

Condensation with Mesitylene.—A mixture of 130 g. of mesitylene and 9.5 g. of α -methoxystyrene was heated to 250° for ten hours. The non-volatile fraction weighed 9.5 g. and manipulation with methanol yielded 20.8% of the theoretical amount of ω -(α -mesityl)-acetophenone; m. p. 54–55°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.7; H, 7.8.

The oxime gave considerable trouble in that a sharp melting point was difficult to attain. The highest value was 118°.

Anal. Calcd. for $C_{17}H_{18}NO$: C, 80.6; H, 7.6. Found: C, 80.4; H, 7.9.

Condensation with Ethylbenzene.—Sixty-five grams of hydrocarbon and 8.6 g. of the ether at 250° for ten hours yielded 3.4 g. (23.6%) of β -phenylbutyrophenone; m. p. 74°; m. p. of the oxime 93.5–94°.⁹

Condensation with Cyclohexane.—A mixture of 8.5 g. of α -methoxystyrene and 263 g. of cyclohexane was heated to 250° for twenty-four hours. Fractionation yielded

(9) Kohler, *Am. Chem. J.*, **31**, 642 (1904).

5.4 g. or 42.7% of ω -cyclohexylacetophenone as a colorless liquid; b. p. 117–118° at 1 mm.; n_D^{25} 1.5330. After freezing it melted at 17–18°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 82.9; H, 9.2.

The oxime formed needles melting at 104.5–105.5°.

Anal. Calcd. for $C_{14}H_{18}NO$: C, 77.4; H, 8.8. Found: C, 77.6; H, 9.1.

For comparison, a sample of the ketone was synthesized by condensing cyclohexylacetyl chloride with phenylzinc chloride. The product, isolated in 64% yield, was identical with the above compound.

Summary

α -Methoxystyrene undergoes a condensation reaction with toluene, mesitylene, ethylbenzene, diphenylmethane, 4-methoxytoluene and cyclohexane. Methane is eliminated and a phenacyl derivative is formed.

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Volatile Flavor and Fixed Acids of Montmorency Cherry Juice¹

BY E. K. NELSON AND A. L. CURL

The juice of Montmorency cherries was obtained by pressing the carefully pitted fruit in Geneva, New York.¹ The juice was pasteurized and shipped to Washington by express, arriving in good condition, with no evidence of fermentation.

ANALYSIS OF THE JUICE

	G. per 100 cc.
Total acidity, as malic	1.4
Total solids	14.7
Total sugars as invert, after inversion	9.91
Alcohol precipitate	0.037
Volatile acids (as acetic)	.0012
Ash	.432

The juice (94 liters) was distilled *in vacuo* at 54°, with a trap surrounded by solid carbon dioxide and alcohol to recover any volatile material which might pass through the condenser. Nineteen liters of distillate was collected. The residual liquor in the still was then devoid of odor. The distillate was cohobated in the same manner until a distillate of 500 cc. was obtained. This final distillate, which had a strong flavor suggestive of benzaldehyde, was treated with 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate and distilled to small volume. The distillate was reserved for further examination. The residual liquor in the distilling flask was extracted with ether. On evaporation of the ether, 0.4098 g. of semicarbazone

was obtained. This, recrystallized once from alcohol, melted at 214°, and a mixture with benzaldehyde semicarbazone showed no depression in melting point. The weight of semicarbazone corresponded to 0.27 g. of benzaldehyde, or 2.8 mg. per liter of cherry juice.

Since the appearance of the flow of the first runnings through the condenser indicated the presence of some alcohol, the distillate from the semicarbazone was carefully distilled through a twenty-inch (51-cm.) Widmer column. A fraction boiling at 75–80° was thus obtained. This was redistilled from a small flask through a Vigreux column and 10 cc. of liquid boiling at 73–76° was recovered. By the colorimetric method² this was found to consist of a mixture of 35% methyl alcohol with 65% of ethyl alcohol.

After distillation of the alcohol (the tails being returned to the aqueous solution), the solution was extracted with ether. On careful evaporation of the ether at room temperature, a very small residue remained which had a strong rose-like odor. This was shaken up with 10% sodium hydroxide solution and the insoluble portion extracted with ether. The ether, on evaporation, left a residue of 0.0067 g. It had a rose-like odor and when oxidized with potassium bichromate and sulfuric acid gave a very faint lemon-like odor, indicating that a very small amount of geraniol might be present.

The sodium hydroxide solution, acidified and extracted with ether, afforded 0.0016 g. of material which did not give a phenol reaction with ferric chloride.

(1) Cherry juice was prepared by E. A. Beavens in the fruit juice laboratory of the Food Research Division in Geneva, New York.

