ACTA CHEMICA SCANDINAVICA 20 (1966) 529–535

The Aroma of Black Currants

III. Chemical Characterization of Different Varieties and Stages of Ripeness by Gas Chromatography

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Six botanical varieties of black currants (*Ribes nigrum* L.) and one variety of five stages of ripeness were investigated by gas chromatography. Both the essential oil and the headspace gas were subjected to analysis using two different stationary phases. Some previously identified aroma compounds were quantitatively determined. Differences in the concentrations of some of these compounds were found between all six varieties and a systematic trend in the concentrations during the ripening process was also shown.

Volatile compounds contributing to the aroma of black currants *var.* Brödtorp have been identified previously.[1,2] As it is well known that botanical varieties of fruits and berries in general have different flavour properties, it was found desirable to study black currants in this respect. At the same time the influence of stage of ripeness on the aroma composition was studied for one variety, for the quantitative composition of the volatile complex will presumably change continuously up to the time of harvest, which is in practice determined by considerations other than objective aroma analysis.

The material studied in this investigation was gathered during one season and from a single area. This, however, does not impair the general validity of any conclusions made for it has been shown that normal variations in growing conditions and climate have only a slight influence on the composition of the volatile fraction. Thus Brödtorp from 1962, 1963, and 1964 grown at one site and Brödtorp from 1962 grown at seven sites with widely different soils showed only small quantitative differences in the components of the essential oils.[3]

Both the essential oil and the headspace gas of the berries were invariably analyzed by gas chromatography using columns of different selectivity. Certain components of the essential oils were quantitatively determined from the chromatograms.

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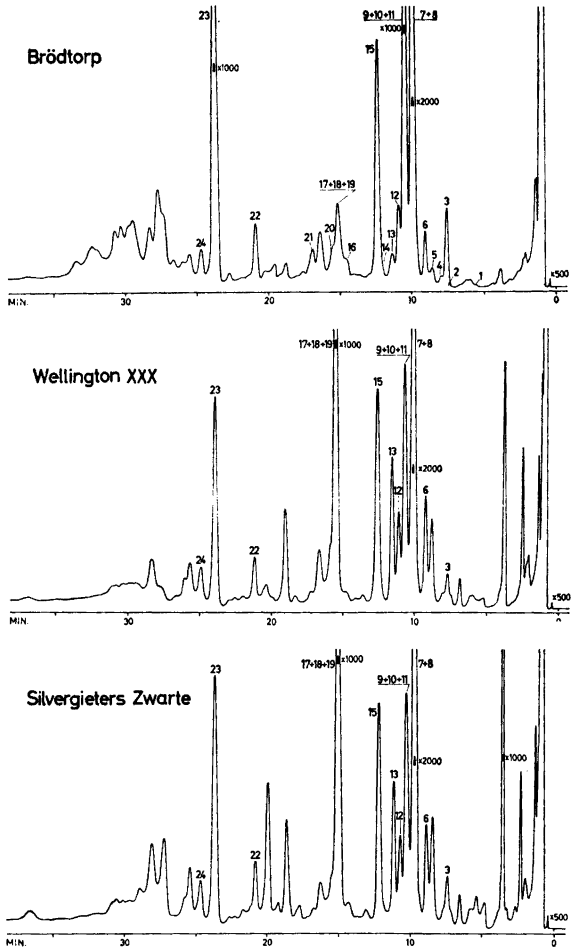

Fig. 1a.

EXPERIMENTAL

Materials. Six varieties of black currants, all fully ripe in a technical sense, were harvested in July 1964. The varieties were: Brödtorp, Silvergieters Zwarte, Wellington XXX, Cotswold Cross, and two hybrids, Wellington XXX × Brödtorp and Cotswold Cross × Brödtorp.

