.09(0)	0.34(0)	–	0.95(0)	–
4-methylpent-3-en-2-one	0.06(0)	0(0.01)	0.06(0)	–	–
octan-2,3-dione	0.25(0)	–	–	–	–
penten-3-one	–	0(0.01)	–	–	–
pent-E3-en-2-one	0.13(0)	–	–	2.00(0)	–
Alcohols					
butanol	–	0.23(0)	–	0.94(0)	–
decanol	0.75(0)	0.53(0)	2.13(0)	1.36(0)	–
dodecanol	7.84(0)	5.06(0)	8.86(0)	7.51(0)	–
ethanol	0(11.08)	0(34.71)	0(39.06)	0(48.96)	(22.74)
heptanol	–	–	–	0.37(0)	–
hexadecanol	0.82(0)	–	–	0.76(0)	–
hexanol	0.19(0)	0.23(0.03)	0.2(0.03)	1.8(0.14)	–
hex-E2-enol	0.07(0)	0(0.03)	0(0.03)	0(0.04)	–
hex-Z2-enol	–	–	–	0(0.03)	(0.02)
hex-E3-enol	–	0(0.01)	–	–	–
hex-Z3-enol	0.06(0)	–	–	–	–

(*continued on next page*)

Table 2 (*continued*)

Component	Solvent extract (headspace extract)				
	A1	A3	A5	A6	A7
3-methylbutanol	0.10(0)	–	–	–	–
2-methylpropanol	–	0(0.01)	–	–	–
nonanol	0.19(0)	–	0.41(0)	–	–
octanol	0.97(0)	1.30(0)	1.76(0)	2.48(0)	–
oct-1-en-3-ol	–	–	–	0.18(0)	–
pentanol	–	–	–	1.90(0)	–
pent-E2-enol	–	0(0.01)	–	–	–
penten-3-ol	0(0.11)	0(0.02)	0(0.06)	–	(0.03)
propanol	–	0.09(0)	–	0.57(0)	–
Acids					
acetic acid	–	0(0.32)	0(0.07)	0(0.17)	–
butanoic acid	–	0.30(0)	–	–	–
Hydrocarbons					
heptadecane	0.39(0)	0.51(0)	–	–	–
hexadecane	0.37(0)	0.60(0)	–	–	–
2,6-dimethyldecane	–	–	0.28(0)	–	–
dodecane	–	0.81(0)	0.16(0)	–	–
2-methylpenta-1,3-diene	–	0(0.18)	–	–	(0.53)
2-methoxy-2-methylpropane	–	–	0(0.10)	–	–
nonadecane	0.37(0)	–	–	–	–
octadecane	–	1.11(0)	–	–	–
pentadecane	0.44(0)	–	–	–	–
tetradecane	–	0.61(0)	–	–	–
tridecane	0.18(0)	–	–	–	–
Sulphur compounds					
bis(1-methylethyl)disulphide	0.22(0)	–	–	1.01(0)	–
Furans					
ethyl 2-furancarboxylate	0.29(0)	–	–	–	–
2-furancarboxaldehyde	–	–	–	–	(0.31)
4-methoxy-2,5-dimethyl-3(2H)-furanone	0.11(0)	–	–	–	–
2-methylfuran	–	0(0.58)	–	–	–
5-methyl-2-furfural	–	0(0.02)	–	–	–
methyl 2-furoate	–	–	–	–	0.22
tetrahydrofuran	0(1.51)	–	–	–	–
Unidentified compounds[a]					
unknown 3	–	–	–	0(0.19)	–
unknown 178	–	–	1.44(0)	–	–

[a] The numbering of these unknown compounds is based upon that in our in-house database of compounds in *Actinidia* species and their genotypes. Retention Indices and mass spectral data are listed in Section 4.6.

isomers of lilac alcohol formate, which were found only in the headspace of the flower samples. We have not found these esters, or linalool oxide in the flowers of any *A. deliciosa* genotypes (unpublished data). Both the linalool oxide isomers were reported in the SDE (simultaneous steam distillation solvent extraction) extract of 'Hayward' flowers (Tatsuka et al., 1990), but were not detected in the flower headspace. Linalool oxide may have been an artefact of the steam distillation process.

Varying numbers of lilac aldehyde and lilac alcohol isomers were found together in the *A. arguta* flower samples. Only one unidentified diastereoisomer of each compound was detected at levels of 0.5% in *Artemesia pallens* (davana) (Misra et al., 1991), while four isomers of both compounds were identified at trace levels in the flowers of apricots (Watanabe et al., 1974). In some *Platanthera* (Orchidaceae) flowers four isomers were present at up to 97% of the volatile production (Tollsten and Bergstrom, 1993). Three of the aldehyde isomers were the major lilac compounds in *Planthera stricta* (Patt et al., 1988), and up to three isomers each of the alcohol and aldehyde were also major components of the scent of *Gaura longiflora* (Kint et al., 1993), and of some *Silene* species (Caryophyllaceae) (Jürgens et al., 2002). These compounds have also been extracted

from Haze (*Rhus succedanea*) honey (Shimoda et al., 1996) and from nodding thistle (*Carduus nutans*) honey (Wilkins et al., 1993). 2,6-Dimethyl-6-hydroxyocta-2,7-dienal (**8**) and the furanoid linalool oxide (**6**) have also been reported from apricot flowers and nodding thistle honey, suggesting these pathways may also operate in those species.

