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Isolation and Identification of Volatiles from Catawba Wine

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The volatile composition of three Catawba wines prepared from grapes grown in the vineyards of the New York State Agricultural Experiment Station during the 1976 vintage were analyzed by instrumental and sensory means. The three wines differed according to the enological technique employed for their production. Volatiles were isolated by solvent extraction, separated and quantified by gas chromatography, and identified by combined gas chromatography–mass spectrometry. Although some variation in volatile composition due to processing technique was observed, sensory analyses comparing the wines with corresponding model solutions indicate that the major identifiable components are of little importance in determining the aroma of Catawba wine as influenced by processing technique.

Catawba vines have been cultivated in the northeastern United States for over 150 years. Currently, in New York, over 10 000 tons are produced annually and over 90% of that is used for wine production (New York State Crop Reporting Service, 1976). Catawba grapes can be used in the production of either white or rosé wines depending upon enological technique, and much of the white wine produced is used in sparkling wine cuvées.

The literature dealing with the volatile composition of wines and wine grapes is extensive. Kahn (1969) and Webb and Muller (1972) have tabulated hundreds of compounds that have been identified in wines and other alcoholic beverages.

Many native American grape varieties including Concord and Catawba have characteristic aroma components that appear to be unique to some varieties with *labrusca* parentage. Although many workers (Holley et al., 1955; Neudoerffer et al., 1965; Stevens et al., 1965; and Stern et al., 1967) have studied the volatile composition of the Concord variety, no such investigations have been conducted with Catawba.

Methyl anthranilate, a compound long thought to be of major importance in the aroma of *labrusca* varieties (Sale and Wilson, 1926), now appears to be far less important than previously thought (Nelson et al., 1977a). Friedman (1976) believes that methyl anthranilate is of little importance in the aroma of Concord grapes, even though its concentration in that variety is relatively high. Amerine et al. (1959) noted that the distinctive Catawba aroma was apparently not due to methyl anthranilate and that other more important compounds must be present.

This report examines the volatile composition of Catawba wines prepared by three different enological techniques. In addition, it attempts to assess the effect of processing technique on the occurrence of these volatiles in Catawba wine.

MATERIALS AND METHODS

Wine Preparation. Catawba grapes were harvested at 16.6° Brix in October of 1976. The fruit was divided into three 20-kg lots for fermentation. From one lot a white Catawba wine was prepared by immediately pressing the crushed grapes while rosé wines were prepared from the other two. One of the rosé wines was prepared by fermenting the juice in contact with the skins for 5 days [rosé (FS)] while the other was thermally vinified [rosé (TV)]. Thermal vinification consists of heating the crushed grapes in a steam kettle to 60 °C for 15 min, followed by immediate pressing. Fermentations were conducted at 20 °C and other standard enological procedures as described by Nelson et al. (1977b) were followed in each case.

Volatile Isolation. The Catawba wine volatiles were isolated using organic solvent extraction with Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane, "Precision Cleaning Agent, Du Pont"). Equal volumes of wine and Freon (2700 mL) were stirred for 1 h. The Freon phase was then drawn off, dried over anhydrous magnesium sulfate, and con-

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Table I. Volatile Components Identified in Catawba Wine

compound	retention time, min	concentration, ppm white	rosé (TV)	rosé (FS)
(a) ethyl acetate	3.25	0.15	0.15	0.02
(b) isobutyl acetate	6.22	0.03	0.04	0.03
(c) ethyl butyrate	6.74	0.17	0.12	0.09
(d) isoamyl acetate	9.14	2.57	3.19	1.68
(e) isoamyl alcohol	11.37	6.27	3.19	1.68
(f) ethyl hexanoate	12.84	0.57	0.49	0.47
(g) hexyl acetate	14.07	0.04	0.13	0.20
(h) ethyl lactate	16.18	0.17	0.24	0.45
(i) *n*-hexanol	16.43	0.34	0.12	0.75
(j) *cis*-3-hexene-1-ol	17.41	0.06	0.03	0.13
(k) ethyl octanoate	19.61	1.16	0.74	0.55
(l) linaloöl	23.18	0.02	0.05	0.10
(m) butyric acid	24.13	0.04	Tr[a]	0.12
(n) γ-butyrolactone	25.02	nd[b]	Tr	0.06
(o) ethyl decanoate	26.07	0.53	0.33	0.26
(p) diethyl succinate	27.39	0.30	0.56	0.95
(q) 2-phenylethyl acetate	31.70	1.09	3.79	2.90
(r) hexanoic acid	32.76	3.23	1.35	5.51
(s) 2-phenylethyl alcohol	33.17	5.00	7.45	7.50
(t) octanoic acid	38.87	9.20	7.35	1.80
(u) methyl anthranilate	46.41	nd[b]	0.07	Tr[a]

