Volatiles from Grapes. *Vitis vinifera* (Linn.) *cultivar* Grenache

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An examination of the volatile components found in Grenache grape essence (*Vitis vinifera*) has been performed using an open tubular gas chromatography column coupled to a time-of-flight mass spectrometer. A large number of compounds have been identified, the most abundant being 1-hexanol, 3-methyl-1-butanol, *trans*-2-hexenal, hexanal, and 1-heptanol.

The Grenache wine grape was recommended by Amerine and Winkler in 1944 as a promising variety to be used in the production of rosé wines from the cooler regions of California and as a light dessert wine from the warmer regions. In 1963, they restated their recommendation and described the grape and wines produced from Grenache and other varieties.

As of 1961 (Parr and Fance), 67% of the California Grenache grapes were grown in the Central Valley region—i.e., the warm area classified as region V by Amerine *et al.* (1944). The total acreage of Grenache grapes in California, as of 1964 (Calif. Dept. of Agriculture), was 14,272 acres, falling behind Carignane (26,912 acres) and Zinfandel (23,172 acres) of those listed as wine grapes. However, there are raisin and table varieties, often used for production of wine, which have greater acreage than Grenache—i.e., Thompson Seedless (238,894 acres), Muscat (20,117 acres), Emperor (31,438 acres), and Tokay (23,495 acres). Nevertheless, the relatively large acreage, with the use of Grenache grapes in the production of rosé and light dessert wines, has led us to investigate volatile organic components in the essence from free-run juice.

Experimental

Free-run Grenache grape juice (500 gallons, 22.5° Brix) was obtained as described by Stevens *et al.* (1966), and stripped by the method of Bomben *et al.* (1966). A feed rate of 112 pounds per hour (51.0 kg. per hour) and an evaporation temperature of 60° C. resulted in evaporation of 29.8% of the feed. The 5 gallons of essence (100-fold) were saturated with sodium chloride, and extracted with three portions of isopentane (Phillips, 99%, previously purified by distillation through a 10-plate Oldershaw column). The isopentane extract was dried over anhydrous sodium sulfate, filtered, and evaporated using a 10-plate Oldershaw column. No attempt was made to remove the last traces of isopentane. The isopentane extract consisted mainly of C_5 and C_6 alcohols with smaller amounts of other compounds. To identify the minor components, the isopentane extract was washed with three portions of propylene glycol to remove the alcohols. A chromatogram of the oil remaining after the extraction is shown in Figure 1 in which a hydrogen flame was used as a detector. A 500-foot × 0.02-inch i.d. stainless steel tube coated with GE SF-96(50) silicone oil was used to separate the components. The initial temperature of the column was 30° C., and the column was programmed at approximately 1.5° per minute. The effluent from the column was led directly into the ionization chamber of a Bendix Model 12 mass spectrometer. As the components emerged from the column as indicated by a strip chart recorder monitoring *m/e* 41 and/or an oscilloscope monitoring the mass spectral pattern, a spectrum was run from 20 to 200 mass units in 2.5 seconds. The resulting mass spectra were compared with spectra of known compounds and assignments made. Spectra were obtained from standard sources, literature references, and the authors' instrument using pure compounds. An identification was said to be conclusive when the mass spectral data and retention time by the enrichment technique (McFadden *et al.*, 1965) were in agreement.

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Results and Discussion

A chromatogram of the Grenache grape oil washed with propylene glycol is shown in Figure 1. The peak numbers are for identification and are referred to in Table I and the discussion. Peaks not numbered remain unidentified largely because of insufficient sample to obtain sufficiently intense mass spectra. Washing with propylene glycol removed most of the 2- and 3-methyl-1-butanols with considerable 1-hexanol, and the terpene alcohols were reduced considerably.

The three hydrocarbons, 2-methylpentane (peak 3), 3-methylpentane (peak 4), and methylcyclopentane (peak 7), were present in the solvent. Hexane and cyclohexane (peaks 5 and 10) were also detected in a solvent control experiment, but in much smaller proportions than in the grape oil. Fairly large quantities of hexane and cyclohexane were also in the oil from Muscat of Alexandria (Stevens *et al.*, 1966). The occurrence of hydrocarbons in Grenache and Muscat was remarkably similar, perhaps indicating a common source of contamination, such as the solvent.

As with the Muscat of Alexandria, the oil from Grenache grapes consisted mainly of alcohols. 1-Hexanol (peak 29) is predominant and 3-methyl-1-butanol (peak 15) the next most abundant (not apparent in Figure 1). Considerable *cis*-3-hexen-1-ol (peak 25) has been found, with smaller quantities of 2-methyl-1-butanol (peak 16), *trans*-3-hexen-1-ol (peak 22, not confirmed by retention data), *trans*-2-hexen-1-ol (peak 30), 2-heptanol (peak 31), 1-heptanol (peak 36), 2-ethyl-1-hexanol (peak 43), 1-octanol (peak 45), and 1-nonanol (peak 50). Terpene alcohols linaloöl, α-terpineol, citronellol, nerol, and geraniol were identi-

