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The Aroma of Finnish Wild Raspberries, Rubus idaeus, L.

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Das Aroma von finnischen wilden Himbeeren, Rubus idaeus, L.

Zusammenfassung. Die flüchtigen Aromastoffe der wilden Himbeere wurden gaschromatographisch-massenspektrometrisch bestimmt. Insgesamt 75 Bestandteile wurden identifiziert, entsprechend einem Gehalt an ätherischem Öl von etwa 64 ppm. Mehr als 40 Komponenten wurden festgestellt, die bisher nicht in Himbeeren identifiziert worden sind. Zu diesen gehören 5-Methyl-4-hydroxy-3(2H)furanon, 2,5-Dimethyl-4-hydroxy-3(2H)furanon, 2,5-Dimethyl-4-methoxy-3(2H)-furanon und 11 Terpene. Die zwei identifizierten Ester, nämlich 5-Hydroxyoctansäureethylester und 5-Hydroxydecansäureethylester, sind bisher in keinen natürlichen Produkten gefunden worden. Diese Ester sind sehr unstabil und werden beim Verarbeiten der Beeren leicht zu den entsprechenden δ-Laktonen umgewandelt.

Summary. Volatile components of fresh wild raspberries were studied by combined gas chromatography-mass spectrometry. A total of 75 components were identified, corresponding to about 64 ppm of raspberry oil in the press juice. More than 40 compounds not reported previously as raspberry volatiles were detected. These included 5-methyl-4-hydroxy-3(2H)furanone, 2,5-dimethyl-4-hydroxy-3(2H)furanone, 2,5-dimethyl-4-methoxy-3(2H)furanone, and 11 terpenes. Two of the identified esters, ethyl 5-hydroxyoctanoate and ethyl 5-hydroxydecanoate, have not previously been identified in natural products. These esters are very unstable, forming the corresponding δ-lactones during processing of the berries.

Volatile components of cultivated raspberries have been studied extensively during the last decades. In the studies of Schinz and Seidel [1, 2], Winter et al [3, 4], and Bohnsack [5, 6], numerous aroma compounds have been isolated and characterized by classical methods. In a more recent work of Winter and Enggist [7] 39 neutral volatiles were identified.

4-(4-Hydroxyphenyl)butan-2-one (raspberry ketone) together with α- and β-ionones have been found to be the character impact compounds of the aroma of raspberries.

It is well-known that the flavour of fresh wild raspberries is much stronger and more pleasant than that of raspberry cultivars. The aroma of wild raspberries is, however, very sensitive to heat and storage. Even deep freezing destroys the pleasant aroma nuances of the fresh berries. This is obviously partly due to the increased enzyme activity during thawing of the berries.

The aim of this investigation was to study the possible qualitative and quantitative differences between volatiles of wild and cultivated raspberries and also to explain the chemical and enzymatic reactions which may occur during the processing or storage of the berries.

Experimental

About 2 kg of both wild and cultivated (cultivars Ottawa and Preussen) raspberries were used in this study. The berries were pressed immediately after harvesting in a hydraulic press, and the juices were extracted with pentane/ethyl ether (1 + 2) as described previously [8]. The juices were, however, not neutralized with sodium hydrogen carbonate. The extracts, containing both neutral components and free fatty acids, were concentrated and analyzed in a combined gas chromatograph-mass spectrometer (JEOL JMS-D1OO) using glass capillary columns (30 m, i.d. 0.3 mm) coated with FFAP. The mass spectra were recorded at 70 eV. For the quantitative determination of the individual components, the same capillary columns were used on a Carlo Erba, Fractovap 2350 gas chromatograph combined with a Varian C DS 111 computing integrator. The temperature was programmed from 50 °C to 200 °C at 6 °C/min.

Ethyl 5-hydroxyoctanoate and ethyl 5-hydroxydecanoate were synthetized from the corresponding 5-hydroxyacids by diazoethane treatment in ether according to the method used by Näf-Müller and Willhalm [9] in the syntheses of the correspondingly methyl esters. Because of the instability of the esters, the isolations were performed

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Table 1. Volatile components identified in wild raspberries, *Rubus idaeus*, L. and their approximate concentrations in the press juice (ppm)