2.2.2. Other terpenes

6-Methylhept-5-en-2-one was present in all bar one (A1) of the solvent extracts at $<0.5\%$ and in all of the headspace samples at $<1\%$. This oxidation product of α-farnesene (Filmer and Meigh, 1971) is a suspected causal agent in superficial scald, a storage disorder of long-term cool-stored apples (Mir et al., 1999). Geranylacetone was detected in the solvent and the headspace extracts of most of the flower samples. It is also thought to be a terpene oxidation product, one possible precursor being squalene (Fruekilde et al., 1998). Geranylacetone is found in fruits and essential oils (Bauer et al., 1997), and is an important component in the aroma of fresh tomatoes (Hayase et al., 1984).

Flowers of the related *A. arguta* var. *purpurea* were distinct from those of the other genotypes. Terpenes that were either absent from or were minor components of the flowers of the *A. arguta* var. *arguta* genotypes, made up 60% of the *purpurea* headspace (unpublished data). The major terpenes in this variety were germacrene D (25.2%), δ-cadinene (10.9%), α-copaene (7.75%), γ-muurolene (4.3%), β-caryophyllene (3.6%), epi-bicyclosesqui-phellandrene (2.5%), α-muurolene (2.2%), α-caryophyllene (1.9%), and 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-naphthalene (1.5%). Germacrene D is a major component of the aroma of some rose varieties (Guterman et al., 2002; Vainstein et al., 2001) and *Cyphomandra sciadostylis* flowers (Sazima et al., 1993), and β-caryophyllene is a major odourant in carnations (Clery et al., 1999).

2.2.3. Benzenoid compounds

2-Phenylethanal was a small component (0.13%) of one flower solvent extract (A5). The dominant benzene compound was its reduction product, 2-phenylethanol (3-18% in solvent extracts; 1–17% in headspace extracts). Its ester, 2-phenylethyl acetate, was found in the headspace of two flower samples at 0.1 and 0.3%. 2-phenylethanol and 2-phenylethyl acetate have both been reported in 'Hayward' flowers (Tatsuka et al., 1990).

The above 2-phenylethyl compounds are probably metabolites of phenylalanine via cinnamic acid and phenylacetic acid (Lapadatescu et al., 2000; Silk et al., 2001; Yaylayan and Keyhani, 1998). Benzoic acid, benzyl alcohol, and therefore benzyl benzoate are also thought to be metabolites of phenylalanine (Lapadatescu et al., 2000). Benzoic acid based compounds are important components of carnation perfume (Clery et al., 1999).

2-(4-Hydroxyphenyl)ethanol (or tyrosol) has antioxidant properties and is the major phenol in olive oil (Giovannini et al., 1999). Tyrosol was present in five samples at levels between 1.4 and 11.4%. 2-(4-Methoxyphenyl)ethanol was in most of the samples, ranging from 5.5 to 31.1%. These two compounds are probably metabolites of tyrosine, the 4-hydroxy analogue of phenylalanine. These compounds, and structural relatives, were reported as odourants in the hot water extract of the pleasant smelling wood-rotting fungus *Gloeophyllum odoratum* (Rosecke and Konig, 2000). Despite their abundance in the solvent extracts of *A. arguta* flower samples, they were not detected in the headspace.

2.2.4. Esters, aldehydes, ketones, alcohols, and acids

Many of the aldehydes were present in both the fruit and the flower samples, although they predominated in the fruit. The most prevalent aldehydes in the flower samples were heptanal and nonanal. Heptanal was a minor component but nonanal was consistently present in the solvent extracts (up to 15.5%) and in the headspace (up to 2.1%).

Straight-chain aldehydes are metabolites of fatty acids such as oleic acid (Schmidt and Monroe, 1976). The branched-chain 3-methylbutyl and 2-methylbutyl compounds are metabolites of L-Leucine and L-isoleucine degradation, respectively (Mosandl, 1992; Myers et al., 1970; Rettinger et al., 1991; Rowan et al., 1996). 3-Methylbutanal was present in several of the headspace samples (2.6–20.5%), but not in the solvent extracts. Its reduction product, 3-methylbutanol, was detected in several solvent extracts (0.04–0.44%), but in only one of the headspace samples at 21%. Akin to 3-methylbutanal, 2-methylbutanal was found only in the headspace, but at much lower concentrations (0.5–1.8%) than 3-methylbutanal. 2-methylbutanol was also only found in the headspace, but at quite high levels (4.7–20.2%).