[a] Only trace quantity detected. [b] Not detected.

centrated in a rotary evaporator with water bath at 20 °C. The final extract concentration was 13 500-fold (0.2 mL), and each extract had a characteristic Catawba-like aroma while the aqueous phase was nearly odorless.

Instrumental Analysis. The Catawba extracts were analyzed by combined gas chromatography–mass spectrometry using 3-μL injections. The system consisted of a Varian Series 1400 gas chromatograph with a 4 m × 2 mm i.d. glass column packed with 10% SP-1000 on 100–120 mesh Chromosorb W. A temperature program from 60 to 200 °C at 4 °C/min was employed. The gas chromatograph was interfaced through a Llewellyn type methyl silicone membrane separator to a Bendix Model 12 Time-of-Flight mass spectrometer equipped with CVC Mark IV solid state electronics and with a computerized data collection system. Spectra were taken at 70 eV and identification was done by comparison of experimental spectra with published spectra and with those of authentic standards. Comparison of component retention times with those of the authentic standards was considered to be confirmatory. Quantification of volatile components was done using a Hewlett-Packard 5830 A gas chromatograph. Chromatographic conditions were the same as above except that a stainless steel column of the same dimensions was used. Quantitative estimation was done by comparing the peak area of 2-phenylethyl alcohol, a major component, with that of an internal standard (*n*-decanol) added to the Freon extract at a level of 2 ppm relative to the original wine. The concentrations of the other components were then calculated directly using relative peak area ratios.

Sensory Evaluation. The odors of the individual components in the three extracts were characterized by the authors using a sniffing device (Acree et al., 1976) attached to the effluent port of a Packard Model 800 gas chromatograph. Chromatographic conditions were the same as in the GC–MS system.

In order to examine the role, if any, of the identified compounds in determining Catawba odor, model wine solutions were prepared using 12% v/v ethanol–1% w/w tartaric acid, purified Concord grape anthocyanin pigment, and the identified volatiles in distilled water. The volatiles were added to the three model solutions at the level determined for each compound in the corresponding authentic wine. The concentration of each compound added to model solutions are listed in Table I. All compounds identified were added to the corresponding model solution, except when only a trace was detected none was added. To eliminate panel bias due to color differences, pigment was added to the wines and to the model solutions at levels such that each sample had a typical rosé color. An experienced 12-member panel completed three sets of randomized triangle difference tests. Only odor was considered by the panel so the samples were not tasted. The Catawba wines were first tested against each other, and then the model solutions were examined for aroma differences. Finally each wine was tested against its corresponding model solution. Samples were presented at room temperature in standard wine glasses in individual tasting booths. Sample size was 50 mL.

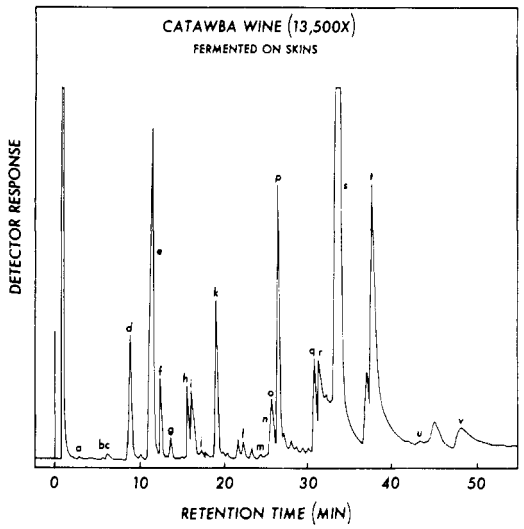

Figure 1. Chromatogram of the 13 500-fold Freon extract of Catawba wine fermented in contact with the skins.

