

## Supplementary materials

# Characterization of Botanical Origin of Italian Honey by Carbohydrate Composition and Volatile Organic Compounds (VOCs)

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## Supplementary Table

**Table S1.** Eighty volatile organic compounds identified in floral honey samples by HS-SPME-GC/MS, reporting retention time and molecular weight of each aromatic compound.

Compound	Retention time (min)	Molecular weight
Octane	2.1	114
Ethyl Acetate	2.6	88
Butanal, 3-methyl-	2.9	86
Ethanol	3.5	46
2,3-Butanedione	3.7	86
Pentanal, 3-methyl-	4.6	100
Propanal, 2-methyl-	6.8	72
Dodecane	8.6	170
D-Limonene	8.7	136
$\gamma$ -Terpinene	10.4	136
o-Cymene	11.4	134
Octanal	12.2	128
2-Nonanone	16.1	142
1,3,8-p-Menthatriene	16.2	134
Nonanal	16.3	142
Tetradecane	16.6	198
p-Mentha-1,5,8-triene	17.4	134
trans-Linalool oxide (furanoid)	18.2	170
Acetic acid	19.1	60
Furfural	19.2	96
Decanal	20.5	156
Pentadecane	20.7	212
Benzaldehyde	21.3	106
Lilac aldehyde A	22.1	168
Lilac aldehyde C	22.5	168
Linalool	22.7	154
Lilac aldehyde B	22.9	168
Propanoic acid, 2-methyl-	23.6	88
Lilac aldehyde D	23.8	168
Terpinen-4-ol	24.5	154
Hexadecane	24.7	226
1,5,7-Octatrien-3-ol, 3,7-dimethyl- (Hotrienol)	25.1	152
Butanoic acid	25.8	88
Benzeneacetaldehyde	26.0	120
Butanoic acid, 2-methyl- and Butanoic acid, 3-methyl-	27.4	102
Terpineol	28.3	154
2-Furanmethanol	28.6	98
2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	30.6	134
1-Nonanol	30.8	144
Pentanoic acid, 3-methyl-	31.8	116
Hexanoic acid	33.7	116
1-Decanol	34.8	158
Nonadecane	35.8	268
Lilac alcohol A	36.8	170
Creosol	37.2	138

**Table S1 (Continued).** Eighty volatile organic compounds identified in floral honey samples by HS-SPME-GC/MS, reporting retention time and molecular weight of each aromatic compound.

Compound	Retention time (min)	Molecular weight
Benzylalcohol	37.6	108
Hexanoic acid, 2-ethyl-	38.1	144
Heptanoic acid	38.2	130
3,7-Octadiene-2,6-diol, 2,6-dimethyl-	38.6	170
Phenylethylalcohol	40.8	122
Cinnamaldehyde (E)	42.0	132
Octanoic acid	44.8	144
Heneicosane	46.9	296
m-Guaiacol	47.8	124
p-Cymene	47.9	134
Caprolactam	48.7	113
Eugenol	48.9	164
3-Phenylpropanol	49.1	136
Nonanoic acid	49.4	158
Thymol	50.1	150
n-Decanoic acid	52.5	172
Eicosane	53.2	282
Heptadecane	53.3	240
Octadecane	53.3	254
Geranic acid	54.1	168
Diethyl Phthalate	54.4	222
Benzoic acid	55.9	122
2,7-Octadiene-1,6-diol, 2,6-dimethyl-	56.2	170
Dodecanoic acid	57.2	200
Benzeneacetic acid	58.5	136
5-Hydroxymethylfurfural	58.6	126
Dibutyl phthalate	60.7	278
Tetradecanoic acid	60.9	228
trans-Cinnamic acid	63.7	148
n-Hexadecanoic acid	64.6	256

**Table S2.** Data of mean area value, standard deviation, and relative standard deviation (RSD%) of 24 identified volatile organic compounds calculated on seven replicates (n=7) of a multifloral honey.