Black currants *var.* Brödtorp were picked in July 1964 at five successive stages of ripeness:

Date of harvest	*Ripening stage*
July 3	Unripe (40 % w/w fully green berries)
July 9	Half ripe (15 % fully green and 35 % fully black berries)
July 16	Fully ripe (75 % fully black berries)
July 22	Half overripe
July 27	Overripe

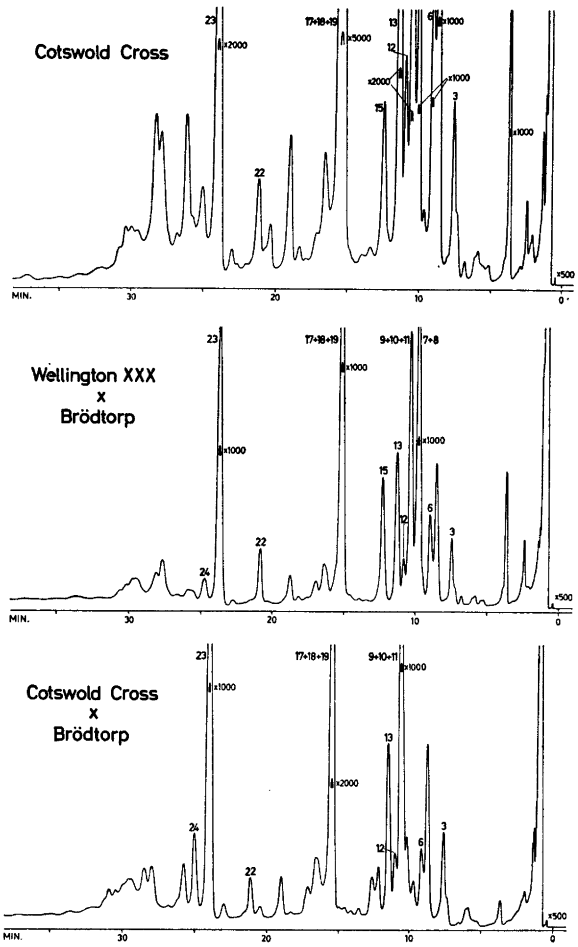

Fig. 1b.

Fig. 1, a,b. Gas chromatograms on silicone oil SF 96 of the essential oils of six varieties of black currants.

1. *cis*-3-Hexen-1-ol, 2. Benzaldehyde, 3. α-Pinene, 4. Camphene, 5. 1-Octen-3-ol, 6. Myrcene, 7. 3-Carene, 8. *p*-Cymene, 9. Limonene, 10. β-Phellandrene, 11. *cis*-β-Ocimene, 12. *trans*-β-Ocimene, 13. γ-Terpinene, 14. Methyl benzoate, 15. Terpinolene, 16. Ethyl benzoate, 17. Terpinen-4-ol, 18. *p*-Cymen-8-ol, 19. Methyl salicylate, 20. α-Terpineol, 21. Citronellol, 22. Citronellyl acetate, 23. Caryophyllene, 24. Humulene.

The berries were frozen immediately after they had been gathered and were stored at −40°C until used (April—May, 1965).

Sample preparation. The concentration method for the essential oils has been described elsewhere.[1] The following major modifications were made: 3 kg of the berries, preserved by addition of 3 g NaF, were extracted with four 1000 ml portions of pentane. The total extraction time was 46 h. 1500 ml steam distillate was collected, and the aqueous phase

was extracted with two 100 ml portions of diethyl ether. The final volume of each concentrate was 200 μl.

For headspace analysis, the berries were homogenized with a mixture of solid CO_2 The carbon dioxide was evaporated at −20°C, and 20 ml injection bottles were filled with 10 g each of the resulting powder. The bottles were closed with rubber caps and stored at −30°C until used.

Gas chromatography. The essential oils were analyzed in a Perkin-Elmer model 800 on two different stainless steel columns, 1/8″ × 2 m:

(a) 15 % silicone oil SF 96 on Chromosorb W AW DMCS 60−80 mesh. Column temperature: Programmed 70−195°C at 4.2°C/min.
(b) 5 % Castorwax on Chromosorb G AW DMCS 80−100 mesh. Column temperature: Programmed 70−205°C at 4.2°C/min.

Injector temperature 225°C; carrier gas nitrogen 33 ml/min; sample size, 0.8 μl in both cases.

The relative amounts of the various components were determined by cutting out and weighing the peaks of separate chromatograms run at a high paper velocity, 2″/min. The amount of essential oil in the concentrates was calculated from the sum of the peak weights and the weight of the solvent peak.

