Volatiles from Grapes

Comparison of Grenache Juice and Grenache Rosé Wine

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The volatiles in grenache grape juice and grenache rosé wine made from the same batch of juice were compared. The investigation was aided by the use of gas chromatography coupled to a Time-of-Flight mass spectrometer. Several differences were noted; the most apparent was the loss of aldehydes and hexanol upon fermentation and the formation of lower alcohols and acetals.

In a continuing effort to elucidate volatile organic material in grapes and grape products, we have extended our work to comparing the volatiles from grenache grapes and the wine (rosé) produced from the same batch of juice. The volatile constituents of the grenache juice have been reported (Stevens *et al.*, 1967); however, the constituents in the wine and juice from the same source have not been compared.

Webb (1967) lists five classifications of flavor compounds found in wines. The first consists of compounds produced by the plant, which come through the processing unchanged. Numbers two through five consist of compounds produced during fermentation and aging. An analysis of the must and wine should prove helpful in distinguishing which components in the wine are from the raw material. This type of investigation does not differentiate between classifications two through five.

EXPERIMENTAL

Grenache grapes, from which was obtained 450 gallons of free-run juice (25° Balling), were harvested near Fresno, Calif., in October 1966. Two hundred gallons of the juice was shipped to Albany, Calif., in a refrigerated van and extracted as described below. The remaining must (250 gallons) was fermented by Western Grape Products, Kingsburg, Calif., under the standard conditions for making grenache rosé wine and the finished product was returned to Albany, Calif., in a refrigerated van in December 1966.

Each sample was extracted with approximately 10 gallons of freshly distilled trichlorofluoromethane (Freon 11). The procedure employed allowed extraction of the material without formation of an emulsion. The extractor consisted of a series of concentric perforated sheet metal (stainless steel) tubes which slowly rotated within a large glass tube (Figure 1). The glass tube was a standard pipe section 36 inches long and 9 inches in inside diameter. The three concentric perforated tubes had 4-, 6-, and 8- inch diameters, respectively, and were held in place by end brackets fastened to the center drive shaft. Each end of the pipe was sealed with a stainless steel end plate using a Teflon gasket.

The shaft was rotated at a maximum rate (approximately 10 to 20 r.p.m.) to attain optimum extraction yet minimize emulsion formation. Although no quantitative data are available on the efficiency of the extractor, the flow of the sample was set at 2 gallons per hour and the flow of the solvent about 1/10 of that rate.

After extraction, the Freon extracts were concentrated with

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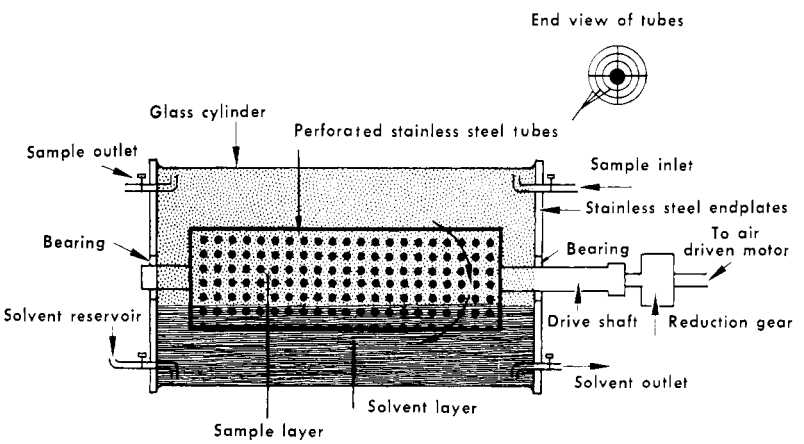