Terpene hydrocarbons	
α-Pinene	tr
α-Phellandrene	tr
Limonene	tr
α-Terpinolene	0.7
Sabinene	tr
trans-Caryophyllene	1.2
Humulene	tr
α-Elemene	0.1
	2.0
Alcohols	
Ethanol	tr
2-Methylpropanol	tr
2-Methylbutan-1-ol	tr
1-Pentanol	tr
3-Methyl-2-buten-1-ol	3.2
1-Hexanol	1.4
trans-3-Hexen-1-ol	0.7
cis-3-Hexen-1-ol	7.0
trans-2-Hexen-1-ol	tr
Linalool	0.8
4-perpineol	0.5
α-Terpineol	0.7
cis-Sabinol	0.2
Nerol	0.4
Geraniol	0.5
Menthanol	tr
	15.4
Acids	
Acetic acid	16.0
Propanoic acid	tr
Butanoic acid	0.9
2-Methylbutanoic acid	tr
3-Methyl-2-butenoic acid	tr
3-Methyl-3-butenoic acid	tr
Hexanoic acid	6.7
Octanoic acid	tr
Decanoic acid	tr
Tetradecanoic acid	tr
Hexadecanoic acid	tr
	23.6
Esters	
Ethyl acetate	tr
3-Methyl-2-buten-1-yl formate	tr
3-Methyl-2-buten-1-yl acetate	tr
cis-3-Hexen-1-yl formate	tr
cis-3-Hexen-1-yl acetate	tr
Ethyl 5-hydroxyoctanoate	1.3
Ethyl 5-hydroxydecanoate	0.8
	2.1
Carbonyls	
Hexanal	tr
trans-2-Hexenal	tr
6-Methyl-5-hepten-2-one	3.2
Acetoin	3.6
Piperitone	0.2
α-Ionone	0.4
β-Ionone	0.5
	7.9
Aromatic compounds	
Xylene	tr
p-Cymene	0.9
Benzaldehyde	0.2
Benzyl acetate	tr
Benzyl alcohol	3.5
2-Phenylethanol	0.5
2-Methoxy-4-vinylphenol	tr
2-Methoxy-5-vinyl phenol	tr
3,4-Dimethoxybenzaldehyde	tr
Eugenol	tr
4-Vinylphenol	0.3
trans-Cinnamyl alcohol	tr
Benzoic acid	tr
Vanillin	tr
Gingerone	0.3
Raspberryketone	3.1
	8.8
Heterocycles	
Linalool oxides	tr
2,5-Dimethyl-4-methoxy-3(2H) furanone	tr
5-Methyl-4-hydroxy-3(2H) furanone	0.1
2,5-Dimethyl-4-hydroxy-3(2H) furanone	0.1
γ-Hexalactone	0.7
δ-Hexalactone	0.6
γ-Octalactone	0.4
δ-Octalactone	0.7
δ-Decalactone	1.0
δ-Dodecalactone	0.2
	3.8

without delay. The products always contained a small amount of the corresponding δ-lactone, but the esters were well resolved from the δ-lactones in a FFAP coated glass capillary column. The mass spectra of the synthetized reference compounds were identical with those recorded in the analyses of the raspberry concentrates. Ethyl 5-hydroxydecanoate: M^+ 216 (0.01%), *m/e* 99 (100), 88 (65), 71 (36), 55 (36), 145 (30), 41 (28), 43 (27), 116 (24), 70 (24); ethyl 5-hydroxyoctanoate: M^+ 188 (0.01%), *m/e* 99 (100), 88 (58), 55 (56), 71 (25), 43 (23), 70 (16), 60 (15), 41 (15), 16 (12), 125 (12), 145 (10). The mass spectra of both ethyl 5-hydroxy octanoate and ethyl 5-hydroxydecanoate contain intense ions at *m/e* 88 (characteristic for ethyl esters), 116 and 145, which are not present in the mass spectra of the corresponding δ-lactones [10, 11].

Results and Discussion

The volatile compounds identified in the press juice of the wild raspberries and the approximate concentrations of the main components are presented in Table 1.

The high content of free fatty acids, especially of acetic and hexanoic acids, is characteristic for raspberry volatiles, as shown previously by many authors [12, 13]. The content of volatile acids is also very high in wild raspberries (24 ppm), corresponding to about 37% of the total volatiles. In the cultivars Ottawa and Preussen, the free fatty acids amounted to 40 to 43% of the total volatiles. 3-Methyl-2-butenoic and 3-methyl-3-butenoic acids were identified only in wild raspberries. These acids have been identified previously in arctic bramble (*Rubus arcticus*, L.) by Kallio [14, 15] and in hybrids between arctic bramble and raspberry by Pyysalo [13].

Several terpene and sesquiterpene hydrocarbons are reported here for the first time as raspberry volatiles. These include α-pinene, α-phellandrene, limonene, sabinene, α-terpinolene, *trans*-caryophyllene, humulene, and α-elemene. None of these terpene hydrocarbons were identified in the raspberry cultivars studied. Several terpene and sesquiterpene hydrocarbons remained unidentified because of their low concentration in the aroma oil. The content of terpene hydrocarbons was low, only 3.1%, of which *trans*-caryophyllene alone amounted to 1.9%.

