

## The Aroma of Black Currants

### I. Higher Boiling Compounds

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With gas chromatography, infrared spectrophotometry and mass spectrometry black currants (*Ribes nigrum* L. var. Brödtorp) were analyzed for volatile compounds with boiling points above 150°C. The following twentyfive compounds were identified: myrcene (1.4%), *cis*- $\beta$ -ocimene (2.6), *trans*- $\beta$ -ocimene (2.9), limonene (3.8),  $\beta$ -phellandrene (5.3),  $\gamma$ -terpinene (0.7), terpinolene (4.9), *p*-cymene (0.9), *m*-cymene (0.4),  $\alpha$ -pinene (7.0), car-3-ene (25.9), camphene (0.6), citronellol (1.4),  $\alpha$ -terpineol (0.5), terpinen-4-ol (3.3), *p*-cymen-8-ol (2.9), citronellyl acetate (2.5), caryophyllene (11.6), humulene (0.2), benzaldehyde (0.1), methyl benzoate (0.1), ethyl benzoate (0.2), methyl salicylate (0.5), *cis*-hex-3-en-1-ol (0.1), and oct-1-en-3-ol (0.3).

As a link of an investigation on the flavour of black currants an analysis of the essential oil of the leaves was published by Andersson, Bosvik and von Sydow.<sup>1</sup> Previous to that paper Glichitch and Igolen<sup>2</sup> described some volatile compounds in the essential oil of the buds. These results will be discussed later and compared with the data presented here.

The concentrate of volatiles was fractionated by gas chromatography on a polar column and fractions were condensed. For infrared spectrophotometric identification the collected fractions were rechromatographed on a nonpolar column. The mass spectrometric analysis was carried out directly on the collected fractions in a combined gas chromatograph-mass spectrometer.

Owing to differences in volatility of the aroma compounds the concentration procedure used for those components of the volatile complex that had a high boiling point differed from that used for those with a lower boiling point. The present study is concerned with the volatile compounds with a boiling point above 150°C. The analysis of the low boiling fraction is under way and the results will be presented later.

## EXPERIMENTAL

*Materials.* Ripe berries of *Ribes nigrum* L. var. Brödorp were picked in the middle of August 1962 and were stored at  $-40^{\circ}\text{C}$  until used (June 1963).

Reference compounds for infrared spectrophotometry and mass spectrometry were available except for *p*-cymen-8-ol and 1-methyl-4-isopropenylbenzene. These compounds were synthesized from *p*-methyl acetophenone by action of the methyl Grignard reagent ( $\text{CH}_3\text{Mg I}$ ). The reaction mixture contained a small amount of the dehydration product 1-methyl-4-isopropenylbenzene, which was separated from the main product, *p*-cymen-8-ol, by preparative gas chromatography.

*Concentration of the volatiles.* The concentration procedure used consisted of a batch extraction of the berries with pentane, followed by evaporation of the solvent and steam distillation of the residue.

4 kg of the berries was minced and 10 g of sodium benzoate was added to suppress fermentation. The resulting mash was treated with a depectinizing enzyme for 24 h at room temperature and then extracted with redistilled pentane in a simple batch extractor, consisting of a 5 l separatory funnel rotated by means of a pneumatic motor. Seven 800 ml portions of pentane were used, and the total extraction time was 26 h. The pentane was evaporated on a water bath ( $45^{\circ}\text{C}$ ) through a short Vigreux column with a small reflux. The evaporation residue (250 ml) was first washed with sodium carbonate to remove the added benzoic acid as well as other acidic compounds, and then washed twice with water.

The washed extracts from four extraction batches were pooled and further concentrated to a final volume of 100 ml in a rotary vacuum evaporator at  $15^{\circ}\text{C}$ . The resulting concentrate, which contained large amounts of non-volatile material, was then subjected to steam distillation at atmospheric pressure, and 1200 ml distillate was collected. The distillate, consisting of an aqueous phase and a small pentane phase, was saturated with ammonium sulphate and extracted with three 200 ml portions of diethyl ether. The ether-pentane extract was dried over sodium sulphate, and the solvents were removed in a rotary vacuum evaporator at  $15^{\circ}\text{C}$ .