2.2.5. Unknown compounds

Eight other compounds labelled as unknowns 156-9 and 204-7 (Table 1) were variously present in eight of the nine solvent extracted genotypes (0.03–10.4%). They had very similar mass spectra, and therefore are either isomers of the one compound or of a number of very similar compounds. To be isomers of the one compound, they must be diastereoisomers of a molecule with four chiral centres (optical isomers not being resolvable by this GC column). Their mass spectra were most similar to that of epoxy-linalooloxide (3,7-dimethyl-1,2,6,7-diepoxyoctan-3-ol). However, the mass spectra and GC retention times of an authentic sample of epoxy-linalooloxide isomers differed from those of these unknown compounds. The retention indices and mass spectral data for these and other 'unknown' compounds (Tables 1 and 2) are listed in Section 4.6.

2.2.6. Organoleptic properties

The aroma impacts of volatile compounds in these samples are discussed in terms of their odour activity values (OAV) (Rothe and Thomas, 1963). The OAV is the concentration/threshold where the threshold is the lowest concentration of volatile compound that is detectable by humans (Mayol and Acree, 2001). Other authors have used the terms "odor unit" (Guadagni et al., 1966) and "aroma value" (Kollmannsberger and Berger, 1992).

Lilac aldehyde (**12**) and lilac alcohol (**13**) have fresh, floral fragrances (Wakayama and Namba, 1974; Wakayama et al., 1973; Watanabe et al., 1974). We do not have their aroma threshold values (TVs) and can't determine their contribution to the flowers' aroma profiles. Apart from uncertainty about the lilac compounds, the fresh-floral aroma of linalool probably prevailed in many of the flowers. The concentrations measured by headspace (16–1900 ng per litre) and solvent (105 and 4300 ng g^{-1}) extraction were well above the threshold values of 0.6 ng l^{-1} and 6 ng ml^{-1}, respectively (Rychlik et al., 1998). The maximum OAV of 720 for the A2 genotype probably made this the most fragrant of the flowers. Linalool also had the highest OAVs for the A9 (OAV = 338), A8 (OAV = 192), and A6 (OAV = 34) flowers.

The A4 and A9 flowers would have the second most intense aromas. The A9 aroma was from linalool and A4 was from the malty-smelling (Rychlik et al., 1998) 3-methylbutanal (OAV = 360, 1620 ng l^{-1}). The A1 flowers were also dominated by 3-methylbutanal, but at modest levels (OAV = 28, 126 ng l^{-1}).

The main A5 flower odourant was 2-phenylethanal with its honey-like or flowery aroma and an odour threshold (in water) of 4 ng g^{-1} (Rychlik et al., 1998). At a concentration of 232 ng g^{-1} its OAV was 58. The mild rose (Bauer et al., 1997) or spicy, honey-like aroma (Rychlik et al., 1998) of 2-phenylethanol dominated in A7 flowers with a modest OAV of 26. Its high concentration of 26000 ng g^{-1} was offset by its high aroma threshold of 1000 ng g^{-1}. In both these genotypes, geranylacetone and linalool each had OAVs of about half that of the dominant 2-phenyl- compounds and were probably secondary contributors to the aroma. The 2-phenyl- compounds were present in A1, A4, A6, and A8 flowers as non-dominant contributors to their aromas.

The A3 flower aroma was jointly dominated by geranylacetone [OAV = 18.5, 1110 ng g^{-1}, TV = 60 ppb (Buttery et al., 1971)] and 2-phenylethanol (OAV = 17.6). Geranylacetone is used in perfumery for its fresh-green, slightly penetrating, rose-like odour. The geranylacetone OAV of 86.5 was five times greater in A2 flowers but was overshadowed by the very high linalool concentration.

6-Methylhept-5-en-2-one has a sweet, fruity, green odour with a waxy apple note that contributes to the aroma of pureed 'Hayward' fruit (Jordan et al., 2002). This compound didn't dominate any of the aroma profiles, but probably contributed to the A1 and A3 genotypes in which its OAVs were about 30% of that of the major aroma contributors, 3-methylbutanal and geranylacetone, respectively.

2.3. Fruit

Between 40 and 80 individual compounds were detected in the extracts from five different fruit genotypes (Table 2). These were primarily a mix of esters, aldehydes and alcohols, with varying levels of monoterpenes.

2.3.1. Terpenes

The fruit contained a smaller and different range of terpenes than the flowers. The fruit of the A6 genotype contained the highest (57% of the solvent and 17% of the headspace extracts) and the A1 genotype fruit had the lowest terpene content at (11% of the solvent and 0.9% of the headspace extracts). This genotype had the largest number of compounds in common between its flowers and fruit, both having small amounts of α- and β-pinene, eucalyptol, linalool, squalene, and 5-methylhept-5-en-2-one. Of the other genotypes only A3 had a terpene (limonene) in both its flowers and fruit. Although camphor was the major terpene (7–37%) solvent extracted from the fruit, it was not detected in the headspace. Camphor was previously reported in *Actinidia* fruit as a glycoside in 'Hayward' fruit (Young and Paterson, 1995).

The headspace of fruit (but not the flowers) of A6 also contained limonene (1.7%), myrcene (1.31%), α-pinene (1.42%), and eucalyptol (3.3%). These terpenes were present to a lesser extent in the fruits of the other genotypes. Linalool (and not the various floral metabolic products) was identified in the solvent extract of two samples and as a very minor component (0.06%) in the headspace of A3. Increased linalool alters the flavour profile of transgenic fruit (Lewinsohn et al., 2001) although the contribution of this compound to the sensory properties of *A. arguta* fruit is likely to be overshadowed by that of the more abundant esters and aldehydes.