The headspace gases were analyzed on two different stainless steel columns, 1/8″ × 2.7 m, in a Wilkens Aerograph model 204 (c) and a Perkin-Elmer model 800 (d):

(c) 18 % polyethylene glycol 1000+0.5 % Tween 80 on Chromosorb W AW DMCS 80−100 mesh. Temperature: Isothermal at 65°C.
(d) 20 % silicone oil DC 550+0.2 % Tween 80 on Chromosorb W AW DMCS 80−100 mesh. Temperature: Programmed 35−95°C at 4.2°C/min, subsequently isothermal at 95°C.

In both cases the carrier gas was moist nitrogen fed at a rate of 30 ml/min. The sample bottles were equilibrated for 25 min fully immersed in a water bath at 50°C. A gas-tight syringe was heated to 60°C and a 2.5 ml sample of headspace vapor was withdrawn and introduced into the column.

Denomination of the chromatographic peaks. For twenty-four components previously identified in black currants [1] the position in the chromatograms were determined by co-chromatography of small amounts of the compounds with an aroma concentrate from black currants *var.* Brödtorp. Three or four compounds with widely different retention times on the actual column were selected for each chromatographic run.

RESULTS AND DISCUSSION

The reproducibility of the concentration procedure and the headspace sampling technique was estimated by measuring the relative standard deviation for the chromatographic peaks of relevant interest. Three samples of berries were used for each of these determinations. The average value found for the preparation of the essential oil was 6 %; that for the headspace sampling technique, 8 %.

The chromatograms on the SF 96 column of the essential oils of the six varieties investigated are shown in Fig. 1. From these chromatograms and the ones obtained on the Castorwax column quantitative data were determined for 3-carene, γ-terpinene, terpinolene, terpinen-4-ol, citronellyl acetate, and caryophyllene. The total amount of essential oil was also determined. These data are presented in Table 1.

Cotswold Cross has roughly three times as much essential oil as the other varieties. Silvergieters Zwarte and Wellington XXX which are of similar botanical origin are both qualitatively and quantitatively very similar, but can be distinguished. The compositions of the monoterpene fractions are almost identical. Compared with these two varieties both Brödtorp and Cots-

Table 1. Quantitative data for some major components in the essential oils of six varieties of black currants.

Variety	Essential oil ppm	3-Carene		γ-Terpinene		Terpinolene		Terpinen-4-ol		Citronellyl acetate		Caryophyllene	
		% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries
Brödtorp	13	18	2.3	0.6	0.1	5.7	0.75	1.1	0.14	1.5	0.19	12	1.6
Wellington XXX	10	14.5	1.4	3.5	0.35	5.0	0.5	12	1.2	1.2	0.12	4.9	0.5
Silvergieters Zwarte	11.5	12.5	1.5	2.9	0.34	4.3	0.5	10	1.2	1.2	0.14	5.1	0.6
Cotswold Cross	31	< 2	<0.6	7.4	2.3	1.5	0.5	26	8.0	1.3	0.40	10.5	3.3
Wellington XXX × Brödtorp	10.5	8.6	0.9	3.7	0.39	3.4	0.35	14	1.5	1.9	0.20	12	1.3
Cotswold Cross × Brödtorp	12	< 1.5	<0.2	3.5	0.42	<0.6	<0.1	13	1.5	1.0	0.13	13	1.5

Table 2. Quantitative data for some major components in the essential oils of black currants *var.* Brödtorp of different ripening stages.

Date of harvest	Ripening stage (see text)	Essential oil, ppm	3-Carene		Terpinolene		Terpinen-4-ol		Citronellyl acetate		Caryophyllene	
			% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries	% in oil	ppm in berries
July 3	Unripe	10	14.5	1.5	2.6	0.25	1.5	0.15	1.5	0.15	12	1.2
July 9	Half ripe	11.5	15	1.7	3.6	0.40	1.1	0.13	1.4	0.16	11.5	1.3
July 16	Fully ripe	12	15.5	1.9	3.6	0.40	1.2	0.14	1.5	0.18	12.5	1.5
July 22	Half overripe	13	17	2.2	4.4	0.55	1.1	0.14	1.5	0.20	13	1.7
July 27	Overripe	13.5	18	2.5	7.8	1.1	1.0	0.14	1.6	0.22	14	1.9

