

Composition of Montmorency Cherry Essence.

1. Low-boiling Components

SUMMARY—The low-boiling neutral components of a commercial Montmorency cherry essence were concentrated by distillation. Individual components were separated and identified by combined gas chromatography and mass spectrometry. The identifications were confirmed by gas co-chromatography with known compounds. Ethanol and methanol were the most abundant low-boiling substances. These compounds were estimated to comprise 9 and 0.5% of the essence, respectively. The next most abundant compound was acetaldehyde. Other compounds present included diethyl ether, propionaldehyde, acetone, isobutyraldehyde, methyl acetate and ethyl acetate. The estimated concentrations of these compounds in the original essence are given in each instance.

INTRODUCTION

A NUMBER of investigations have been made on the volatile constituents of cherries and related products. Nelson et al. (1939) identified benzaldehyde in Montmorency cherry juice and isolated a small amount of a yellow oil with an odor they considered suggestive of geraniol. Serini (1957) identified 2,3-butylene glycol and acetylmethyl carbinol from sweet cherries. Waser et al. (1937) found terpineol in cherry wine. Mohler (1934) found that the flavor components of cherry brandy included a low-boiling fraction containing aldehydes and esters, an intermediate boiling fraction of unidentified substances that produced the characteristic cherry brandy aroma and a high-boiling fraction that contained high-boiling alcohols, benzaldehyde, coumarin and vanillin. More recently, Lovric (1962) identified hydroxymethylfurfural in heat-processed red tart cherries.

The development of gas chromatography and its combined use with mass spectrometry has led to increased knowledge of many flavor compositions. Mehltz et al. (1962), Kovacs et al. (1964) and Spanyol et al. (1964) made gas chromatographic studies of the volatile materials of cherries but the compounds were not identified.

This paper is the first of a series on the composition of Montmorency cherry aroma. The objective is to improve the flavor of the processed fruit, as most production of this variety is used for baking or other heat treatment processes. The present paper is concerned with the identification of the low-boiling constituents of Montmorency cherry essence, a commercial flavor concentrate produced by

stripping and rectification of Montmorency cherry juice.

MATERIALS & METHODS

Cherry essence

Commercial grade 150-fold Montmorency cherry essence was obtained from the A. F. Murch Company, Paw Paw, Mich., and was prepared by the procedure developed by Claffey et al. (1958). The degree of vaporization of the juice was 25%. The essence had a strong, pleasant "cooked cherry" aroma typical of pasteurized cherry juice. It was shipped in 1 gal polyethylene bottles and stored in these containers at 34°F until used.

Gas-liquid chromatography

Two gas-liquid chromatographic units were used in this investigation. The first assembly, used principally for analytical determinations, consisted of an F&M 720 gas-liquid chromatograph equipped with the F&M 700 Module (F&M Corporation, Avondale, Pa.). This combination permitted dual column operation with flame ionization detectors. Stainless steel columns containing either Carbowax 20-M or "Tris" (1,2,3-tris-2-cyanoethoxypropane) liquid phases were used for the gas chromatography.

The main column for the analytical determinations was 50' × 1/8" O.D. containing 10% Carbowax 20-M (the standard "Hi-Pak" column produced by the F & M Corp.). A second pair of columns was used, consisting of stainless steel, 6' × 1/8" O.D., and containing 20% "Tris" on 80-100 mesh Chromosorb Z support. These were also purchased from the F & M Corporation.

The second gas chromatograph was an F & M 810 unit used in conjunction with the mass spectrometer Model 21-103C, Consolidated Electrodynamics, Inc. Columns containing the same liquid phases (Carbowax 20-M and "Tris") were used for preparative scale separations with this instrument. Both

the thermal conductivity and flame ionization detectors were used, the latter with a 1:100 stream splitter. A portion of the gas emerging from the exit port of the gas chromatograph was conducted to the mass spectrometer through heated conduit tubes.

Infra-red analysis

Materials were collected for analysis in a Perkin-Elmer 237B by passing the effluent gas from the exit port of the gas chromatograph through a "U"-shaped length of capillary tubing with the loop immersed in a dry ice-acetone bath.