2.3.2. Benzenoid compounds

2-Phenylethanol and 2-phenylethanal, which impacted upon the aroma profiles of a number of flower samples, were not detected in either the solvent or headspace extracts of the fruit samples. Similarly, of the tyrosine derivatives found in the flowers only a small amount of tyrosol (0.88%) was identified in the A3 fruit. Ethyl and methyl benzoate were not present in the flowers, but were the major benzenoid compounds in the fruit samples, particularly in the solvent extracts of A1 and A3 (Table 2).

2.3.3. Esters

Although esters had a minimal presence in the flowers, "fruity" esters were the major aroma contributors in *A. arguta* fruit. The most prominent compounds were the high molecular weight esters such as methyl hexadecanoate, the oleates, linoleates, and linolenates (solvent extracts only), with considerable contributions from ethyl butanoate and ethyl hexanoate (Table 2). The esters constituted 9% of the A6 fruit solvent extract and 60–70% of the solvent extracts from the other three fruit samples analysed by this method. The headspace extracts had large percentages of the volatile esters and little or none of the long-chain esters. Ethyl butanoate dominated headspace extracts, with concentrations between 2% (A1) and 66% (A7). It was only detected in the solvent extract of A1 fruit as a major component at 7.6%. Ethyl butanoate is a major odourant from ripe 'Hayward' fruit (Bartley and Schwede, 1989; Gilbert et al., 1996; Jordan et al., 2002; Young et al., 1983), particularly in fresh fruit (Paterson et al., 1991). Esters increase as fruit ripen (Paterson et al., 1991; Young and Paterson, 1985), and this is possibly the reason for the difference between A1 and the other fruits in this study, especially as the aldehydes were dominant in A1, although all fruit were ripened to similar softness.

Ethyl hexanoate was a major component (29.8%) in the A3 fruit solvent extract. The headspace of this fruit had very high concentrations of esters that were not present in the other four fruit. Ethyl 2-methylpropanoate and ethyl 2-methylbutanoate were 24.7 and 6.5%, respectively, of the headspace in this sample.

2.3.4. Aldehydes, ketones, alcohols, and acids

Hex-E2-enal and hexanal are important contributors to kiwifruit flavour (Jordan et al., 2002), increasing amounts resulting in greater perceived intensity of kiwifruit flavour (Gilbert et al., 1996). Hex-E2-enal was not found in the flower samples but was in the fruit at 0.96–3.8% for solvent extracts and 1–58% for headspace extracts. Hexanal was a minor component in the flowers, but ranged from 0.13% (A5) to 22.5% (A1) of the fruit headspace and 0.14% (A3) to 1.9% (A6) of the fruit solvent extract. These compounds increase with tissue maceration in kiwifruit (Paterson et al., 1991) and inhibitors of lipoxygenase severely suppress the formation of hex-E2-enal (Bartley and Schwede, 1989). However trapping of volatiles from intact *A. arguta* fruit also reveals their presence (unpublished data).

Hex-Z3-enal was present in two headspace samples (A1 and A6) at 0.29 and 0.02%, hex-E3-enal (0.08%) in the A1 fruit headspace, and nona-E2,Z6-dienal (0.13%) in the A1 solvent extract. Hexanal, hexenal, and nona-E2,Z6-dienal are all products of lipoxygenase breakdown of long-chain fatty acids such as linolenic acid (Matheis, 1995).

2.3.5. Organoleptic properties

The aroma of A3 fruit was probably the most intense because of the very sweet, fruity odours of ethyl 2-methylpropanoate (OAV = 25×10^4, 38,234 ng l^{-1}) and ethyl 2-methylbutanoate (OAV = 7×10^4, 10,114 ng l^{-1}) (Rychlik et al., 1998). The next aroma contributor in this fruit was the "fruity" ethyl butanoate which had an equivalent headspace concentration (34840 ng l^{-1}), but an aroma threshold approximately 75 times greater than ethyl 2-methylpropanoate (Rychlik et al., 1998), thus producing an OAV of ca. 0.3×10^4. All three of the above compounds have been identified in 'Hayward' fruit, but ethyl butanoate was the only ester judged to contribute to kiwifruit flavour (Young and Paterson, 1990).

In all other fruit samples, except A1, ethyl butanoate was the main aroma compound with OAVs of ca. 3000. The green, leaf-like smelling hex-Z3-enal was the main headspace compound from A1 fruit (50 ng l^{-1}). With a low aroma threshold of 0.22 ng l^{-1} (Rychlik et al., 1998) it had an OAV (230) over twice that of ethyl butanoate (100). This compound has been reported in 'Hayward' fruit, but did not contribute to its aroma or flavour (Young and Paterson, 1990). The headspace also contained hexanal (OAV = 99, 3960 ng l^{-1}), hex-E2-enal (OAV = 41, 10160 ng l^{-1}), and in the solvent extract, nona-E2,Z6-dienal (OAV = 59, 0.59 ng g^{-1}). These three compounds have tallowy/leaf-like, apple-like/leafy/green/fatty/unripe-fruit (concentration dependent), and cucumber-like notes, respectively (Rychlik et al., 1998). They would reinforce the green notes from hex-Z3-enal.

