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The Aroma of Cranberries

II. *Vaccinium macrocarpon* Ait.

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The volatiles of American cranberries (*Vaccinium macrocarpon* Ait. *var.* Early Black) have been analyzed using gas chromatography and mass spectrometry. 89 compounds amounting to 83 % of the essential oil have been conclusively identified. Of these are 19 aliphatic alcohols, 20 aliphatic aldehydes and ketones, 19 terpene derivatives, 19 aromatic compounds, and 12 other compounds. α-Terpineol (23.7 %) is dominating but 2-methylbutyric acid, the most important aroma compound of *Vaccinium vitis-idaea* L., is negligible. In view of the similarities between the two essential oils, this difference is likely to be the major cause for the difference in aroma.

In part I of this series [1] the essential oil of *Vaccinium vitis idaea* L. (mountain cranberries, red worthleberries, cowberries or lingonberries, in Swedish: lingon) was investigated using gas chromatography and mass spectrometry. In this paper similar data on *V. macrocarpon* Ait. (cranberries, large or American) will be presented and in a further report *V. myrtillus* L. (blueberries, in Swedish: blåbär) will be dealt with. A comparison of data obtained from juice of *V. vitis-idaea* L., *V. macrocarpon* Ait.[2] and *V. oxycoccus* L. will also be made in a later report.

The technique used in this investigation is the same as the one reported in Part I[1] with the exception that the first fractionation was made in a way to give more fractions of smaller retention intervals (35 fractions instead of 19). Due to the sensitivity of the combined gas chromatograph-mass spectrometer much less material was extracted in this investigation giving pure fractions so small that infrared spectrophotometry was not practical to use. The mass spectrometric data obtained were, however, in most cases quite sufficient to allow positive identification.

EXPERIMENTAL

Materials. American cranberries (*Vaccinium macrocarpon* Ait. *var.* Early Black) from New Jersey, USA, were harvested in September 1966 and transported and stored at −20°C or lower until used in December the same year.

Concentration of volatiles. The essential oil was concentrated by a method described by Andersson and von Sydow [3] modified by Anjou and von Sydow.[1] 28 kg of the berries yielded 3.6 kg of press residue. The final specimen volume after the extraction and distillation procedures was 125 µl. The content of remaining solvent was determined by gas chromatography.

With regard to volatile acids no appreciable amounts were found in the press residue.

Gas chromatography. The equipment consisted of an Aerograph model 202 (hot-wire detector) and a Perkin-Elmer model 800 (flame ionization detector). The columns used were:

a) 20 % methyl silicon oil SF 96 on Chromosorb W AW 60—100 mesh, 3/8″ × 3 m Al-tubing (denotion: SF 96 column).
b) 5 % carbowax 20 M on Chromosorb W AW DMCS 80—100 mesh, 1/8″ × 3 m stainless steel tubing (denotion: CW 20 M column).

The concentrate from the press residue was separated into 35 fractions on the SF 96 column. The temperature was programmed 50—200°C at 3°/min, the helium carrier gas flow rate was 200 ml/min and the sample size 100 µl. The fractions were collected in liquid air chilled glass U-tubes and each fraction was then dissolved in 25 µl ether.

These fractions were investigated using the CW 20 M column in Perkin-Elmer 800. The nitrogen carrier gas flow rate was 25 ml/min and the temperatures were selected between 40° and 220°C depending on the fraction examined. Temperature programming was usually used.

The relative amounts of the various fractions were estimated from the areas of the chromatographic peaks by cutting out and weighing them.

Mass spectrometry. The fractions were also analyzed in a combined gas chromatograph-mass spectrometer, LKB 9000. The gas chromatographic separation was done

Table 1. Aliphatic alcohols.

Compound	%	Fraction	% in *V. vitis-idaea*
1-Pentanol	0.8	7E	1.7
1-Hexanol	0.07	10F	2.3
1-Octanol	1.2	16L	0.7
1-Nonanol	0.5	19E	0.3
1-Decanol	0.2	20I	—
1-Undecanol	0.1	22H	—
3-Methyl-1-butanol	0.2	6G	0.8
2-Pentanol	1.0	4C	0.8
2-Octanol	0.03	14I	—
3-Pentanol	0.1	4B	0.3
3-Hexanol	0.03	7C	—
3-Heptanol	0.03	10E	—
3-Octanol	0.02	14H	—
2-Methylcyclohexanol	0.03	12E	—
3-Methylcyclohexanol	0.01	12F	—
2-Methyl-3-buten-2-ol	1.6	1D	3.6
3-Methyl-3-buten-2-ol	0.2	3E	0.4
3-Hexen-1-ol	0.01	10G	1.0
1-Octen-3-ol	0.6	13I	0.5

