J. Sci. Food Agric. 1983, **34**, 992–998

The Aroma of Blueberries

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(Manuscript received 3 August 1982)

The volatile components of bilberry, bog blueberry and cultivated high-bush blueberry (cv. Rancocas) were analysed by gas chromatography and mass spectrometry. Several new compounds not reported previously as blueberry volatiles were detected. These included methyl and ethyl 2-hydroxy-3-methylbutanoate, methyl and ethyl 3-hydroxy-3-methylbutanoate, 2-phenylethyl formate, methyl salicylate, farnesol, farnesyl acetate, vanillin, myristicine, 4-vinylphenol, 2-methoxy-5-vinylphenol, citronellol, hydroxycitronellol and some γ- and δ-lactones. The character impact compounds of bilberry were found to be the above-mentioned hydroxy esters together with 2-phenylethanol and its esters and the γ- and δ-lactones, whereas myristicine, citronellol, hydroxycitronellol, farnesol and farnesyl acetate were typical of the aroma of high-bush blueberry.

1. Introduction

Several wild berries belonging to the genus *Vaccinium* are grown in the temperate regions of northern Europe and North America. Among the species with blue berries are bilberry (*V. myrtillus* L.) and bog blueberry (*V. uliginosum*, L.) in Europe and highbush blueberry (*V. corymbosum*, L.) and some low-bush blueberries, (e.g. *V. angustifolium*, L., *V. australe*, Small and *V. lamarckii* Camp) in America. The cultivation of high-bush blueberry is very extensive in the US and nowadays also in Central Europe. Several cultivars have been obtained by crossing *V. corymbosum*, L. with *V. lamarckii* Camp. and *V. australe* Small. These high-bush blueberry varieties, which have very large berries with pleasant aromas are not, however, very hardy under the climatic conditions prevailing in Finland,[1] which makes their cultivation unreliable and uneconomical in this country.

The tetraploid ($2n=48$ chromosomes) high-bush blueberry has many characteristics, such as vigorous bushy growth, high fruit yield and large berry size, making it more suitable for cultivation than the North European *Vaccinium* species. The only European tetraploid *Vaccinium* species is the bog blueberry, which is fully hardy throughout Finland. Bog blueberry has somewhat smaller berries than high-bush blueberry, and the berries are almost aromaless. To obtain more hardy varieties with attractive aroma and taste characteristics, attempts have been made by Hiirsalmi[1–3] to cross the high-bush blueberry with the bog blueberry. Some of these crosses are now being cultivated experimentally.

The purpose of this investigation was to compare the characteristic flavour compounds of high-bush blueberry, bilberry and bog blueberry. The aromas of bilberry and high-bush blueberry have been investigated previously by von Sydow *et al.*[4,5] and Parliment *et al.*,[6] respectively, but because different isolation and concentration techniques were used, comparison of the results is very difficult.

2. Experimental

2.1. Samples

About 1 kg of bilberries, bog blueberries and high-bush blueberries (cv. Rancocas) were used in this study. The berries were harvested in autumn 1981 and stored at -30°C until used.

2.2. Isolation and concentration of the volatiles

After thawing, the berries were pressed in a hydraulic press. Isolation and concentration of the aroma compounds were performed as described previously.[7]

2.3. Gas chromatography and mass spectrometry

The aroma concentrates were analysed in a combined gas chromatograph-mass spectrometer (Hewlett-Packard 5992) 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 individual components the same capillary column was used in a Micromat 412 integrating gas chromatograph (Orion Analytica). The temperature was programmed from 60°C to 200°C at 6°C min^{-1}. Identifications were made by comparing the measured spectra and gas chromatographic retention times of the blueberry volatiles with those of either commercial or synthetic reference compounds.

2.4. Synthesis of the reference compounds

Methyl and ethyl 2-hydroxy-3-methylbutanoates were obtained by direct esterification of the corresponding acid with methanol or ethanol. The mass spectrum of methyl 2-hydroxy-3-methylbutanoate was: M^+ 132(0%); *m/e* 73(100), 43(51), 55(49), 90(43), 41(28), 39(20), 45(19), 57(14) and that of ethyl 2-hydroxy-3-methylbutanoate was: M^+ 146(0%); *m/e* 73(100), 55(40), 76(33), 43(33), 41(16), 45(14), 39(10), 57(9).