The headspace of A6 fruit contained myrcene, limonene, α-pinene, and eucalyptol at above threshold levels but with modest OAVs. It is probable that only the mint-like aroma of eucalyptol contributed significantly to the aroma profile of the fruit. Its OAV of ca. 1670 [5020 ng l^{-1}, TV = 3 ng l^{-1} (Rychlik et al., 1998)] was half that of ethyl butanoate. Myrcene and eucalyptol have not previously been reported in 'Hayward' fruit.

3. Concluding remarks

A number of compounds different to those found in the fruit and flowers of commercial kiwifruit (*A. deliciosa* 'Hayward') were extracted from *Actinidia arguta*. They are likely to contribute to both the characteristic flavour of the fruit and to the very differently perfumed flowers. A striking difference between fruit and flowers is the presence of many linalool derived compounds in the flowers, but only linalool in the fruit. Sequencing of an EST library for *A. arguta* petals (A1) has revealed a strong presence of amino acid transporters; many have homologues in *Arabidopsis* (unpublished data). This parallels the presence of a number of aroma impact

compounds that derive from phenylalanine and tyrosine. We also discovered a group of apparently highly-related unknown compounds present in the flowers. Establishment of their identity will define their impact on floral aroma and the potential for discovery of new pathways.

4. Experimental

4.1. Plant material

In 2000 and 2001 flowers and fruit were obtained from 9 genotypes of *Actinidia arguta*. The genotypes sampled from were, *A. arguta* (Sieb. et Zucc.) Planch. et Miq.var *arguta* designated as A1 (Hortgem Tahi) (Female), A2 (Female), A3 (Female), A4 (Female), A5 (Female), A6 (Female), A7 (Female), A8 (Male), and A9 (Male), all of which were obtained from the HortResearch orchard in Te Puke, New Zealand. Of these genotypes, A5 and A6 were siblings, and A1 was the offspring of A4 and A9.

4.2. Headspace sampling

Headspace sampling and analysis was undertaken at the Mount Albert Research Centre, Auckland, New Zealand.

4.2.1. Flower volatiles

Branches containing flowers were transported with stems in water immediately after harvest to Auckland. Whole flowers (2.5–5 g) that were 50–75% open, and in good quality, were picked just under the receptacle and placed into a 250 ml Quickfit® Erlenmeyer flask to which was fitted a headspace adapter with an air inlet and outlet. A volatile trapping cartridge (s.s. tubing packed with 100 mg of Chromosorb 105™ absorbent) was fitted to the air outlet port of the adapter. The closed system was allowed to equilibrate for 30 min at room temp. (ca. 23 °C), after which 1.5 l of clean air was passed through the Erlenmeyer flask at 25 ml min^{-1} and was vented through the trapping cartridge. Traps were stored at −15 °C before GC-FID/MS analysis (storage was less than 2 weeks).

4.2.2. Fruit pulp

Each of 10 fruit [mixture of ripe stages with no unripe or overripe fruit included (Hassall et al., 1998)] was cut longitudinally in half and one half of each fruit was used for headspace sampling. The other halves were frozen in liquid N_2 for solvent extraction. The 10 fruit halves were combined by forcing them through a 2 mm sieve into an ice-cooled beaker in which the pulp was thoroughly mixed for 10 s. Approximately 1–1.5 g of this pulp was weighed into a 50 ml Quickfit® test tube containing a magnetic stirrer bar, and fitted with a headspace adapter. The fruit volatiles were sampled from the stirred pulp for 20 min at 23 °C by the same method as used for flower volatiles.

4.2.3. Analysis of headspace samples

Volatile compounds were thermally desorbed from the headspace traps at 175 °C and were cryo-focussed at the beginning of the GC column (Young, 1981). The column outlet was split between the GC (Hewlett Packard 5890) FID detector (for quantitation) and VG-70SE (VG-Micromass, Manchester, UK) mass spectrometer (for component identification) with an electron impact ionisation potential of 70 eV. Separations were carried out in a 30 m×0.32 mm i.d., 0.5 μm J & W DBWax capillary column starting at 30 °C for 6 min, increasing by 3 °C min^{-1} to 102 °C, 5 °C min^{-1} to 190 °C, and held for 5 min. The carrier gas was He at 30 cm s^{-1}, and the FID and mass spectrometer transfer line were at 220 °C. Quantification of compounds was carried out using an average detector response based on methyl butanoate, ethyl butanoate, hexanol and methyl benzoate. Component identification was by comparison with spectra in the Mass Spectral Database (1998 NIST and an in-house database), retention indices (in-house database) and in some cases direct GC-MS comparison with authentic standards.

4.3. Solvent extraction

All of the solvent extract analysis was undertaken at the Palmerston North Research Centre, Palmerston North, New Zealand.