Total 6.7

on a modified carbowax 20 M column (5 % FFAP on Chromosorb W AW DMCS 80—100 mesh, 1/8″ × 2.65 m stainless steel tubing). This column has almost the same separation characteristics as the CW 20 M column. The temperatures were selected in the same way as on the CW 20 M column giving almost identical gas chromatograms. Mass spectra were recorded at 70 eV. The separator temperature was usually 200°C and the ion source temperature 270°C. The fractions were identified by comparison with own reference spectra or spectra given in the literature.

RESULTS

The essential oil was separated in 35 fractions on the SF 96 column. Each of these fractions was subjected to analysis in the combined gas chromatograph-mass spectrometer using the FFAP column. In almost all instances this gave sufficient separation of the peaks enabling positive identification by mass spectrometry. For a quantitative estimation of the compounds the 35 fractions were gas chromatographed separately on a CW 20 M column using flame ionization detector. The data obtained were invariably checked by the retention times observed on the different columns. The identified compounds are presented in Tables 1—5, in which the numerals refer to the 35 main frac-

Table 2. Aliphatic aldehydes and ketones.

Compound	%	Fraction	% in *V. vitis-idaea*
Pentanal	0.4	3A	1.3
Hexanal	0.7	7B	1.6
Heptanal	0.2	10C	0.3
Octanal	0.7	14F	0.4
Nonanal	1.0	17H	2.4
Decanal	0.4	19B	0.4
Undecanal	0.2	21D	—
Dodecanal	0.04	23G	—
(2-Methyl butanal)	0.2		
trans-2-Heptenal	0.4	12D	0.5
trans-2-Octenal	0.4	15J	0.3
trans-2-Nonenal	0.08	18G	0.3
trans-2-Decenal	0.5	20G	0.4
trans,trans-2,4-Heptadienal	0.1	14K	0.1
2,4-Decadienal	0.09	21J	0.5
2-Octanone	0.005	12C	—
2-Tridecanone	0.2	25H	—
2-Pentadecanone	0.05	28F	—
2-Octadecanone	0.3	31G	0.01
6-Methyl-5-hepten-2-one	0.3	13G	0.4
Diacetyl	0.4	3A	0.3

Total 6.7

tions obtained on the SF 96 column and the letters to the subfractions in alphabetical order obtained on the CW 20 M column. The concentrations given refer to the total neutralized ether free concentrate. As several fractionations are involved and since the separations were often not complete the figures given are only approximate. For comparison, the amounts of the compounds found also in lingonberries have been included in Tables 1—5.

Altogether 126 compounds have been identified. Of these are about 25 aromatic hydrocarbons which may originate from the solvent. Benzene, *o*-xylene and styrene are the major ones. It is also doubtful whether the phthalates and some of the phenols originate from the cranberries. It is definitely established, however, that at least 89 compounds comprising 68 % of the concentrate originate from the cranberries. The amount corresponds to not less than 83 % of the essential oil.

Of major compounds not identified there is one of 0.8 % namely 26 N corresponding to fraction 15 S for lingonberries.[1] There are four compounds of 0.5—0.4 % not identified and below that concentration but still observable by gas chromatography a few hundred compounds more not identified.

Table 3. Terpenes.

Compound	%	Fraction	% in *V. vitis-idaea*
Myrcene	0.06	14B	0.02
Limonene	0.4	15B	0.3
α-Terpinene	0.07	17D	—
α-Pinene	0.1	12A	0.9
3-Carene	0.08	15A	0.3
Camphene	0.002	12A	0.1
Linalool	0.3	17L	0.3
Nerol	0.6	20L	—
4-Terpinenol	0.02	19	0.9
α-Terpineol	23.7	19G	0.7
1,8-Cineole	0.7	15C	0.2
trans-Linalool oxide	0.2	16J	—
cis-Linalool oxide	0.3	16K	—
α-Cedrene	0.01	24B	—
trans,trans-Farnesol	0.02	26K	—
Cedrenol	0.1	27D	—
Pimaradiene	1.0	33G	0.1
(−)-Kaurene	1.1	34M	—
Manoyloxide	0.3	33J	0.8

Total 29.1

DISCUSSION

With the technique used in this investigation several of the low boiling compounds are missed and the composition of the essential oil investigated is not necessarily representative for the aroma of the whole fruit or the juice. It is felt however, that the major aroma producing compounds are included in the data presented here. A comparison with data from the press juice [2] will be presented later.