48 kg of the berries yielded 440 mg (9.1 ppm of the fresh weight) containing 10–15 % of residual solvents (diethyl ether and pentane). The oil was stored in a sealed ampoule under nitrogen at  $-25^{\circ}\text{C}$  until analyzed.

*Gas chromatography.* The equipment consisted of a Perkin–Elmer model 116 C Fractometer with a thermistor detector, and helium was used as carrier gas. Three packed columns (aluminium tubing, 3.9 m long, 4 mm inside diameter) were employed: (a) 15 % LAC 446 polyester on 60–80 mesh acid washed Embacel kieselguhr (denotation: LAC column)

(b) 10 % DC 200 silicone oil on 60–100 mesh Embacel (denotation: DC column)

(c) 10 % SAIB (sucrose diacetate hexaisobutyrate) + 5 % Quadrol (N,N,N',N'-tetrakis (2-hydroxypropyl)ethylene diamine) on 60–80 mesh Embacel (denotation: S column).

The oil was roughly separated into 25 fractions with use of the LAC column, operated at  $115^{\circ}\text{C}$  and with a helium flow of 60 ml/min. The fractions were collected in capillary U-tubes, chilled by liquid air or ice-water. The amount of material obtained from fifteen successive collections of some of the smaller fractions was not sufficient for infrared analysis, and then the entire yields were reserved for combined gas chromatography-mass spectrometry. The main part of each of the larger fractions was separated into subfractions on another column, and the subfractions were examined by infrared spectrophotometry. The DC column was used in most cases; the S column only in the few cases, where the DC column did not give satisfactory separation. In each particular case the column temperature was chosen to give a satisfactory separation within a reasonable time of analysis. The minor part of each fraction was reserved for combined gas chromatography-mass spectrometry.

The relative amounts of the various fractions were estimated from the chromatographic peak areas.

The reference compounds for infrared spectrophotometry were, when necessary, purified by preparative gas chromatography on the DC or S column. No decompositions or isomerisations on these columns could be detected under the experimental conditions used in this investigation, except for *p*-cymen-8-ol, a small part of which was dehydrated to 1-methyl-4-isopropenylbenzene.

Table 1. Analytical data and identified compounds of the higher boiling fraction of the aroma of black currants.