<b>Volatile compound</b>	<b>Mean</b>	<b>Std Dev</b>	<b>RSD %</b>
Octane	3753826	677092	18
$\gamma$ -Terpinene	3168509	114746	4
Octanal	2392483	258763	11
2-Nonanone	2235022	143391	6
Nonanal	16689855	1406944	8
Acetic acid	7702118	344264	4
Furfural	57421079	3992440	7
Decanal	5206367	240636	5
Benzaldehyde	1,91E+08	15223791	8
Lilac aldehyde C	2618819	227678	9
Linalool	11761973	1201352	10
1,5,7-Octatrien-3-ol, 3,7-dimethyl- (hotrienol)	1,6E+08	9594495	6
Benzeneacetaldehyde	24809299	763505	3
Terpineol	9029434	698375	8
Heptanoic acid	7228056	598734	8
Phenylethyl alcohol	19807629	846223	4
Octanoic acid	49753568	2011451	4
Nonanoic acid	60961622	5071476	8
Thymol	35527182	1191042	3
n-Decanoic acid	20925199	757184	4
Geranic acid	11508485	343189	3
Benzoic acid	37680359	1778475	5
Dodecanoic acid	8296098	918573	11
Tetradecanoic acid	2778336	441329	16

**Table S3.** Melissopalynological analysis of the floral honey samples; principal (>45%) and/or accompanying pollen (15-45%), and important minor pollen types (3-15%).

Sample	Floral type	Family	Principal pollen (>45%) and/or accompanying important pollen (15-45%)	Important minor pollen (3-15%)
M36	Multifloral	Ericaceae	42.50%	
		Salicaceae	<i>Salix</i> (38.0%)	
		Hippocastanaceae		<i>Aesculus</i> (5.7%)
		Rosaceae		<i>Malus/Pyrus</i> (3.8%)
		Asteraceae		<i>T-Form</i> (3.5%)
M37		Ericaceae	36.50%	
		Fabaceae		<i>Trifolium repens</i> (12.8%)
		Asteraceae		<i>T-Form</i> (9.1%)
		Rosaceae		<i>Rubus</i> (6.8%)
		Apiaceae		5.70%
		Rosaceae		4.30%
		Ranunculaceae		<i>Clematis</i> (3.1%)
M38		Ericaceae	32.60%	
		Rosaceae	<i>Rubus</i> (16.0%)	
		Asteraceae		<i>A-Form</i> (9.6%)
				<i>T-Form</i> (3.2%)
		Buddlejaceae		<i>Buddleja</i> (8.1%)
		Fabaceae		<i>Trifolium pretense</i> (4.2%)
				<i>Trifolium repens</i> (3.7%)
		Lauraceae		3.20%
M39		Rosaceae		<i>Malus/Pyrus</i> (3.0%)
		Ericaceae	62.80%	
		Fagaceae		<i>Castanea sativa</i> (12.1%)
		Apiaceae		<i>A/H-Form</i> (4.0%)
		Ranunculaceae		<i>Clematis</i> (3.5%)
		Boraginaceae		<i>Echium</i> (3.3%)
		Fabaceae		<i>Trifolium repens</i> (3.3%)
M41		Ericaceae	55.60%	
		Apiaceae		<i>A/H-Form</i> (8.8%)
		Asteraceae		<i>T-Form</i> (3.8%)
		Rosaceae		<i>Rubus</i> (3.8%)
		Salicaceae		<i>Salix</i> (3.2%)
		Scrophulariaceae		<i>Rhinanthus</i> (3.2%)
M42		Ericaceae	35.50%	
		Apiaceae		<i>A/H-Form</i> (10.9%)
		Rosaceae		<i>Rubus</i> (8.1%)
				Others (5.5%)
		Fabaceae		<i>Trifolium repens</i> (7.3%)
				<i>Lotus</i> (4.5%)
		Polygonaceae		<i>Fagopyrum esculentum</i> (3.3%)
		Scrophulariaceae		<i>Rhinanthus</i> (3.1%)

**Table S3 (continued).** Melissopalynological analysis of the floral honey samples; principal (>45%) and/or accompanying pollen (15-45%), and important minor pollen types (3-15%).