Figure 1. Horizontal extractor

Table I. Compounds Found in Grenache Juice and Grenache Rosé Wine

Retention Time, Min.	Juice	Rel. Amt.	Retention Time, Min.	Wine	Rel. Amt.
			10.8	Ethanol	12
14.3	Ethyl acetate	50	14.5	Ethyl acetate	12
16.2	3-Methylbutanal	10			
16.8	2-Methylbutanal	6.2	16.5	2-Methyl-1-propanol	0.2
17.5	Cyclohexane[a]	4.2	18.3	2-Methyl-2-propanol	Tr.
19.0	1-Pentanal	2.1			
19.1	3-Pentanone	2.1			
20.5	Ethyl propionate	11.5	20.6	Ethyl propionate	0.9
20.6	1-Propyl acetate	11.5	20.9	1-Propyl acetate	1.2
22.0	2,4,5-Trimethyl-1,3-dioxolane	3.2	22.3	2,4,5-Trimethyl-1,3-dioxolane	3
22.5	2-Methyl-3-pentanone[b]	Tr.			
22.6	1,1-Diethoxyethane	Tr.	22.8	1,1-Diethoxyethane	1
23.5	3-Methyl-2-pentanone[b]	Tr.			
24.2	Ethylmethyl-1,3-dioxolane[b]	Tr.			
24.3	3-Methyl-1-butanol	5	24.4	3-Methyl-1-butanol	12
24.5	2-Methyl-1-butanol	5	24.6	2-Methyl-1-butanol	
25.6	Toluene	1.7	27.0	Ethyl-*tert*-butyl ether[b]	0.2
28.1	Hexanal	16.5	27.9	Ethyl *s*-butyl ether[b]	Tr.
28.6	Ethyl butyrate	Tr.	29.0	Ethyl butyrate	5
30.1	Butenyl acetate[b]	Tr.	30.4	Butyl acetate	0.5
33.0	*cis*-2-Hexenal	2.5	31.6	2,4-Dimethyl-5-ethyl-1,3-dioxolane[b]	Tr.
33.8	*trans*-2-Hexenal	83	33.6	1-Ethoxy-1-propoxyethane	Tr.
35.5	Ethylbenzene	Tr.	36.5	Formate[b]	Tr.
36.5	*m*-Xylene	1.6	37.0	*m*-Xylene	Tr.
36.9	3-Methyl-1-butyl acetate	2.5	37.5	3-Methyl-1-butyl acetate	100
37.2	1-Pentyl acetate	Tr.	37.9	1,1-Dipropoxyethane	Tr.
37.5	*cis*-3-Hexen-1-ol[b]	Tr.			
38.1	Hexanol	100	38.6	Hexanol	Tr.
38.6	2-Hexen-1-ol	Tr.			
39.0	Dimethylbenzene[b]	Tr.	41.2	An acetal	Tr.
42.7	Hexyl formate	Tr.			
47.0	Ethyltoluene or trimethylbenzene	Tr.			
48.0	1,3,5-Trimethylbenzene	Tr.			
49.0	*o*-Ethyltoluene	Tr.			
49.3	Octanol	Tr.			
49.5	An acetal	Tr.	49.4	An acetal	Tr.
50.6	C_3 benzene	Tr.			
50.7	Ethyl hexanoate	Tr.	51.5	Ethyl hexanoate	5
51.5	*cis*-3-Hexenyl acetate	Tr.			
52.3	1-Hexyl acetate	Tr.	53.1	1-Hexyl acetate	3.5
52.6	Diethyl- or *n*-propylmethylbenzene[b]	Tr.	53.5	An acetal	Tr.
53.9	Alkyl benzene	Tr.	64.3	An acetal	Tr.
55.2	Limonene	1.5	73.1	Ethyl octanoate	2.5
70.5	Terpinen-4-ol	Tr.	79.0	β-Phenylethyl formate	0.5

[a] Retention data only.
[b] Mass spectral data only.

the aid of a 10-plate Oldershaw distillation column to approximately 1 liter each. The extracts were further concentrated with a short distillation column and vacuum-transferred at 10^{-4} mm. of Hg and room temperature to separate the volatiles from the nonvolatiles. The resulting extracts were approximately 100 ml. of 5% concentration of aroma material in Freon.