| Fraction LAC No. | Sub-fraction DC or S No. | %     | Infrared data  | Mass spectrometry data                               | Identified compound                                    | %                               |
|------------------|--------------------------|-------|--|--|--|---------------------------------|
| 1                | I                        | 0.2   | <i>a</i> -pinene   | C <sub>10</sub> H <sub>16</sub> (thujene)            | <i>a</i> -pinene<br>camphene                           | 7.0<br>0.6                      |
|                  | II                       | 7.0   |  |  |  |                                 |
|                  | III                      | 0.6   |  | C <sub>10</sub> H <sub>16</sub>                      |  |                                 |
|                  | IV                       | trace |  |  |  |                                 |
| 2                | I                        | 1.4   | myrcene  | myrcene  | myrcene  | 1.4                             |
|                  | II                       | 25.9  | car-3-ene  | car-3-ene  | car-3-ene  | 25.9                            |
| 3                | I                        | 3.8   | limonene   | (limonene)   | limonene   | 3.8                             |
|                  | II                       | 7.9   | $\beta$ -phellandrene<br>and <i>cis</i> - $\beta$ -ocimene | and<br>C <sub>10</sub> H <sub>16</sub>               | $\beta$ -phellandrene<br><i>cis</i> - $\beta$ -ocimene | 5.3<br>2.6                      |
|                  |                          | III   | 2.9  | <i>trans</i> - $\beta$ -ocimene                      | <i>trans</i> - $\beta$ -ocimene                        | <i>trans</i> - $\beta$ -ocimene |
|                  | IV                       | 0.7   |  | $\gamma$ -terpinene                                  | $\gamma$ -terpinene                                    | 0.7                             |
| 4                | I                        | 1.3   | <i>p</i> - and <i>m</i> -cymene                            | cymene   | <i>p</i> -cymene<br><i>m</i> -cymene                   | 0.9<br>0.4                      |
|                  | II                       | 4.9   | terpinolene  | (terpinolene)  | terpinolene  | 4.9                             |
|                  | III                      | trace |  | C <sub>10</sub> H <sub>14</sub> O                    |  |                                 |
| 5                | I                        | 0.1   | oct-1-en-3-ol  | <i>cis</i> -hex-3-en-1-ol                            | <i>cis</i> -hex-3-en-1-ol                              | 0.1                             |
|                  | II                       | 0.4   |  | octadienol   |  |                                 |
|                  | III                      | 0.1   |  | C <sub>10</sub> H <sub>18</sub>                      |  |                                 |
| 6                | I                        | 0.3   | oct-1-en-3-ol  | oct-1-en-3-ol<br>(heptanal) and<br>other compound(s) | 0.3  |                                 |
|                  | II                       | 0.7   | saturated aliphatic aldehyde                               |  |  |                                 |
| 7                | I                        | 0.6   |  | (1-methyl-4-iso-propenylbenzene)                     |  |                                 |
| 8                | I                        | 0.3   |  | unknowns   |  |                                 |
| 9                | I                        | 0.2   |  | unknown  | benzaldehyde   | 0.1                             |
|                  | II                       | 0.1   |  | C <sub>10</sub> H <sub>16</sub> O                    |  |                                 |
|                  | III                      | 0.1   |  | C <sub>10</sub> H <sub>16</sub> O                    |  |                                 |
|                  | IV                       | 0.1   |  | unknowns   |  |                                 |
| 10               | I                        | 0.1   |  | benzaldehyde   | benzaldehyde   | 0.1                             |
|                  | II                       | 0.3   |  | monoterpene derivative                               |  |                                 |
| 11               | I                        | 3.3   | terpinen-4-ol  | terpinen-4-ol  | terpinen-4-ol  | 3.3                             |
|                  | II                       | 0.6   | aliphatic unsaturated acetate                              | monoterpene derivative                               |  |                                 |
|                  |                          | III   | 0.7  | unsaturated hydrocarbon                              |  |                                 |
|                  | IV                       | 11.6  | caryophyllene  | caryophyllene  | caryophyllene  | 11.6                            |
| 12               | I                        | 0.1   | aliphatic acetate with vinylic double bond                 | methyl benzoate                                      | methyl benzoate  | 0.1                             |
|                  | II                       | 1.0   |  | monoterpene derivative                               |  |                                 |
|                  |                          | III   |  | 2.0  |  |                                 |
| 13               | I                        | 0.2   | ethyl benzoate   | ethyl benzoate                                       | ethyl benzoate   | 0.2                             |

Table 1. Cont.