M44	Fagaceae	<i>Castanea sativa</i> (81.1%)	
	Salicaceae		<i>Salix</i> (10.2%)
	Rosaceae		<i>Malus/Pyrus</i> (3.0%)
M3-18	Ericaceae	70.90%	
	Rubiaceae		8.70%
	Fabaceae		<i>Trifolium repens</i> (4.8%)
M5-18	Fagaceae	<i>Castanea sativa</i> (81.1%)	
	Vitaceae		<i>Parthenocissus</i> (3.0%)
M6-18	Fagaceae	<i>Castanea sativa</i> (81.1%)	
	Asteraceae		<i>A-Form</i> (4.1%)
M7-18	Fagaceae	<i>Castanea sativa</i> (78.4%)	
	Ericaceae		14.10%
	Tiliaceae		<i>Tilia</i> (3.1%)
M9-18	Fagaceae	<i>Castanea sativa</i> (75.6%)	
	Tiliaceae		<i>Tilia</i> (3.1%)
M16-18	Ericaceae	55.50%	
	Rosaceae		<i>Rubus</i> (5.7%)
			<i>Fragaria-Potentilla</i> (4.8%)
	Tiliaceae		<i>Tilia</i> (4.4%)
	Ranunculaceae		<i>Clematis</i> (3.5%)
	Scrophulariaceae		<i>Rhinanthus</i> (3.5%)
M19-18	Ericaceae	25.30%	
	Rosaceae		<i>Rubus</i> (13.6%)
			<i>Malus/Pyrus</i> (5.1%)
	Fabaceae		<i>Onobrychis</i> (9.6%)
	Salicaceae		<i>Salix</i> (9.6%)
	Ranunculaceae		<i>Clematis</i> (7.1%)
M20-18	Ericaceae	80.40%	
	Rosaceae		<i>Rubus</i> (11.1%)
M21-18	Ericaceae	80.10%	
	Rosaceae		<i>Rubus</i> (5.7%)
	Fabaceae		<i>Tripholium repens</i> (4.1%)
M23-18	Fagaceae	<i>Castanea sativa</i> (73.7%)	
	Tiliaceae	<i>Tilia</i> (16.5%)	
	Rosaceae		<i>Rubus</i> (3.4%)
M46 C	Fagaceae	<i>Castanea sativa</i> (19.9%)	
	Fabaceae	<i>Tripholium repens</i> (19.2%)	
		<i>Robinia</i> (3.5%)	
	Scrophulariaceae	<i>Verbascum</i> (18.5%)	
	Rosaceae		<i>Rubus</i> (11.1%)
			Others (4.5%)
	Ranunculaceae		<i>Clematis</i> (4.2%)
	Rubiaceae		3.80%

**Table S3 (continued).** Melissopalynological analysis of the floral honey samples; principal (>45%) and/or accompanying pollen (15-45%), and important minor pollen types (3-15%).

M46 P	Fagaceae	<i>Castanea sativa</i> (19.3%)	
	Scrophulariaceae	<i>Verbascum</i> (17.9%)	
			<i>Rhinanthus</i> (6.1%)
	Fabaceae	<i>Tripholium Repens</i> (15.2%)	
		<i>Robinia</i> (3.4%)	
	Rosaceae		<i>Rubus</i> (10.8%)
M46 D			Others (4.4%)
	Caesalpiniaceae		<i>Gleditsia</i> (4.1%)
	Rubiaceae		3.70%
	Rosaceae	<i>Rubus</i> (21.3%)	
	Fagaceae	<i>Castanea sativa</i> (18.4%)	<i>Malus/Pyrus</i> (3.7%)
	Scrophulariaceae		<i>Rhinanthus</i> (12.5%)
M47C	Fabaceae		<i>Tripholium Repens</i> (11.4%)
			<i>Robinia</i> (4.4%)
	Ranunculaceae		<i>Clematis</i> (8.1%)
	Cornaceae		<i>Cornus</i> (4.0%)
	Rubiaceae		3.70%
	Salicaceae		<i>Salix</i> (3.3%)
M47P	Fagaceae	<i>Castanea sativa</i> (41.2%)	
	Rosaceae		<i>Malus/Pyrus</i> (11.1%)
			<i>Prunus</i> (4.6%)
			Others (3.8%)
	Salicaceae		<i>Salix</i> (6.8%)
	Fabaceae		<i>Robinia</i> (5.7%)
M47 D	Cruciferae		4.30%
	Rubiaceae		4.10%
	Asteraceae		<i>T-Form</i> (3.3%)
	Fagaceae	<i>Castanea sativa</i> (41.3%)	
	Rosaceae		<i>Prunus</i> (8.6%)
			<i>Malus/Pyrus</i> (7.6%)
M47 P			<i>Rubus</i> (6.3%)
	Rhamnaceae		5.80%
	Rubiaceae		4.60%
	Cruciferae		3.50%
	Asteraceae		<i>T-Form</i> (3.3%)
M47 D	Fagaceae	<i>Castanea sativa</i> (50.4%)	
	Rhamnaceae		6.60%
	Rosaceae		<i>Malus/Pyrus</i> (6.9%)
			<i>Rubus</i> (6.4%)
			<i>Prunus</i> (5.6%)
	Rubiaceae		3.70%
	Fabaceae		<i>Robinia</i> (3.4%)