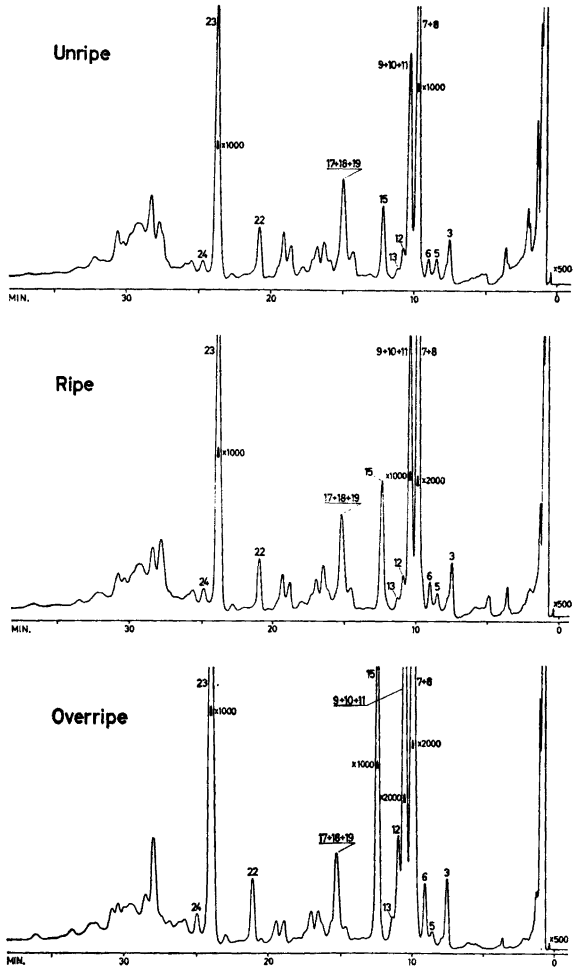

Fig. 2. Gas chromatograms on silicone oil SF 96 of the essential oils of black currants *var.* Brödtorp of different ripening stages. For peak numbering see Fig. 1.

wold Cross contain much more caryophyllene. Brödtorp is characterized by low concentrations of γ-terpinene and terpinen-4-ol. Cotswold Cross has even relatively high concentrations of these compounds and a low concentration, both absolute and relative, of 3-carene.

Some of these characteristic features can be easily traced in the hybrids investigated. Thus Wellington XXX $\times$ Brödtorp has high content of γ-terpinene and terpinen-4-ol from Wellington XXX and of caryophyllene from Brödtorp. It is interesting to note that the content of 3-carene is lower than in both parent plants. Cotswold Cross can be traced in its hybrid with

Brödtorp through the low concentrations of 3-carene and terpinolene. The concentrations of γ-terpinene and terpinen-4-ol in the hybrid seem to be close to the mean values found for the parent plants.

In pertinent parts these observations were supported by data obtained with the headspace technique. Thus, the results regarding total amount of volatiles and content of 3-carene were confirmed. With the exception of Wellington XXX and Silvergieters Zwarte all varieties can be distinguished by their headspace chromatograms.

The chromatograms on the SF 96 column of the essential oils of Brödtorp berries harvested at five successive stages of ripeness are shown in Fig. 2. Quantitative data were obtained as before and are given in Table 2. The following observations were in pertinent parts supported by data from the headspace chromatograms. The total amount of essential oil in the berries increased slowly during ripening which was also the case with the monoterpene fraction, as examplified by 3-carene and terpinolene, the latter showing a sharp increase beyond the time of normal technical ripeness. The monoterpene derivative content of the berries seemed to be fairly constant and caryophyllene increased slowly during ripening. Of the more volatile compounds, the majority changes very little during ripening. Exceptions are ethanol and 2-methyl-3-buten-2-ol, which increased considerably during the later part of the ripening process.

On the whole, only minor changes in the volatile fraction of black currants seemed to occur during ripening, in contrast with observations made in banana [4,5] and papaya.[6]

Acknowledgement. We are indebted to Miss B.-M. Andersson and Miss B. Eriksson for skilful technical help. The investigation was supported by grants from the *Swedish Technical Research Council* and the *National Council for Consumer Goods Research and Consumer Information.*

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Received November 5, 1965.