Samples were chromatographed on a 500-foot × 0.02-inch i.d. open tubular column coated with GE SF-96(50) silicone oil containing a trace of Igepal. The initial temperature was 32° C. and was programmed to 172° C. at approximately 1.4° per minute; the flow rate of the carrier gas (helium) was 25 cm. per second. A flame ionization detector (FID) was used for preliminary scanning and for enrichment analyses.

Peak composition was determined by coupling the gas chromatograph effluent to a Bendix Time-of-Flight Model 12 mass spectrometer. A Biemann separator (Watson and Biemann, 1964) was placed between the gas chromatograph and the mass spectrometer inlet to concentrate the organic material further. As the components emerged from the gas chromatograph and entered the mass spectrometer, they were monitored on an oscilloscope and recorded on a high speed oscillographic recorder scanning from 20 to 200 mass units in 2.5 seconds. In addition, the total ion current was recorded on a strip chart recorder, giving a tracing almost identical with the FID tracing.

Mass spectral assignment was verified by enriching the sample with the suspected compound and obtaining an increase in peak height at the appropriate retention time, using an FID.

RESULTS AND DISCUSSION

Juice. Table I lists the compounds found in the grenache juice along with the retention times and relative amounts. 1-Hexanol is found in the juice extract in greatest quantity. Hexanol has been found in practically all of the grapes investigated (Table II). The two fusel oil alcohols, 2- and 3-methyl-1-butanol, are also found in the juice, although the amount is considerably less than that of hexanol. Four other alcohols have been identified in the juice extract, in trace amounts. One of them, terpinen-4-ol, has not previously been identified in grapes.

The juice contains a large amount of ethyl acetate, a situation similar to the concord essence extract (Stern *et al.*, 1967).

Table II. Grape Volatiles Common to Previous Work and Present Investigation

Compound	Concord	Grenache	Riesling	Rotundafolia	Sauvignon Blanc	Zinfandel	Muscat Aleutico	Muscat Early	Muscat Malvasia Bianca	Muscat Alexandria	Muscat Hamburg	Muscat Orange	Muscat P-20-59	Muscat Q-26-39
Ethyl acetate	*a,b,c,d*	*e*	*f*	*g*	*h*					*i*				
3-Methylbutanal	*c*													
2-Methylbutanal		*e*												
Cyclohexane	*d*	*e*												
3-Pentanone										*i*				
Ethyl propionate	*b,c,d*	*e*			*h*									
n-Propyl acetate	*b,d*				*h*									
2,3,5-Trimethyl-1-3-dioxolane		*e*												
1,1-Diethoxyethane	*d*	*e*								*i*				
3-Methyl-1-butanol	*b*	*e*	*f*	*g*	*h*		*j*	*j*	*j*	*i,j,k*	*j*	*j*	*j*	*j*
2-Methyl-1-butanol	*b*	*e*	*f*		*h*		*j*	*j*	*j*	*i,j*	*j*	*j*	*j*	*j*
Toluene	*d*	*e*								*i*				
Hexanal	*d*	*e*					*j*	*j*	*j*	*i,j,k*	*j*	*j*	*j*	*j*
Ethyl butyrate	*b,c,d*	*e*		*g*										
cis-2-Hexenal		*e*												
trans-2-Hexenal	*d*	*e*	*f*	*g*	*h*	*l*	*j*	*j*	*j*	*i,j,k*	*j*	*j*	*j*	*j*
m-Xylene	*d*									*i*				
3-Methyl-1-butyl acetate	*e*		*f*		*h*									
1-Pentyl acetate		*e*			*h*									
cis-3-Hexen-1-ol	*d*	*e*								*i,k*				
1-Hexanol	*d*	*e*	*f*	*g*	*h*		*j*	*j*	*j*	*i,j,k*	*j*	*j*	*j*	*j*
2-Hexen-1-ol	*d*	*e*	*f*				*j*	*j*	*j*	*i,j*	*j*	*j*	*j*	*j*
1,3,5-Trimethyl benzene	*d*													
o-Ethyl toluene		*e*												
Octanol		*e*	*f*											
Ethyl hexanoate	*b,d*				*h*					*k*				
cis-3-Hexenyl acetate		*e*												
n-Hexyl acetate		*e*			*h*		*j*	*j*	*j*	*i,j*	*j*	*j*	*j*	*j*
Limonene		*e*								*i*				