**Table S3 (continued).** Melissopalynological analysis of the floral honey samples; principal (>45%) and/or accompanying pollen (15-45%), and important minor pollen types (3-15%).

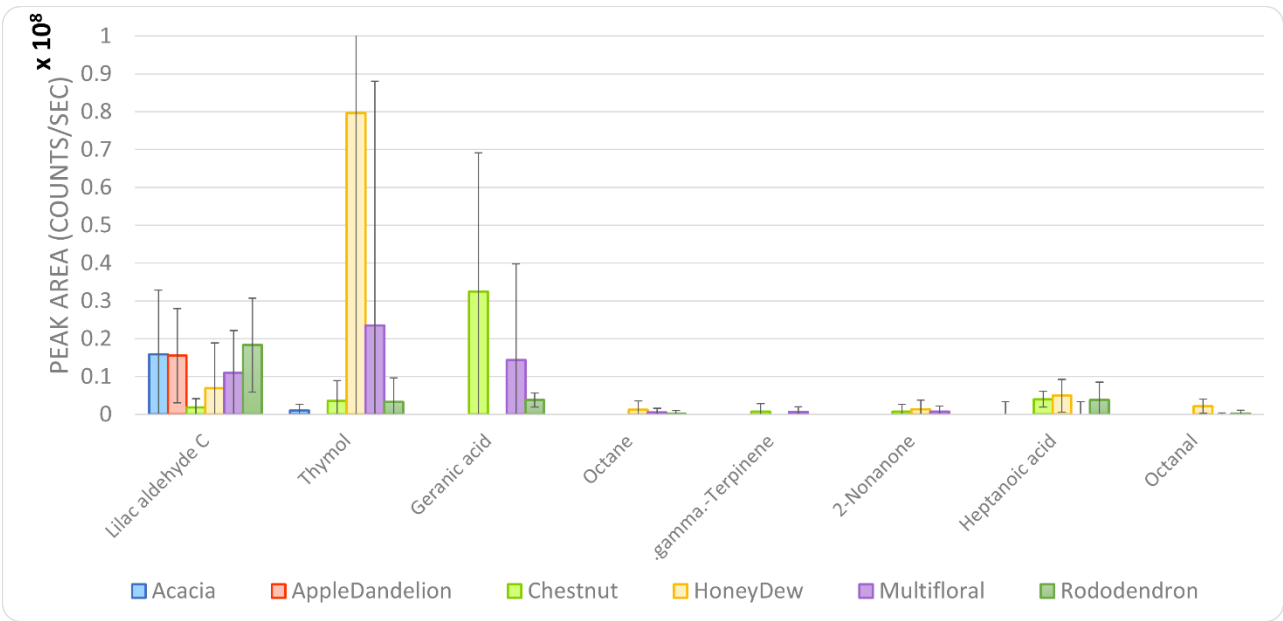
		Rosaceae	<i>Rubus</i> (16.6%) Others (10.3%)	
				<i>Prunus-Gr</i> (3.3%) <i>Malus/Pyrus</i> (5.5%) <i>Robinia</i> (14%) <i>Camerops</i> (11.1%) <i>Ailanthus</i> (11.1%) <i>Aesculus</i> (5.5%) <i>A-H Form</i> (3.7%) <i>Salix</i> (3.7%)
M22-18		Fabaceae Arecaceae Simaroubaceae Hippocastanaceae Apiaceae Salicaceae		
A1-18	Acacia	Fagaceae Fabaceae Rosaceae	<i>Castanea sativa</i> (46.3%) <i>Robinia</i> (22.4%) <i>Rubus</i> (16.1%)	
A11-18		Fagaceae Fabaceae  Rosaceae Scrophulariaceae Rhamnaceae	<i>Castanea sativa</i> (46.6%) <i>Robinia</i> (17.2%)  <i>Tripholium Repens</i> (3.4%) <i>Rubus</i> (7.8%) <i>Rhinanthus</i> (5.0%) 3.80%	
A28-18		Fabaceae Rosaceae  Fagaceae Ebenaceae	<i>Robinia</i> (19.8%) <i>Rubus</i> (19.4%) <i>Malus/Pyrus</i> (19.0%) <i>Castanea sativa</i> (14.1%) <i>Diospyros</i> (4.6%)	
AD43	Apple- Dandelion	Fagaceae Asteraceae Salicaceae Rosaceae	<i>Castanea sativa</i> (32.2%) <i>T-Form</i> (23%) <i>Salix</i> (19.7%) <i>Malus/Pyrus</i> (18.1%)	
AD45		Fagaceae Asteraceae Rosaceae Hydrophyllaceae Simaroubaceae Vitaceae	<i>Castanea sativa</i> (49.5%)  <i>T-Form</i> (14.0%) <i>Malus/Pyrus</i> (12.1%) <i>Phacelia</i> (3.8%) <i>Ailanthus</i> (3.3%) <i>Parthenocissus</i> (3.0%)	
AD25-18		Rosaceae  Vitaceae Fabaceae Arecaceae Hippocastanaceae	<i>Malus/Pyrus</i> (22.6%)  <i>Rubus</i> (11.6%) <i>Parthenocissus</i> (12.5%) <i>Robinia</i> (11.9%) <i>Camerops</i> (9.8%) <i>Aesculus</i> (4.2%)	
R2-18	Rhododendron	Fagaceae Ericaceae	<i>Castanea sativa</i> (64.2%) 31.30%	
R4-18		Ericaceae Fagaceae	87.10%  <i>Castanea sativa</i> (6.5%)	