Classification tests

Qualitative organic classification tests were used together with gas chromatography to indicate the presence of various functional groups. Decrease in the gas chromatographic peak height after reaction indicated the presence of that particular functional group in the compound responsible for that peak. The following classification tests were used (Howard et al., 1967): carbonyl compounds, hydroxyammonium chloride; olefins and aldehydes, potassium permanganate. No satisfactory test for esters has been found. Alcohols were identified by their 3,5-dinitrobenzoate derivatives (Shriner et al., 1956).

Preparation of concentrate

The low-boiling volatile materials were isolated and concentrated by three successive distillations. A 36" glass-spiral Widmer column (Labglass, Inc., Vineland, N.J.) was used for the first two distillations. The third distillation utilized an 18" spinning band column (Nestor Faust Manufacturing Corporation, Newark, Del.). The outlets in all three distillations were protected by a trap immersed in a dry ice-acetone bath. Mechanical stirring was used in all instances to improve efficiency of distillation. Representative results from the distillation of 3370 ml of essence were as follows:

Distillate No. 1—distillation of original essence, collecting all material distilling up to 77°C (i.e., including ethanol). Vol. = 325 ml.

Distillate No. 2—distillation of above distillate, collecting all material distilling up to 70°C (i.e., eliminating most ethanol, but not methanol). Vol. = 18.8 ml.

Distillate No. 3—distillation of distillate No. 2, collecting all material distilling up to 60°C (eliminating most of methanol). Vol. = 1.1 ml.

Table 1—Low-boiling components present in Montmorency cherry essence.

Peak no.	R acetaldehyde	Identity	Estimated concentration in original essence	Method of identification ¹
1	0.73			
2	0.87	Diethyl ether	140 ppm	MS, GC
3	...	Acetaldehyde	485 ppm	MS, GC
4	1.22	Propionaldehyde	less than 5 ppm	MS, GC
5	1.31	Acetone and isobutyraldehyde	16 ppm each (estimated on this column)	MS, GC
6	1.37	Methyl acetate	32 ppm	MS, GC
7	1.46	
8	1.69	Ethyl acetate	295 ppm	MS, GC
9	1.83	Methanol	5000 ppm (0.5%)	MS, GC, IR, CHEM
10	2.02	Ethanol	90,000 ppm (9.0%)	MS, GC, IR, CHEM

¹ MS = mass spectrometry; GC = gas chromatography; IR = infrared; CHEM = chemical derivatives.

RESULTS & DISCUSSION

Quantitative analysis

The concentrations of methanol and ethanol present in the original 150-fold essence were determined by a series of chromatographic runs using propanol-1 as an internal standard according to the method of Dal Nogare et al. (1962). Known quantities of propanol-1 were added to the original essence and also to known mixtures of methanol and ethanol. The concentrations of the alcohols were estimated by comparing the heights of their respective peaks with the height of the propanol-1 peak.

Figure 1 shows the chart obtained by injection of a sample of 150-fold essence directly onto the 50' × 1/8" O.D. Hi-Pak column containing 10% Carbowax 20M. The numbers assigned to the peaks correspond to the numbers in Table 1.

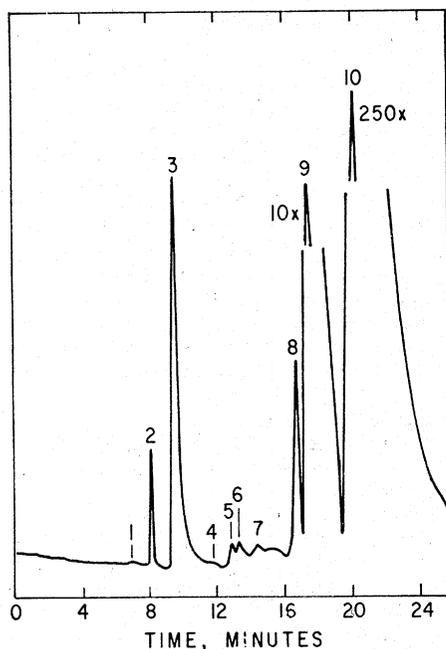


Fig. 1—Chromatogram of low-boiling components in original Montmorency cherry essence using 50' × 1/8" Carbowax 20M column at 65°C.