| Fraction LAC No. | Sub-fraction DC or S No. | %     | Infrared data                                      | Mass spectrometry data                        | Identified compound  | %    |
|------------------|--------------------------|-------|--|---|----------------------|------|
| 14               | II                       | 2.5   | citronellyl acetate                                | citronellyl acetate                           | citronellyl acetate  | 2.5  |
|                  | III                      | trace |  | $C_{15}H_{24}$                                |                      |      |
|                  | IV                       | 0.3   | unsaturated hydrocarbon                            | $C_{15}H_{24}$                                |                      |      |
|                  | V                        | 0.2   | unsaturated hydrocarbon                            | $C_{15}H_{24}$                                |                      |      |
|                  | VI                       | trace |  | $C_{15}H_{24}$                                |                      |      |
|                  | I                        | 0.6   | primary or secondary unsaturated aliphatic alcohol | $C_{10}H_{16}O$                               |                      |      |
| 15               | II                       | 0.2   | humulene   | humulene                                      | humulene             | 0.2  |
|                  | I                        | 0.5   |  | $\alpha$ -terpineol                           | $\alpha$ -terpineol  | 0.5  |
| 16               | I                        | 0.4   | $>C=O$   | $C_9H_{14}O$                                  |                      |      |
| 17               | I                        | 0.9   | tertiary unsaturated aliphatic alcohol             | $C_{10}H_{16}O$ , hydroxyl in isopropyl group |                      |      |
|                  | II                       | 0.3   | $\alpha,\beta$ -unsaturated aliphatic ketone       | $C_{10}H_{14}O$ , ketone                      |                      |      |
|                  | III                      | 1.4   | citronellol  | citronellol                                   | citronellol          | 1.4  |
| 18               | I                        | trace |  | $C_{10}H_{16}O$                               |                      |      |
|                  | II                       | 0.5   | unknowns   | unknowns                                      |                      |      |
| 19               | I                        | 0.2   | $\alpha,\beta$ -unsaturated aliphatic ketone       | $C_{10}H_{14}O$ , ketone                      |                      |      |
|                  | II                       | 0.1   |  | $C_{15}H_{24}$                                |                      |      |
| 20               | I                        | 0.5   | methyl salicylate                                  | methyl salicylate                             | methyl salicylate    | 0.5  |
|                  | II                       | trace |  | $C_{15}H_{24}$                                |                      |      |
| 21               | I                        | trace |  | ester of $C_{10}H_{16}O$                      |                      |      |
|                  | II                       | trace |  | $C_{10}H_{14}O$ , ketone                      |                      |      |
|                  | III                      | trace |  | $C_{15}H_{24}$                                |                      |      |
|                  | IV                       | trace |  | $C_{15}H_{24}$                                |                      |      |
|                  | V                        | trace |  | $C_{15}H_{22}O$                               |                      |      |
| 22               | I                        | 0.1   |  | $C_{10}H_{16}O$ , alcohol                     |                      |      |
|                  | II                       | 0.1   |  | $C_{14}H_{22}$                                |                      |      |
|                  | III                      | 0.6   | unsaturated hydrocarbon                            | $C_{15}H_{24}$                                |                      |      |
|                  | IV                       | 0.7   | unsaturated hydrocarbons                           |   |                      |      |
| 23               | I                        | 0.3   |  | several $C_{15}H_{24}$                        |                      |      |
| 24               | I                        | 2.9   | <i>p</i> -cymen-8-ol                               | <i>p</i> -cymen-8-ol                          | <i>p</i> -cymen-8-ol | 2.9  |
|                  | II                       | 0.3   | unsaturated aliphatic                              | unknowns                                      |                      |      |
| 25               | I                        | 0.2   | unknowns   | unknowns                                      |                      |      |
|                  | II                       | 0.6   | two $>C=O$ , $\alpha,\beta$ -unsaturated           | $M = 150$                                     |                      |      |
|                  |                          | 94.4  |  |   |                      | 80.0 |

*Infrared spectrophotometry.* Infrared spectra were recorded on a Perkin-Elmer model 221 spectrophotometer. The capillary film technique was used when material was sufficient. When the sample quantity was very small the spectra were determined in  $CS_2$  solution in a micro-cavity cell with solvent compensation.

*Mass spectrometry.* The fractions from the LAC column were also analyzed in a combined gas chromatograph-mass spectrometer placed at our disposal by Dr. R. Ryhage, Stockholm. The mass spectrometer was an Atlas CH 4. The technique used was similar to that described previously.<sup>3,4</sup> The separation was made on a DC column (see Gas chromatography).