The alcohol fraction in wild raspberries is 24% of the total volatiles, whereas that of raspberry cultivars is only 10 to 15%. Five of the alcohols identified in wild raspberries have not been found in raspberries in previous studies; these are *trans*-2-hexen-1-ol, *trans*-3-hexen-1-ol, α-terpineol, sabinol, and menthanol.

In addition to the few esters present in cultivated raspberries, small amounts of 3-methyl-2-buten-1-yl acetate, *cis*-3-hexen-1-yl formate and *cis*-3-hexen-1-yl acetate were identified in wild raspberries. Furthermore, two completely new esters, ethyl 5-hydroxyoctanoate and ethyl 5-hydroxydecanoate were found in both wild and cultivated raspberries. These compounds are probably precursors of the corresponding δ-lactones. They are very unstable, loosing ethanol on standing or heating (probably also enzymatically). The concentrations of ethyl 5-hydroxyoctanoate and ethyl 5-hydroxydecanoate in the press juice of wild raspberries were found to be 1.3 and 0.8 ppm, respectively. It is, however, possible that the esters are partially decomposed during the isolation procedure. It seems very probable that δ-lactones and perhaps also γ-lactones are formed according to this mechanism. Ethyl esters of the 5-hydroxyacids have a sweet pineapple-like odour, whereas the corresponding δ-lactones have an intense coconut-like odour.

The concentrations of ethyl 5-hydroxyoctanoate, ethyl 5-hydroxydecanoate and also those of the δ-lactones in the raspberry cultivars studied, are somewhat lower than in wild raspberries. The above-mentioned esters, together with the δ-lactones, probably make a great contribution to the aroma of fresh raspberries. The 5-hydroxyacid esters were completely lost when the berries were deep frozen and thawed. Recently Näf-Müller and Willhalm [9] have identified methyl and ethyl 5-acetoxyoctanoates and decanoates in fresh pineapple-juice.

Several aromatic compounds detected only in the wild berries, and not reported previously as raspberry volatiles, include *p*-cymene, benzyl acetate, eugenol, 4-vinylphenol, 2-methoxy-4-vinylphenol, 2-methoxy-5-vinyl-phenol, 3,4-dimethoxybenzalhyde, vanillin, *trans*-cinnamyl alcohol, and 4-(3-methoxy-4-hydroxyphenyl)butan-2-one (gingerone). The content of 4-(4-hydroxyphenyl)butan-2-one (raspberry ketone) is about 3 times higher in wild raspberries than in cultivar Preussen; in cultivar Ottawa, only traces of this ketone were detected. Gingerone, a methoxy derivative of raspberry ketone, has previously been identified only in ginger oil. Recently, however, Hirvi et al. [16] found this compound also in European cranberry (*Vaccinium oxycoccus,* L.) and in cowberry (*V. vitis-ideae,* L.).

5-Methyl-4-hydroxy-3(2H)furanone, 2,5-dimethyl-4-hydroxy-3(2H)furanone, and 2,5-dimethyl-4-methoxy-3(2H)-furanone are reported here for the first time as raspberry volatiles. 2,5-Dimethyl-4-hydroxy-3(2H)furanone has previously been detected in pineapple [17], in cultivated strawberries [18] and in arctic bramble [15]; 2,5-dimethyl-4-methoxy-3(2H)furanone in mango fruit [19], in arctic bramble [15], in hybrids between arctic bramble and raspberry [13] and in strawberries [8]; 5-methyl-4-hydroxy-3(2H)furanone has been found in roasted beef [20]. These compounds are all unstable to heat and decompose on standing at room temperature. Because the odour-threshold value of 2,5-dimethyl-4-hydroxy-3(2H)furanone is very low (0.00003 ppm), its sweet odour may contribute to the aroma of fresh wild raspberries. The concentrations of the two other furanones are fairly low and obviously below their respective odour threshold concentrations.

The concentrations of α- and β-ionones in the raspberry cultivars are 1.5–2 times higher than in the wild berries. Theaspirane, damascenone, and epoxyionone, reported by Winter et al. [7] as raspberry volatiles, could be identified neither in wild nor in cultivated berries.

With the exception of ionones, the concentrations of individual components present in both wild and cultivated berries were, in general, 3–4 times higher in wild raspberries. In addition to this, the numerous compounds found only in wild berries may contribute to the distinct difference between the aromas of wild and cultivated raspberries. It seems to be a general phenomenon that increase in berry size, obtained by breeding, hybridization or fertilation, inevitably leads to deterioration of the aroma of the berries. Climatic conditions and even geographical situation also have great influence on the aroma of some berries. The berries grown in the Nordic Countries are in general more highly flavoured than those of the same species grown in Central Europe. This may be due to the stronger solar radiation during the summer.

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