[a] Holley *et al.*, 1955.
[b] Stevens *et al.*, 1965.
[c] Neudoerffer *et al.*, 1965.
[d] Stern *et al.*, 1967.
[e] Stevens *et al.*, 1967.
[f] Van Wyk *et al.*, 1967.
[g] Kepner and Webb, 1956.
[h] Chaudhary *et al.*, 1964.
[i] Webb and Kepner, 1957.
[j] Webb *et al.*, 1966.
[k] Stevens, *et al.*, 1966.
[l] Haagen-Smit, *et al.*, 1949.

Ethyl acetate has been reported in several other varieties of grapes (Table II). Ethyl propionate and *n*-propyl acetate also represent rather large percentages of the volatiles found in the juice extract; each has been found previously in grapes (Table II). The remaining esters, except 3-methyl-1-butyl acetate, were found in trace amounts and one of them, hexyl formate, has not been identified as a grape constituent prior to this time.

The aldehydes represent a substantial amount of the grape oil, with *trans*-2-hexenal and 1-hexanal predominating. Also *cis*-2-hexenal has been identified. The two aldehydes, 2- and 3-methylbutanal, have been isolated in rather large amounts, each being the immediate precursor to the two major fusel oil alcohols, active amyl and isoamyl alcohol, respectively. Neudoerffer *et al.* (1965) have tentatively identified 2-methylbutanal in concord grapes, while Stevens *et al.* (1967) found 3-methylbutanal in grenache grapes (Table II). 1-Pentanal, previously unidentified in grapes, has been found. Two acetals have been identified, 2,4,5-trimethyl-1,3-dioxolane and 1,1-diethoxyethane, each probably arising by condensation of acetaldehyde with 2,3-butandiol and ethanol, respectively. A third acetal (retention time 24.2 minutes) appears to be an ethylmethyl-1,3-dioxolane; however, positive identification was not possible.

Very few ketones were found, each in small amounts. 3-Pentanone was identified; it has been found in Muscat of Alexandria by Stevens *et al.* (1966). Two other ketones, 2-methyl-3-pentanone and 3-methyl-2-pentanone, have been tentatively identified and are present in trace amounts.

Of the hydrocarbons present in the juice extract, cyclohexane, toluene, *m*-xylene, and limonene are the only ones present in greater than trace quantities. Each has been identified previously in grapes (Table II).

Wine. Table I lists the compounds identified in the grenache rosé wine extract along with their retention times and relative amounts. In general, the esters comprise the bulk of the extract, with 3-methyl-1-butyl acetate predominating. With the exception of *n*-propyl acetate and β-phenylethyl formate, each of the esters has been previously identified in wine (Table III). The alcohol portion of the esters are all common to either the fermentation product or the starting material (Webb, 1967).

As might be expected, the alcohols represent a fair proportion of the oil, with ethanol predominating and to a lesser