The two major peaks were identified as methanol and ethanol using fractions isolated by gas chromatography. Their identifications as methanol and ethanol by mass spectra were confirmed by infrared analysis and the melting points of their 3,5-dinitrobenzoate derivatives (melting points of 104–105°C and 90–91°C, respectively; unaltered by admixture of the corresponding derivatives of the known compounds). It was estimated that the original essence contained approximately 9.0% ethanol and 0.5% methanol.

The high concentrations of methanol and ethanol that were found in 150-fold cherry essence may not be representative of the composition of the juice of fresh, sound fruit. Ethanol, for example, may be formed by reactions occurring after the fruit is crushed, either by fermentation of sugars or by hydrolysis of esters. Thus a slight build-up to 0.06% ethanol by incidental fermentation would result in 9.0% ethanol in the 150-fold essence after concentration. Traces of methanol could arise from the enzymic cleavage of the methoxy groups present in cherry pectins.

The low concentrations of the minor components in the original essence made it necessary to concentrate them by the series of distillations described in Materials and Methods. This also reduced the preponderance of ethanol and methanol in the concentrates. The final product, Distillate No. 3, was chromatographed and the results are shown in Figure 2. The components were identified by mass spectral analysis of the gas emerging from the Carbowax 20M and the "Tris" columns. The concentration of each component was estimated by comparing the peak height with that produced by a standard solution containing 100 ppm. of that component. A 50' × 1/8" Carbowax 20M column was used because of the excellent separation and the sharpness of the peaks obtained. The compounds identified in the distillate are indicated in Table 1, together with the estimated concentrations in the original essence and the retention distances relative to acetaldehyde on a Carbowax 20M column. The identity of Peak 1 has not been established.

The presence of diethyl ether (Peak 2) was unexpected as this compound is not a product of normal plant metabolism. The possibility that it represents a breakdown

product of ethanol arising during the analysis from degradation of ethanol in the injection port was eliminated by a duplicate determination injecting purified ethanol into the volume. It is possible that diethyl ether is formed by degradation of ethanol during distillation.

Acetaldehyde (Peak 3) was the main component emerging before methanol. The odor of acetaldehyde was easily detected in control solutions that contained the same concentration as found in the original essence. Peak 4 was identified as propionaldehyde.

Acetone and isobutyraldehyde (2-methylpropanal) formed a single peak (Peak 5) on the column containing Carbowax 20M (Fig. 2) but formed well separated peaks on the "Tris" column. The peak heights on the latter column indicated that acetone and isobutyraldehyde are present in approximately equal amounts in cherry essence. Methyl acetate, the component of the next peak, was somewhat more abundant. The identity of Peak 7 has not been established.

Ethyl acetate, next to acetaldehyde, is the most abundant of the minor components of cherry essence boiling below methanol. It occurred on the Carbowax 20M column adjacent to the methanol peak, which tended to obscure it. However, on the "Tris" column it occurred as a distinct, separate peak.

Several of these components have definitely perceptible odors in control solutions at the levels at which they occur in cherry

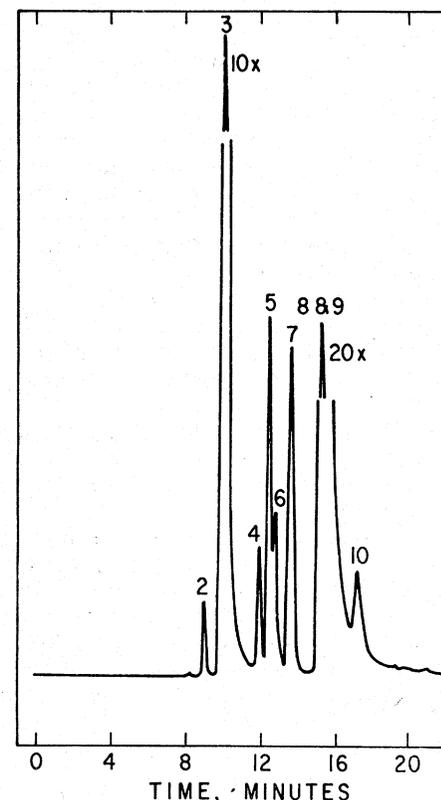


Fig. 2—Chromatogram of concentrated distillate containing low-boiling components in Montmorency cherry essence, using 50' × 1/8" Carbowax 20M column at 75°C.

essence. Their relative contribution to the total "cherry" aroma in the presence of the other components has not yet been evaluated.

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