## RESULTS

The result of the separation of the volatiles on the LAC 446 column is shown in Fig. 1. Fractions were collected as denoted in Fig. 1 and the results will be presented in this order. The data obtained by the different techniques used is summarized in Table 1.

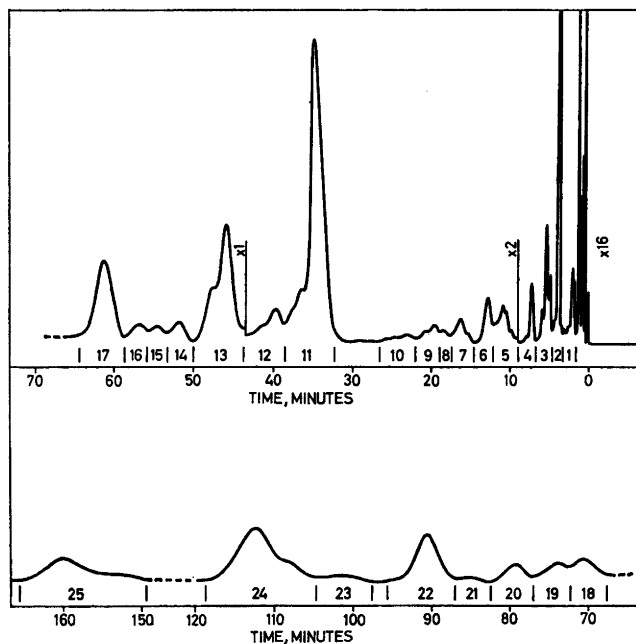


Fig. 1. Black currant volatiles separated by gas chromatography on the LAC column.

*Fraction No. 1.* This fraction was rechromatographed on the S column, before IR (infrared spectrophotometry or spectrum) of the largest subfraction (II), which was shown to be  $\alpha$ -pinene. This was confirmed by MS (mass spectrometry or spectrum) which also resulted in the conclusive identification of camphene (III) and a tentative identification of thujene (I).<sup>4</sup> A fourth subfraction consisted of one or more  $C_{10}H_{16}$  unidentified compounds.

*Fraction No. 2.* This fraction was shown by IR and MS to consist entirely of myrcene (I) and car-3-ene (II),<sup>4</sup> the latter being the most abundant compound in the concentrate investigated of which it represented 25.9 %.

*Fraction No. 3.* Subfractions I and II were not separated on the DC column connected to the mass spectrometer. The MS of this peak showed this fraction to consist entirely of  $C_{10}H_{16}$  compounds, one of which was thought to be limonene ( $m/e = 68$  strong).<sup>4</sup> Subfractions III and IV were conclusively shown to be *trans*- $\beta$ -ocimene and  $\gamma$ -terpinene, respectively.

In order to obtain a better separation for IR the whole fraction was rechromatographed on the S column, which yielded four subfractions: I consisting of pure limonene, II of a 67:33 mixture of  $\beta$ -phellandrene and *cis*- $\beta$ -ocimene and III, in accordance with MS, of *trans*- $\beta$ -ocimene.

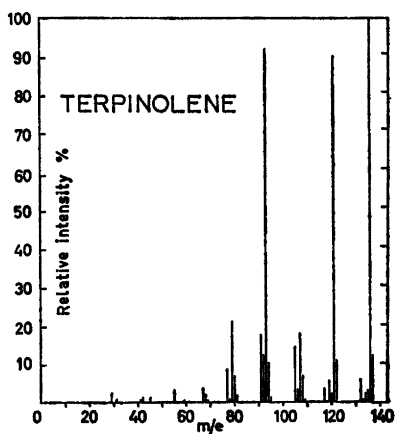


Fig. 2. Mass spectrum of terpinolene.