4.3.1. Flowers

Approximately 1 g of flower petals were removed from the flowers after their headspace was sampled. The petals were rinsed in 2 ml of 50:50 pentane/Et_2O (GPR, BDH) which had been purified by distillation and by passing through a column of activated alumina (Perrin and Armarego, 1988). The volume of the solvent extract was reduced to ca. 50 μl under a gentle stream of N_2. Samples were stored at −18 °C.

4.3.2. Fruit pulp

Approximately 40 g of fruit was diced and placed in a Waring Commercial Blendor with an equivalent volume of absolute EtOH (Analar, 99.7–100%, BDH) and macerated for 10–15 s. The EtOH was retrieved by filtration of the pulp over 30 min at room temp. on a 9 cm Buchner funnel using a coarse filter paper (Whatman No. 4). Fine solids and high molecular weight waxes were removed from the EtOH extract by vacuum distillation (1 Pa) at 40 °C, with condensation into a receiving flask cooled in liquid nitrogen. This was effected using a solvent assisted flavour evaporation (SAFE) apparatus (Engel et al., 1999). The EtOH distillate was rapidly stirred for 1 h with and equivalent volume of pentane (purified as described in Section 4.3.1). Pentane

extracts were reduced to ca. 5 ml by rotary evaporation and were dried by passing through a small column of anhydrous $MgSO_4$ before the volume was further reduced to ca. 50 μl under a gentle stream of nitrogen.

4.3.3. Analysis of solvent extracts

Chromatographic separations were in a 30 m×0.25 mm i.d.×0.25 μm film thickness SP10-Wax (Supelco, Belefonte) or ZBWax capillary column (Phenomenex, Torrance, CA). The He head pressure was 52 kPa (7.5 psig), and the injection port was at 220 °C. The temp. program was 5 min at 40 °C, increasing by 5 °C min^{-1} to 200 °C, 15 °C min^{-1} to 240 °C, and held for 20 min. The GC and mass spectrometer were the same models as used for the analyses of headspace samples.

Compounds were quantified by comparing their total ion current intensity with that of ethyl butanoate for esters, hexanol for alcohols, acids and aldehydes, and α-pinene for terpenes and hydrocarbons. Percentage compositions were calculated excluding the solvent peaks. Component identification was by comparison with spectra in the Mass Spectral Database (NIST, 1992), and in some cases direct GC (retention indices) and MS comparison with authentic standards. A number of unknown compounds are listed in Tables 1 and 2. The numbering for these compounds is based upon that in our in-house database of compounds in *Actinidia* species and their genotypes.

4.4. Synthesis of lilac aldehydes and alcohols

Mixtures of four diastereoisomeric pairs of lilac aldehydes (**12a–d**) and alcohols (**13a–d**) were prepared by a modification of the procedure of Wilkins et al. (1993).

4.4.1. (*E*)-2,6-Dimethyl-6-hydroxyocta-2,7-dienal (*8*)

SeO_2 (1.3 g, 11.7 mmol, 98%, Sigma) was added, in one portion, to a soln. of linalool (2.0 g, 12.9 mmol, 97%, Aldrich) in dry dioxane (10 ml) under an atmosphere of dry N_2 at room temp. The mixture was stirred under reflux for 90 min and the formation of aldehydic compounds monitored by TLC (Merck 1.05554, hexanes/Et_2O 4:1) using an acidified ethanolic soln. of 2,4-DNP (Krebs et al., 1969). The reaction mixture was cooled to room temp., diluted with CH_2Cl_2 (50 ml) and washed with H_2O (50ml). The aqueous layer was separated and re-extracted with CH_2Cl_2 (50 ml). The combined organic phases were washed with satd. brine (50 ml), dried over $MgSO_4$, filtered under reduced pressure and concentrated in vacuo to give a pale yellow oil that was purified by flash chromatography on silica gel (95 g, Merck 1.09385) eluting with hexanes/Et_2O 4:1. The aldehydic fractions were combined and subjected to short path distillation (0.1 mm Hg, Kugelrohr) to give the title compound (0.38 g, 19%) as a colourless oil. Data was consistent with that reported earlier (Wilkins et al., 1993).