**Table S3 (continued).** Melissopalynological analysis of the floral honey samples; principal (>45%) and/or accompanying pollen (15-45%), and important minor pollen types (3-15%).

R14-18		Ericaceae	84.60%	
		Rosaceae		<i>Rubus</i> (5.5%)
		Fagaceae		<i>Castanea sativa</i> (4.4%)
R17-18		Ericaceae	82.60%	
		Rosaceae		<i>Rubus</i> (3.7%)
R18-18		Ericaceae	91.00%	
		Campanulaceae		3.90%
R24-18		Ericaceae	91.10%	
		Fagaceae		<i>Castanea sativa</i> (7.2%)
R27-18		Ericaceae	69.60%	
		Fagaceae		<i>Castanea sativa</i> (23.0%)
HD15-18	Honeydew		Honeydew elements (HDE/P=3.13)	
HD26-18			Honeydew elements (HDE/P=3.57)	
HD29-18			Honeydew elements (HDE/P=7.61)	
C40	Chestnut	Fagaceae		<i>Castanea sativa</i> (90.0%)
C8-18		Fagaceae		<i>Castanea sativa</i> (98.0%)
C12-18		Fagaceae		<i>Castanea sativa</i> (97.8%)
C13-18		Fagaceae		<i>Castanea sativa</i> (91.7%)
C52 C		Fagaceae		<i>Castanea sativa</i> (97.0%)
C52 P		Fagaceae		<i>Castanea sativa</i> (96.4%)
C52 D		Fagaceae		<i>Castanea sativa</i> (95.1%)

Supplementary figures



**Figure S1** Eight less intense and not statistically significant VOCs in honey samples. Error bars represents standard deviations.