*Fraction No. 4.* Subfraction I was shown by MS to be cymene (the difference between the MS of the isomers is only slight). The infrared spectrum revealed the presence of both *p*- and *m*-cymene in the proportions 7:3. The largest subfraction (II) consisted entirely of terpinolene, as shown by IR and MS (Fig. 2). MS of the trace fraction III gave the molecular formula  $C_{10}H_{14}O$ . The general nature of the MS and the peak  $m/e = 132$  suggested that this compound is a monoterpene alcohol or aldehyde, but the retention time on the LAC 446 column excluded the alcohol.

*Fraction No. 5.* This small fraction was divided into three parts on the DC column. MS of I was identical with that of *cis*-hex-3-en-1-ol.<sup>7</sup> MS of II showed that this fraction is probably one of the isomers of octadienol, and that III is a  $C_{10}H_{16}$  monoterpene hydrocarbon. The retention data from the DC column originally suggested *allo*-ocimene, but MS ruled out this possibility.

*Fraction No. 6.* Subfraction I was shown by IR and MS to be oct-1-en-3-ol.<sup>1,8</sup> IR of II indicated the presence of a saturated aliphatic aldehyde, and MS suggested that heptanal is a possible component of this subfraction.

*Fraction No. 7.* The main part of this fraction was tentatively shown by MS to be 1-methyl-4-isopropenylbenzene.

*Fraction No. 8.* This fraction was not resolved on any of the columns used, and could not be identified by MS.

*Fraction No. 9.* Of the four subfractions obtained I and IV were not identified. MS of II and III indicated the molecular formula  $C_{10}H_{16}O$  and a monoterpene aldehyde or alcohol for both, although the MS's were different.

*Fraction No. 10.* Subfraction I was shown by MS to be benzaldehyde. MS of II resembled that of a monoterpene hydrocarbon, but this possibility was ruled out by retention data. This subfraction is more likely a monoterpene ester, several of which have a tendency to give a hydrocarbon MS under the experimental conditions used (*cf.* fraction 13: II).

*Fraction No. 11.* This large fraction was subfractionated into four parts of which I was shown by IR and MS to be terpinen-4-ol.<sup>5</sup> IR of II indicated the presence of aliphatic unsaturated acetate, and the MS made it plausible that this compound is a monoterpene ester. MS of III was that of a sesquiterpene hydrocarbon, which was supported by the IR data. Identification was not possible, however. Subfraction IV, which represented 11.6 % of the total, was shown by IR and MS to be caryophyllene (Fig. 3).

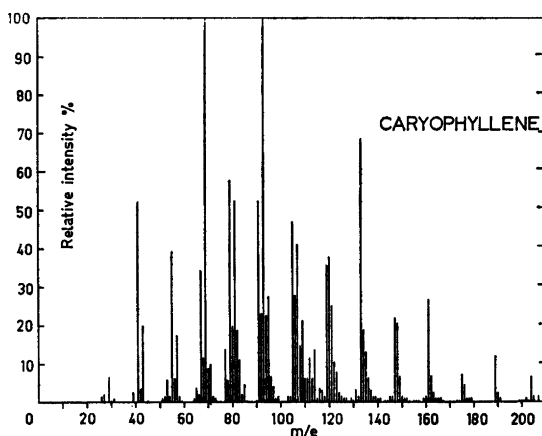


Fig. 3. Mass spectrum of caryophyllene.

*Fraction No. 12.* Subfraction I was shown by MS to be methyl benzoate. II is very likely a monoterpene ester, a conclusion drawn in the same way as for fraction No. 11: II. IR of III closely resembled that of No. 11: III. The two MS's are, however, quite different, but still those of sesquiterpene hydrocarbons.

*Fraction No. 13.* IR and MS of subfractions I and II conclusively revealed that these are ethyl benzoate and citronellyl acetate, respectively (Fig. 4). Besides these two fractions four small sesquiterpene hydrocarbon fractions were found by MS.