Methyl and ethyl 3-hydroxy-3-methylbutanoates were synthesised by the Reformatsky reaction from methyl or ethyl bromoacetate and acetone. The mass spectrum of methyl 3-hydroxy-3-methylbutanoate was: M^+ 132(0%), *m/e* 43(100), 59(70), 85(28), 117(23), 74(19), 45(13), 42(10), 41(9) and that of ethyl 3-hydroxy-3-methylbutanoate was: M^+ 146(0 %), *m/e* 43(100), 59(78), 85(51), 131(33), 60(23), 88(20), 42(13), 101(11). Hydroxycitronellol was obtained by sodium borohydride reduction of hydroxycitronellal in methanol. Its mass spectrum was: M^+ 174(0%); *m/e* 59(100), 43(40), 41(21), 55(16), 70(10), 42(8), 69(8), 58(6), 39(5). *Trans*-2-Hexenoic acid was synthesised by the Knoevenagel reaction from malonic acid and *n*-butyraldehyde. Its mass spectrum was: M^+ 114 (15%), *m/e* 73(100), 42(71), 40(65), 41(64), 55(48), 67(36), 99(30), 45(28).

2.5. Sensory evaluation

The odours of the new pure synthetic compounds were characterised by 10 panellists with previous experience in odour determinations. The panellists were asked to give a verbal characterisation of the odours of the samples. The samples were diluted with odour-free water to their approximate threshold range and were presented in beakers fitted with plateglass covers.

3. Results and discussion

The volatile components identified in the press juices of bilberry, bog blueberry and high-bush blueberry (cv. Rancocas) and the approximate concentrations of the main compounds are presented in Table 1. The main volatile compound of all the berries investigated was benzyl alcohol, which has also been shown previously to be typical for the berries of *V. vitis-idaea* L.,[8] *V. oxycoccos* L.[9] and *V. macrocarpon* Ait.[9] von Sydow *et al.*[4] found that benzyl alcohol in bilberries accounted for only 0.6% of the total volatiles, the main volatile compound being nonanal (7.1%). In this study, traces of nonanal were found only in bilberry. In general, the aroma compositions of all three berries had many similarities. Among the alcohols, 1-hexanol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 2-phenylethanol, linalool and α-terpineol were all present in approximately the same concentrations in all the berries studied. The same was also true of butanoic acid, hexanoic acid and phenol. Typical compounds for the aroma of bilberries were *trans*-2-hexenal, *trans*-2-hexenoic acid, phenylacetaldehyde, methyl salicylate, 2-phenylethyl formate and 2-phenylethyl acetate and the methyl and ethyl esters of 2- and 3-hydroxy-3-methylbutanoic acids together with γ- and δ-lactones. Ethyl 2-hydroxy-3-methylbutanoate has only been identified previously in some wines and brandies (Schreier *et al.*).[10–13] Most of the sensory panellists characterised, the odour of an aqueous solution of ethyl 3-hydroxy-3-methylbutanoate as bilberry-like and some of them also found this odour quality in the solutions of other hydroxyesters. These esters may therefore contribute in part to the typical aroma of bilberry. On the other hand, the characteristic compounds for highbush blueberry were hydroxycitronellol, farnesyl acetate, farnesol and myristicine. The odour of hydroxy-

Table 1. Compounds identified in the press juices of bilberry, bog blueberry and high-bush blueberry and the approximate concentrations of the main compounds