4.4.2. Preparation of lilac aldehydes (*12*)

NaH (0.19 g, 7.9 mmol) was washed with anhydrous THF (2×5 ml) and dried under a stream of N_2. A soln. of (E)-2,6-Dimethyl-6-hydroxyocta-2,7-dienal (**8**) (0.38g, 2.2 mmol) in MeOH (15 ml, ANALAR, BDH) was added cautiously over 5 min and the reaction stirred for a further 30 min at room temp. The disappearance of starting material was monitored by TLC (hexanes/EtOAc 1:1) and products were visualised by treatment with acidified ethanolic vanillin (Krebs et al., 1969). The reaction mixture was diluted with Et_2O (50 ml) and washed with H_2O (50 ml). The aqueous layer was separated and re-extracted with a further aliquot of Et_2O (50 ml). The combined organic phases were washed with satd. brine (50 ml), dried over $MgSO_4$, filtered under reduced pressure and concentrated in vacuo to give the crude product mixture as a yellow oil. Purification by short path distillation (0.1 mm Hg, Kugelrohr) gave the four lilac aldehydes (**12**) as a mobile oil (0.33 g, 87%) that were characterised by mass spectrometry (Kint et al., 1993; Wakayama and Namba, 1974; Wilkins et al., 1993), H^1 NMR (270 MHz, $CDCl_3$) (Wilkins et al., 1993), and ^{13}C NMR (270MHz, $CDCl_3$): δ 9.24, 9.91, 10.31, 10.40 (b-CH3), 26.12, 26.52, 26.72, 27.04 (5-CH3), 28.60, 29.18, 29.34, 29.97 (C-3), 36.57, 36.85, 37.38, 37.59 (C-4), 50.66, 51.02, 51.68, 51.88 (C-2), 78.26, 78.53, 79.06, 79.53 (**C**HCHO), 82.74, 83.03, 83.25, 83.29 (C-5), 111.35, 111.44, 111.44, 111.62 (CH=**C**H2), 143.09, 143.22, 143.79, 144.00 (**C**H=CH2), 204.01, 204.19, 204.25, 204.29 (CHO).

4.4.3. Preparation of lilac alcohols (*13*)

$NaBH_4$ (0.4 g, 10.5 mmol) was added to a soln. of lilac aldehydes (**12**) (0.19 g, 1.13 mmol) in MeOH (7.5 ml) and the reaction monitored by TLC. After 30 min the reaction mixture was quenched by the cautious addition of satd. NH_4Cl soln. (5 ml), diluted with H_2O (10 ml) and subjected to an ethereal work-up and short path distillation, as described above, to give a mixture of the four lilac alcohols (0.186 g, 1.09 mmol, 96%) that were characterised by mass spectrometry (Kint et al., 1993; Wilkins et al., 1993), H^1 NMR (270 MHz, $CDCl_3$) (Wakayama et al., 1973), and ^{13}C NMR (270 MHz, $CDCl_3$): δ 12.02, 12.38, 13.41, 13.60 (b-CH3), 26.72, 26.84, 27.18, 27.33 (5-CH3), 30.63, 30.63, 31.06, 31.06 (C-3), 36.35, 36.91, 37.24, 37.71 (C-4), 38.15, 38.72, 40.94, 41.04 (C-2), 66.02, 66.12, 67.88, 68.50 (**C**HCH2OH), 81.78,82.13, 85.27, 85.66 (**C**H2OH), 82.46, 82.82, 83.43, 83.57 (C-5), 111.28, 111.28, 111.43, 111.72(CH=**C**H2), 143.20, 143.29, 143.88, 144.01 (**C**H=CH2).

The retention times and mass spectra of these authentic compounds were used to confirm their presence in the extracts of the *A. arguta* flowers. The configurations of the aldehydes (or their respective enantiomers) and their order of elution on polar GC columns, are 1: (β*S*,2*S*,5*S*), 2: (β*R*,2*S*,5*S*), 3:

(βR,2R,5S), and finally 4: (βS,2R,5S) (Tollsten and Bergstrom, 1993; Wakayama and Namba, 1974). The alcohols eluted thus, b: (βR,2S,5S), d:(βS,2R,5S), a: (βS,2S,5S), and finally c:(βR,2R,5S) (Tollsten and Bergstrom, 1993; Wakayama et al., 1973). These authors gave the configuration of one enantiomer of each diastereoisomer, but acknowledged that they did not know which enantiomer, or even whether both enantiomers of each diastereoisomer were present.

The elution order of the lilac aldehydes was determined by comparing the GC retention times of the alcohols produced by $LiAlH_4$ reduction of both natural and synthetic aldehydes (Wakayama and Namba, 1974). Tollsten and Bergstrom (1993) appear to have interpreted these results to assign the configurations of the aldehydes based upon those of their alcohols. However, according to the CIP (Cahn-Ingold-Prelog) rules (March, 1985), reduction of the lilac aldehydes to their alcohols will change the β*S* designation of the aldehyde to the β*R* for the alcohol and visa versa for the β*R*. It is unclear whether the stereochemical consequences of the reduction of the aldehydes to the alcohols was considered by these workers.

4.5. Synthesis of epoxy-linalooloxide

Linolool was epoxidised by a modification of the method used to prepare α-farnesene epoxide (Fielder and Rowan, 1994). Linalool (87 mg, 0.56 mmol, 97%, Aldrich) was added, at room temp., to a stirred slurry of 3-chloroperoxybenzoic acid (0.4 g, 2.2 mmol, 75%, Pfaltz & Bauer Inc.) in freshly distilled CH_2Cl_2 (10 ml) and the disappearance of starting material monitored by TLC (hexanes/EtOAc 1:1) as described above. After 5 h the reaction mixture was filtered under reduced pressure, washed with satd. $NaHCO_3$ (15 ml), H_2O (10 ml) and brine (10 ml), dried over $MgSO_4$, filtered and concentrated in vacuo to give a mixture of products that was characterised by GC-MS. Analysis of the product mixture identified the major components as the *cis*- and *trans*-linaloloxides (68%). It was assumed that these compounds were the *cis* and *trans* isomers of 6,7-epoxylinalool (**4**). Other major products were the *cis* and *trans* isomers of the pyranoid form of linalool oxide (**5**) (27%), also known as epoxylinalol, and four isomers of epoxy-linalool-oxide (**7**) (3%). The mass spectra of (**4**), (**5**) and (**7**) were fully consistent with spectra reported in the 1998 NIST database.