*Fraction No. 14.* The major part of this fraction (I) was shown by IR to be a primary or secondary unsaturated aliphatic alcohol with a terminal meth-

ylene group. The MS was similar to, but not identical with, that of carveol.<sup>5</sup> II was shown by IR and MS to be humulene (Fig. 5).

*Fraction No. 15.* This fraction was pure and shown by MS to be  $\alpha$ -terpineol.<sup>5</sup>

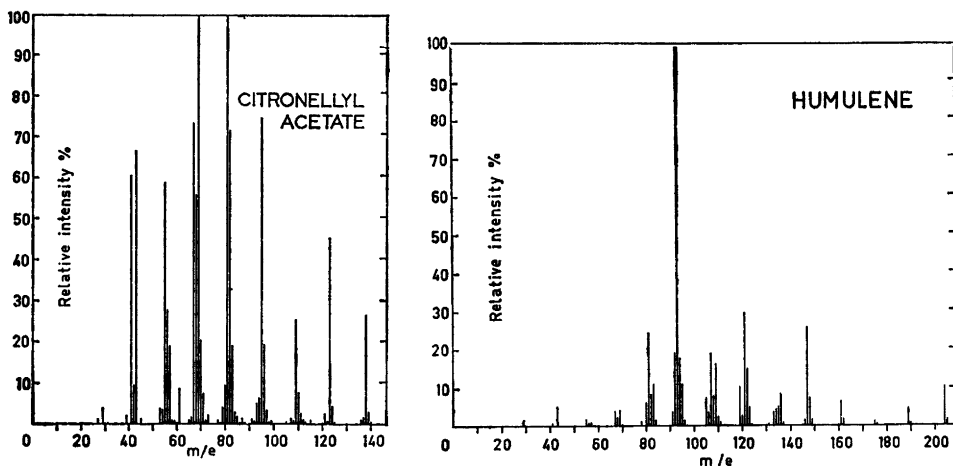


Fig. 4. Mass spectrum of citronellyl acetate. Fig. 5. Mass spectrum of humulene.

*Fraction No. 16.* This fraction consisted almost entirely of a compound, the IR of which showed the presence of a carbonyl group with a double bond in the  $\alpha,\beta$ -position. MS gave the molecular formula  $C_9H_{14}O$ .

*Fraction No. 17.* IR of subfraction I showed this compound to be a tertiary unsaturated aliphatic alcohol. MS indicated the molecular formula  $C_{10}H_{16}O$ . The very strong peak  $m/e = 59$  and the appearance of the MS together with the IR data suggest that this compound is a "dehydro- $\alpha$ -terpineol".<sup>5</sup> II is an  $\alpha,\beta$ -unsaturated aliphatic ketone with the formula  $C_{10}H_{14}O$  as indicated by IR and MS. The MS closely resembled that of piperitenone.<sup>6</sup> Subfraction III was shown by IR and MS to be citronellol.<sup>5</sup>

*Fraction No. 18.* This fraction consisted of several unknown compounds, one of which (I) is a monoterpene alcohol or aldehyde with the formula  $C_{10}H_{16}O$ .

*Fraction No. 19.* I is closely related to, but not identical with, No. 17: II, as shown by IR and MS. II is an unknown sesquiterpene hydrocarbon.

*Fraction No. 20.* The main part of this small fraction was methyl salicylate (MS and IR). It also contained a trace component, which is a sesquiterpene hydrocarbon (MS).

*Fractions Nos. 21, 22 and 23.* None of the components of these fractions could be identified. MS and IR gave, however, some information (Table 1).

*Fraction No. 24.* The main part (I) of this fairly large fraction was shown by IR and MS to be *p*-cymen-8-ol (Figs. 6 and 7). The fraction also contained several unknown compounds.