	Concentration (mg kg^{-1})		
Compound	Bilberry	Bog blueberry	High-bush blueberry
Terpene hydrocarbons			
α-Pinene	–	–	+
Myrcene	–	–	+
Limonene	+	+	+
Caryophyllene	–	–	+
Alcohols			
Butan-1-ol	0.001	–	0.016
Butan-2-ol	0.010	–	0.013
2-Methylbutan-1-ol	+	–	–
3-Methylbutan-1-ol	–	+	–
Pentan-1-ol	0.050	+	0.020
1-Penten-3-ol	–	–	+
Hexan-1-ol	0.020	0.020	0.070
cis-3-Hexan-1-ol	0.060	0.070	0.050
trans-2-Hexen-1-ol	0.010	0.010	0.020
Octan-1-ol	–	+	+
Linalool	0.004	+	0.050
Nonan-1-ol	–	–	+
α-Terpineol	0.015	0.020	0.020
Myrcenol	–	+	–
Nerol	0.002	+	+
Citronellol	0.001	–	0.010
Geraniol	+	–	0.030
Hydroxycitronellol	–	–	0.045
Farnesol	–	–	0.040
	0.173	0.12	0.384
Carbonyl compounds			
Hexanal	–	+	+
trans-2-Hexenal	0.06	+	0.020
Acetoin	+	–	–
Nonanal	+	–	–
	0.06		0.020
Acids			
Acetic acid	0.32	1.1	0.70
Butanoic acid	0.13	0.005	0.010
2-Methylbutanoic acid	0.060	0.020	0.050
Pentanoic acid	+	–	+
Hexanoic acid	0.040	0.070	0.050
trans-2-Hexenoic acid	0.030	–	–
	0.580	1.195	0.810

Table 1—*continued*

Compound	Concentration (mg kg^{-1}) Bilberry	Bog blueberry	High-bush blueberry
Aromatic compounds			
Benzyl alcohol	0.080	0.070	0.080
2-Phenylethanol	0.020	0.015	0.030
3-Phenylpropan-1-ol	0.003	–	+
trans-Cinnamylalcohol	+	0.010	0.030
Guaiacol	–	+	–
Phenol	0.030	0.060	0.060
p-Cresol	0.001	–	–
Pyrocatechol	–	+	–
2-Methoxy-5-vinylphenol	+	0.060	+
4-Vinylphenol	0.010	0.070	0.070
Thymol	–	–	+
Eugenol	0.010	–	0.012
Isoeugenol	+	–	+
Myristicine	–	–	+
Benzaldehyde	+	0.040	+
Phenylacetaldehyde	0.003	–	–
trans-Cinnamaldehyde	+	–	+
Vanillin	0.015	+	0.010
Methyl salicylate	0.001	–	–
2-Phenylethyl formate	0.002	–	–
2-Phenylethyl acetate	+	–	–
	0.175	0.325	0.292
Esters			
Hexyl acetate	–	–	+
cis-3-Hexenyl acetate	+	–	–
trans-2-Hexenyl butyrate	–	–	+
Methyl 2-hydroxy-3-methylbutanoate	0.020	–	–
Methyl 3-hydroxy-3-methylbutanoate	+	–	–
Ethyl-2-hydroxy-3-methylbutanoate	+	–	–
Ethyl 3-hydroxy-3-methylbutanoate	0.010	–	–
	0.030		
Other compounds			
1,8-Cineol	+	–	+
α-p-Me_2-styrene	+	–	+
γ-Butyrolactone	+	–	–
γ-Octalactone	0.045	–	–
γ-Decalactone	0.022	–	–
γ-Dodecalactone	+	–	–
δ-Decalactone	+	–	–
Pentylfuran	+	+	+
Hydroxyisocarvomentol	+	–	+
Farnesylacetate	–	–	0.070
	0.067		0.070

citronellol was considered to be blueberry-like. However, this and many other compounds were present below their threshold concentrations (threshold concentration of hydroxycitronellol = 5 mg kg^{-1} in water), and it is possible that synergism may play an important role in the overall impression of odour of blueberries. Hydroxycitronellol has not previously been found in any fruits or berries. The concentrations of acetic acid, benzaldehyde, 4-vinylphenol and 2-methoxy-5-vinylphenol were highest in the bog blueberry. The two last-named compounds have been identified previously in cloudberry (*Rubus chamaemorus* L. *Rosaceae*) by Honkanen and Pyysalo.[14] These two compounds are probably formed by enzymic decarboxylation of 4-hydroxy- and 3-hydroxy-4-methoxycinnamic acid.

von Sydow *et al.*[4] found considerable amounts (4.7% of total volatiles) of 2-phenylethyl benzoate in bilberries. This compound has not been detected in any of the berries used in the present study.

Acknowledgements

The authors are indebted to Dr Heimo Hiirsalmi, Agricultural Research Centre, Institute of Horticulture, Piikkiö, Finland for helpful co-operation, valuable discussions and for supplying berries.

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