The cranberries studied here contained 1.1 ppm essential oil of the fresh weight which is about the same amount as in lingonberries.[1]

From Tables 1—5 and by comparison with the data obtained for lingonberries it can be seen that qualitatively the two essential oils are rather similar. The quantitative differences are, however, quite appreciable particularly for

Table 4. Aromatic compounds.

Compound	%	Fraction	% in *V. vitis-idaea*
Benzaldehyde	1.1	12G	3.3
Acetophenone	0.2	15N	1.1
Benzyl alcohol	9.0	15S	40.2
2-Phenyl ethanol	1.4	17U	0.7
Phenol	0.03	14M	0.2
Cresol	0.08	16S	—
(Dimethyl phenol)[a]	0.04	18V	—
(*m*-or-*p*-Ethyl phenol)[a]	2.1	18X	0.3
(Trimethyl phenol)[a]	0.06	20T	—
(Trimethyl phenol)[a]	0.1	20U	—
Thymol	0.1	21R	0.08
Carvacrol	0.5	21S	0.1
Eugenol	0.2	23P	1.0
o-Hydroxydiphenyl	0.7	25V	0.07
4-Ethyl-2-methoxy-phenol	0.7	21P	0.1
Methyl benzoate	0.6	16M	1.5
Ethyl benzoate	0.7	18L	0.2
Benzyl benzoate	1.2	29G	0.2
Benzyl salicylate	0.4	32M	0.3
Benzyl formate	0.03	15O	0.1
(Dimethyl phthalate)[a]	0.02	23R	—
(Diethyl phthalate)[a]	0.3	26R	0.02
(Di-isobutyl phthalate)[a]	0.2	31K	—
(Di-butyl phthalate)[a]	2.8	32L	0.8
Ethyl cinnamate	0.003	24K	—
Benzothiazole	0.6	19J	—
Dibenzofuran	0.008	25S	—
	Total 22.5		

[a] may originate from pentane solvent.

Table 5. Other compounds.

Compound	%	Fraction	% in *V. vitis-idaea*
Ethyl acetate	0.8	1A	4.1
Methyl butyrate	0.07	5A	—
Ethyl butyrate	0.03	7A	—
Isopropyl butyrate	0.4	9A	—
(Hexyl butyrate)	0.1	19A	—
2-Butyl furan	0.02	10A	—
2-Pentyl furan	0.2	14C	0.1
Furfural	0.4	8E	0.5
2-Hexyl thiophene	0.03	20D	—
2-Heptyl thiophene	0.005	22G	—
Isophorone	0.2	17N	—
Indene	0.07	15K	—
1-Octadecene	6.1	30B	—

Total 8.4

some of the more abundant compounds. Thus α-terpineol is the major component in cranberries (23.7 %) compared with 0.7 % in lingonberries. On the other hand benzyl alcohol, present in 40.2 % in lingonberries, amounts to 9.0 % in the essential oil of cranberries. Of great importance is also that 2-methylbutyric acid is missing or present in very small amounts in cranberries. If these three compounds are excepted the amount of the different chemical groups of aroma compounds are rather similar in cranberries and lingonberries.

With regard to the aliphatic alcohols (Table 1) the main differences in concentration are that hexanol and 3-hexen-1-ol are much less abundant in cranberries.

Among the monoterpenes (Table 3) no carbonyl compounds were identified in cranberries while three such compounds were found in lingonberries totalling 0.7 %. The large difference in content of α-terpineol has already been pointed out. As second monoterpene alcohol in quantity nerol was identified in cranberries (0.6 %) but this compound was not found in lingonberries. In cranberries 4-terpinenol was found in much smaller quantities than in lingonberries and perilla alcohol and borneol was not found at all. The identified sesquiterpenes are not the same in the two berries while the diterpenes pimaradiene and manoyloxide were found in both.

Beside benzyl alcohol (Table 4), acetophenone, anisaldehyde and eugenol are all less abundant in cranberries than in lingonberries. Contrary, carvacrol and some other ones are more abundant.

Several butyrates have been identified in cranberries. None was found in lingonberries.

As 2-methylbutyric acid and α-terpineol both have high specific odour intensity [4,5] the difference in aroma between cranberries and lingonberries may well be explained by the difference in concentrations of these compounds, particularly with reference to the fact that other quantitative and qualitative differences in chemical composition do not seem to be important for the aroma. A further support is the fact that a change of pH in cranberries results in a much less noticeable change in the aroma than is the case for lingonberries.[1,5]

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