4.6. MS and RI Data for unknown compounds in Tables 1 and 2

Unknown 3: RI-wax = 1021, *m/z* (rel. int.): 93 (100), 91 (38), 77 (36), 92 (32), 41 (11), 39 (11), 136 (10), 79 (10), 94 (8), 83 (8), 53 (6), 105 (5).

Unknown 6: RI-wax = 1263, *m/z* (rel. int.): 69 (100), 41 (55), 107.1 (13.1), 81 (12.6), 39 (11.1), 53 (9.2), 150.1 (9), 79 (7.4), 67 (7.2), 82.1 (7.1), 135.1 (6.3), 70 (5.6).

Unknown 7: RI-wax = 1149, *m/z* (rel. int.): 55 (100), 67 (91), 43 (67), 123 (62), 68 (55), 39 (27), 41 (24), 81 (19), 53 (19), 82 (17), 32 (14.3), 96 (14.2).

Unknown 25: RI-wax = 1101, *m/z* (rel. int.): 81 (100), 57 (76), 32 (53), 109 (44), 138 (31), 43 (27), 39 (21), 79 (20), 41 (20), 53 (19), 123 (18), 67 (16).

Unknown 27: RI-wax = 1168, *m/z* (rel. int.): 67 (100), 123 (73.2), 68 (62.4), 96 (20.1), 81 (19.5), 95 (18), 82 (15.8), 71 (14.9), 79 (9.1), 111 (8.7), 109 (7.8), 93 (7.7).

Unknown 33: RI-wax = 1317, *m/z* (rel. int.): 69 (100), 41 (54.3), 81 (16.8), 39 (10.2), 150 (9.7), 53 (8.4), 82 (8.3), 79 (7), 107 (6.2), 67 (6.2), 70 (5.5), 135 (3.9).

Unknown 34: RI-wax = 1451, *m/z* (rel. int.): 119 (100), 134 (55.8), 117 (20.3), 91 (16), 133 (12), 120 (10.4), 132 (9.8), 77 (9), 115 (7.4), 105 (6.1), 39 (5.6), 103 (5.6).

Unknown 47: RI-wax = 1328, *m/z* (rel. int.): 43 (100), 41 (44.1), 55 (31), 71 (25), 39 (19.9), 29 (14.6), 42 (12.3), 70 (11.4), 56 (5.8), 30 (5.1), 45 (4.3), 62 (4.2).

Unknown 59: RI-wax = 1140, *m/z* (rel. int.): 67 (100), 55 (90.6), 43 (76.3), 123 (66), 68 (55.1), 39 (29.1), 41 (28), 53 (22.8), 81 (20.2), 96 (19), 82 (19), 54 (15.9).

Unknown 93: RI-wax = 1930, *m/z* (rel. int.): 81 (100), 41 (87), 58 (77), 55 (73), 67 (67), 111 (67), 39 (56), 109 (55), 43 (54), 71 (51), 93 (47), 110 (33).

Unknown 95: RI-wax = 2085, *m/z* (rel. int.): 81 (100), 67 (74), 82 (54), 41 (53), 55 (39), 95 (38), 109 (33), 69 (26), 68 (25), 71 (24), 39 (23), 43 (23).

Unknown 100: RI-wax = 2520, *m/z* (rel. int.): 69 (100), 95 (72), 41 (68), 81 (68), 93 (38), 67 (37), 55 (35), 136 (25), 137 (19), 68 (18), 121 (18), 107 (16).

Unknown 106: RI-wax = 2220, *m/z* (rel. int.): 71 (100), 43 (50), 55 (33), 41 (32), 69 (20), 56 (16), 81 (15), 31 (13), 68 (12), 72 (11), 39 (10), 67 (10).

Unknowns 204, 156, 205, 206, 157,158, 207,159: RI-wax = 2110, 2120, 2150, 2175, 2185, 2210, 2215, 2280, *m/z* (rel. int.): 43 (100), 81 (38), 143 (33), 41 (28), 55 (23), 127 (18), 83 (15), 125 (14), 67 (14), 31 (13), 69 (12), 39 (12).

Unknown 178: RI-wax = 1440, *m/z* (rel. int.): 108 (100), 41 (88), 69 (82), 109 (75), 95 (56), 67 (51), 152 (49), 137 (46), 81 (35), 93 (31), 39 (30), 55 (25).

Unknown 227: RI-wax = 2287, *m/z* (rel. int.): 69 (100), 41 (38.7), 81 (29.5), 93 (19.2), 55 (14), 136 (14), 67 (10), 95 (9.8), 137 (8.3), 68 (8.2), 91 (7.9), 53 (7.7).

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