RESULTS AND DISCUSSION

In the white Catawba wine, 36 compounds were present in concentrations sufficient for quantitative estimation. In the rosé wine fermented in contact with the skins and in the thermally vinified rosé wine 42 and 50 compounds were detected, respectively. Of these, 19 compounds found in the white wine were identified and 21 compounds in the other two extracts were identified. Methyl anthranilate and γ-butyrolactone were not detected in the white Catawba wine. The compounds that were identified were generally those present in the largest quantities. The identified compounds had a total concentration that was nearly constant at 30.8 ppm in all three wines and represented from 95.7 to 97.5% of the total extractable volatiles.

Figure 1 shows a chromatogram of the 13 500-fold extract of the wine fermented in contact with the skins. The letters "a" through "v" correspond to the identified compounds listed in Table I with their concentrations in the different wines. The concentrations of the majority of the compounds appear to be little affected by enological technique. However, the acetate esters, particularly isoamyl acetate and 2-phenylethyl acetate are distinctly more abundant in the thermally vinified wine. Decanoic acid (v) was identified in each of the wine extracts but its concentration could not be reliably estimated due to excessive chromatographic tailing.

Many strongly odorous compounds were detected by gas chromatographic effluent sniffing. Some, with extremely low apparent thresholds, were present in concentrations

Table II. Results of Randomized Triangle Tests Comparing the Aroma of Catawba Wines and of Model Solutions

comparison	correct responses[a]	significance
wines vs. wines		
white vs. rosé (TV)[b]	10	0.001
white vs. rosé (FS)[c]	9	0.01
rosé (TV) vs. rosé (FS)	9	0.01
models vs. models		
white vs. rosé (TV)	9	0.01
white vs. rosé (FS)	7	NS[d]
rosé (TV) vs. rosé (FS)	9	0.01
wines vs. models		
white	11	0.001
rosé (TV)	12	0.001
rosé (FS)	10	0.001

[a] Maximum number of correct responses is 12. [b] Thermally vinified rosé wine. [c] Rosé wine fermented in contact with the skins. [d] Not significant.

too low to give any detector response. No single compound was thought to have a distinctly Catawba-like aroma.

The results of the triangle difference tests are shown in Table II. The panel found that the aroma of each Catawba wine was significantly different from that of the other two wines (99% level of confidence or better). Clearly, if processing technique had no significant effect on Catawba wine aroma, further sensory investigation would be unproductive but this is apparently not the case. The panel was then asked to distinguish among the three model solutions. The aroma of the solution imitating the thermally vinified wine was significantly different from that of the other two solutions (99% level of confidence). Apparently some compositional difference in the identified compounds is organoleptically significant and peculiar to the thermally vinified wine. Although proof is not yet available, the most obvious compounds to which this difference can be attributed are isoamyl acetate and 2-phenylethyl acetate because of their high concentration in that sample. The solutions corresponding to the wine fermented in contact with the skins and the white wine were indistinguishable by the panel. This indicates that the identified compounds, even though they represent over 95% of the total extractable volatiles, do not account for the significant aroma differences that occur in Catawba wine due to processing technique.

In the final triangle test each wine was judged against its corresponding model solution. A highly significant difference (99.9%) was found in each case. The three model solutions were, in fact, very poor imitations of the authentic wine. The high concentration of acetate esters in the thermally vinified wine may contribute to its distinctive aroma but it certainly does not define that aroma. It appears that the identified components, although they do contribute aroma, contribute little or nothing to Catawba varietal character as influenced by enological technique.

The nature of wine and wine-grape aroma is not well understood. Brander (1974) has suggested that essentially the same volatile components are present in all wine varieties and that the aroma differences among varieties are due to these components being present in differing ratios. On the other hand, Stern (1975) stresses the importance to wine aroma of compounds present in trace quantities. The concentrations of these compounds is often too low to give any detector response whatsoever with current methodology, but they may be of great organoleptic importance if they have sufficiently low thresholds.

The major volatile components detected and identified in the three Catawba wines do contribute aroma to those wines. However, the model solutions containing these compounds at their appropriate concentrations are easily distinguished from the authentic wine. It can be concluded that the unidentified trace components, although they comprise less than 5% of the total Freon-extractable volatiles, are of critical importance to the aroma of Catawba wine as influenced by processing technique.

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