Table III. Wine Volatiles Common to Previous Work and Present Investigation

Compound	Apple	Cabernet Sauvignon	Grape	Muller Thurgau	Passion Fruit	Rotundifolia	Sake	Sauvignon Blanc	Sherry	Sylvaner	Sugar	Champagne	Riesling
1,1-Diethoxyethane		*a*	*b*		*c*	*d*		*e*	*f*				
Ethanol	*g*	*a,h,i*	*b,j*	*k*	*c*	*d*		*e*	*l*	*k*	*m,n,o*	*p*	*i*
2-Methyl-1-propanol	*g*	*a,h,i*	*b,j*	*k*	*c*			*e*	*f,q*	*k,r*	*m,n,o*	*p,s*	*i*
3-Methyl-1-butanol	*g*	*a,h,i*	*b,j*	*k*	*c*	*d*		*e*	*f,q*	*k,r*	*m,n,o*	*p,s*	*i*
2-Methyl-1-butanol		*a,h*	*b,j*		*c*	*d*		*e*	*f,q*				
1-Hexanol	*q*	*a,h*			*c*	*d*		*e*	*f,q*			*p*	
Ethyl acetate	*g*	*a,h*	*t*		*c*	*d*		*e*	*f,l,q*	*r*	*m,o*	*p,s*	
Ethyl propionate			*t*					*e*		*r*		*p*	
Ethyl hexanoate		*a*			*c*				*f,q*	*r*	*o*	*p,s*	
Butyl acetate	*g*												
3-Methyl-1-butyl acetate	*g*	*a*	*i*		*c*			*e*	*f,q*		*o*		
Hexyl acetate		*a*						*e*	*f,q*				
Ethyl octanoate	*g*	*a*			*c*		*u*	*e*	*f,q*	*r*	*o*	*p,s*	
Ethyl butyrate								*e*					

[a] Webb *et al.*, 1964.
[b] Lipis and Mamakova, 1963.
[c] Muller et al., 1964.
[d] Kepner and Webb, 1956.
[e] Chaudhary *et al.*, 1968.
[f] Webb *et al.*, 1964.
[g] Matthews *et al.*, 1962.
[h] Webb et al., 1963.
[i] Pisarnitskii, 1964.
[j] Sihto *et al.*, 1962.
[k] Drawert 1962.
[l] Diemair and Schams, 1960.
[m] Wick *et al.*, 1964.
[n] Smith and Coffman, 1960.
[o] Suomalainen and Nykänen, 1964.
[p] Rodopulo and Egorov, 1964.
[q] Webb and Kepner, 1962.
[r] Mecke *et al.*, 1960.
[s] Rodopulo and Pisarnitskii, 1963.
[t] Bayer and Bässler, 1961.
[u] Yamamoto, 1961.

extent 3- and 2-methyl-1-butanol. Small amounts of 2-methyl-1-propanol and 2-methyl-2-propanol have also been identified, the latter not previously identified in wines.

A number of acetals have been identified in the wine extract, with 2,4,5-trimethyl-1,3-dioxolane predominating. This was previously found in Flor Sherry Wine (Webb *et al.*, 1967). The two acetals, 1-ethoxy-1-propoxyethane and 1,1-dipropoxyethane, are also new additions to the list.

Differences between Juice and Wine. Gross differences exist between the juice and wine extracts. Several reasons may account for this, one of which is the process of fermentation. However, one would expect the wine extract to be predominantly alcohols, with ethanol the most abundant. One possible explanation, to account for this discrepancy, is that the juice was 25° Balling with very little dissolved alcohols and one would expect the organic material to be more easily extracted. In the wine, the concentration of sugar was much lower, whereas the alcohol (ethanol) content was considerably higher and hence extraction of the organic material with Freon would be expected to be more difficult. Consequently, a comparison of the relative amounts of material between the juice and wine extracts may not be valid, and only a qualitative comparison is possible.

No free aldehydes were found in the wine extract, although several were present in the juice. There was a large decrease in hexanol content upon fermentation. Part of the loss may have been due to inefficient extraction of the wine; however, Ingraham *et al.* (1961) indicated that hexanol is not a normal product of fermentation but arises from the raw material. In view of the present investigation, this would seem to be the case. This is in contrast with the work of Drawert *et al.* (1965), who, through a series of model experiments, showed that 2-hexenal was converted to hexanol upon fermentation.

In general, 14 components are common to both the juice and wine and apparently the main differences between the two are the loss of aldehydes and the formation of fusel alcohols, esters, and acetals upon fermentation.

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