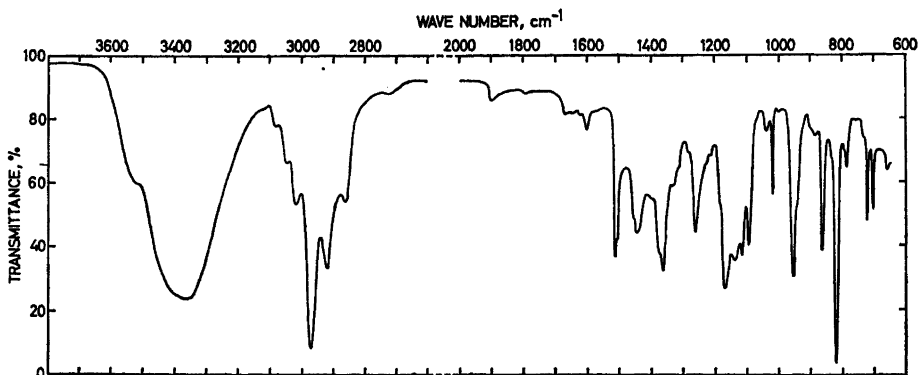


Fig. 6. Infrared spectrum of *p*-cymen-8-ol.

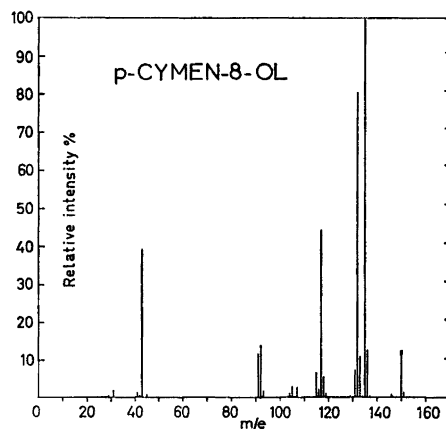


Fig. 7. Mass spectrum of *p*-cymen-8-ol.

*Fraction No. 25.* Besides several unknown compounds this fraction consisted mostly of a compound, the IR of which indicated the presence of two carbonyl groups with double bonds in the  $\alpha,\beta$ -position. MS indicated the molecular weight 150 and that the base peak is  $m/e = 150 - 43 = 107$ . It seems likely that this compound is in some respect related to one or more monoterpene compounds found in this material.

#### DISCUSSION

The higher boiling fraction of the aroma complex of black currants studied here amounts to 9 ppm of the fresh weight as compared with 200 ppm essential oil of the leaves of the same plant.<sup>1</sup> The twenty-five compounds identified represent 80.0 % of the whole fraction. Structural information was obtained

on another thirty-seven compounds representing 13.1 %. Roughly ten more compounds are present, each in amounts exceeding 0.1 % and totalling 1.3 %, as well as a large number of compounds in minute quantities, as revealed by gas chromatography.

The odour of the oil, when diluted in large amounts of air, was reminiscent of that of fresh black currants, though some of the odour "top notes" were apparently missing. In this connection it should be remembered that the present study included none of the low boiling aroma compounds and, secondly, that some chemical changes might have occurred during the concentration procedure.

The presence of methyl and ethyl benzoate could possibly be attributed to the addition of benzoic acid in the concentration step. On the other hand, these compounds frequently occur in plant materials and besides benzoic acid is naturally present in small amounts in black currants.<sup>9</sup>

It might be of some interest to compare the composition of the oil of the leaves<sup>1</sup> with the data presented here. Qualitatively the two oils are quite similar since fifteen of the seventeen compounds identified in the leaves are also found in the berries. Two fairly large components of the leaves were not found in the berries. These are linalool (3.6 %) and geraniol (6.0 %), the latter being a key-substance in the biosynthesis of terpenes. Four monoterpene alcohols were identified in the berries, namely terpinen-4-ol, which was also found in the leaves, and  $\alpha$ -terpineol, citronellol and *p*-cymen-8-ol.

Quantitatively the main general difference between the oils is that there is a larger relative amount of monoterpene hydrocarbons in the berries than in the leaves.

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