(2) "Official and Tentative Methods of Analysis," A. O. A. C., 4th ed., p. 578.

Non-Volatile Acids

The still-residue, left after distilling off 19 liters from the cherry juice, was used for the investigation of the non-volatile acids by the ester distillation method.³ One-fifth of the distillation residue, equal to 19 liters of juice, was used.

The acids, separated from their lead salts, were converted into ethyl esters. The crude weight of the esters was 147 g. The ethyl esters were fractionated through an eight-inch (20-cm.) Widmer column with an electrically heated jacket at 10 mm. The boiling points and yields of the three fractions were as follows:

Fraction 1	84-86°	6.3 g.
Fraction 2	125-128°	125.0 g.
Fraction 3	about 160°	very little

To seven-tenths of a gram of each fraction in 5 cc. of absolute alcohol, 2 cc. of hydrazine hydrate solution was added.

Fraction 1 gave no crystalline hydrazide. Neither oxalic acid nor succinic acid was found. When the fraction was saponified, a crystalline acid was obtained which did not melt. Optical crystallographic examination⁴ showed that this acid is fumaric acid. It is probably formed by the dehydration of malic acid and is not present in the juice.

Fraction 2 gave a copious precipitate, which was shown

(3) Franzen and Helwert, *Z. physiol. Chem.*, **122**, 46-85 (1922); Nelson, *THIS JOURNAL*, **46**, 2337 (1924), and **47**, 568 (1925).

(4) Optical crystallographic examinations were made by G. L. Keenan of the Food and Drug Administration.

by melting point (178.5°) and mixed melting point to be malic hydrazide.

Fraction 3 gave a hydrazide, which, after recrystallization, was shown by optical crystallographic examination to be identical with the hydrated form of citric trihydrazide. The quantity was insufficient for a melting point determination.

Franzen and Helwert³ found a trace of oxalic acid, small amounts of succinic and citric acids, and malic acid predominating, in cherries examined by them. However, neither oxalic nor succinic acid was found in Montmorency cherries by the present writers.

Summary

The flavor of pitted Montmorency cherry juice was found to be due mainly, if not entirely, to benzaldehyde (2.8 mg. per liter in the sample examined) and possibly in part to a trace of an alcohol having a rose-like odor, probably geraniol.

From ninety-four liters of juice there was obtained about 10 cc. of mixed alcohols, boiling at 73-76°, which consisted of 35% methyl and 65% ethyl alcohol.

The non-volatile acids of Montmorency cherries were found to consist chiefly of malic acid, and a very small amount of citric acid.

WASHINGTON, D. C.

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The Cleavage of Benzyldimethylphenylammonium Chloride by Certain Sulfur-containing Salts (I)

BY H. R. SNYDER AND J. C. SPECK

Considerations of the structural similarity between the pyrimidine and benzene rings made it seem likely that the cleavage of thiamin (vitamin B₁) by sodium bisulfite¹ (equation A) is a manifestation of the well-known lability of the bond between the benzyl group and the nitrogen atom of benzylamine derivatives. Von Braun² found that the benzyl group is among the radicals most readily removed in the cleavage of tertiary amines with cyanogen bromide. Embde and Kull³ and more recently Achmatowicz and Lindenfeld⁴ have shown that the benzyl radical is removed readily from quaternary ammonium salts by hydrogenation. Tschugaeff and Chlopin⁵ reported that

(1) Williams, Waterman, Keresztesy and Buchman, *THIS JOURNAL*, **57**, 536 (1935).

(2) Von Braun and Weiszbach, *Ber.*, **63**, 490 (1930).

(3) Embde and Kull, *Arch. Pharm.*, **274**, 173 (1936).

(4) Achmatowicz and Lindenfeld, *Roczniki Chem.*, **18**, 75 (1938); *C. A.*, **32**, 9047 (1938).

(5) Tschugaeff and Chlopin, *Ber.*, **47**, 1272 (1914).

benzyldimethylphenylammonium chloride in aqueous solution converts sodium telluride to benzyl telluride. Baw⁶ observed that the same ammonium salt may be used to benzylate phenols in alkaline solutions. In addition Porai-Koschitz⁷ has studied the benzylating action of this quaternary salt, but the details of his work apparently are not available in this country.

In view of these observations it was desirable to determine whether quaternary ammonium salts containing the benzyl group will undergo scission on mild treatment with sodium bisulfite (equation B).

A study of benzyldimethylphenylammonium chloride (I) has revealed that it is cleaved in the expected manner not only by aqueous sodium bisulfite, but also by solutions of sodium sulfite, so

(6) Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926).

(7) Porai-Koschitz, *C. A.*, **29**, 7957 (1935).