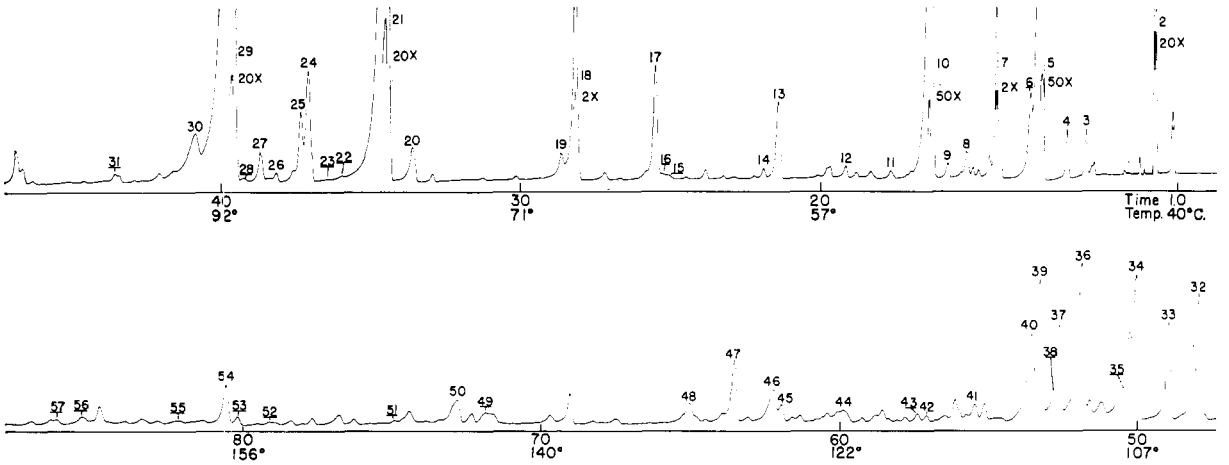

Figure 1. Gas chromatogram of propylene glycol–washed Grenache grape oil
A 500-foot × 0.02-inch i.d. column with SF-96(50) used as a stationary phase

Table I. Compounds Identified in Grenache Oils[a]

Peak No.	Hydrocarbons	Alcohols	Aldehydes and Acetals	Esters	Ketones
1	Isopentane[b]				
2					Acetone
3	2-Methylpentane[b]				
4	3-Methylpentane[b]				
5	Hexane				
6				Ethyl acetate	
7	Methyl cyclopentane[b]				
8	Unknown				
9			2-Methylbutanal		
10	Cyclohexane				
11					2-Pentanone
12				Ethyl propionate	
13			2,4,5-Trimethyl-1,3-dioxolane		
14			1,1-Diethoxyethane		
15		3-Methyl-1-butanol			
16		2-Methyl-1-butanol			
17	Toluene				
18			Hexanal		
19				Ethyl butanoate	
20			*cis*-2-Hexenal[c]		
21			*trans*-2-Hexenal		
22		*trans*-3-Hexen-1-ol[d]			
23	*p*-Xylene				
24				*n*-Amyl acetate	
25		*cis*-3-Hexen-1-ol			
26					3-Heptanone
27					2-Heptanone
28	*o*-Xylene				
29		1-Hexanol			
30		*trans*-2-Hexen-1-ol			
31		2-Heptanol			
32	*n*-Propylbenzene				
33	*p*-Ethyltoluene				

[a] Unless otherwise indicated, identification of each component includes mass spectrum and retention time data. [b] Solvent contaminants. [c] Mass spectrum identical with (or very similar to) *trans*-2-hexenal. Authentic sample not available. [d] Mass spectrum identical with (or very similar to) *cis*-3-hexen-1-ol. Authentic sample not available.

Table I. Continued

Peak No.	Hydrocarbons	Alcohols	Aldehydes and Acetals	Esters	Ketones
34			Benzaldehyde		
35	*o*-Ethyltoluene				
36		1-Heptanol			
37				*cis*-3-Hexenyl-1-acetate	
38	1,2,4-Trimethylbenzene				
39				*n*-Hexyl acetate	
40				*trans*-2-Hexenyl-1-acetate	
41	1,2,3-Trimethylbenzene				
42	Limonene				
43		2-Ethyl-1-hexanol			
44					Acetophenone
45		1-Octanol			
46					2-Nonanone
47			Nonanal		
48		Linaloöl			
49				Benzyl acetate	
50		1-Nonanol			
51		α-Terpineol			
52		Citronellol			
53		Nerol			
54				2-Phenylethyl acetate	
55		Geraniol			
56	2-Methylnaphthalene				
57	1-Methylnaphthalene				

fied, but they represent small percentages of the total oil, in contrast to Muscat oil in which linaloöl and geraniol were two of the major components.

Although only six aldehydes were identified, two of them *trans*-2-hexenal (peak 21) and hexanal (peak 18) represent a large percentage of the oil and probably contribute the green-grass aroma. Smaller amounts of 2-methylbutanal (peak 9), *cis*-2-hexenal (peak 20, not confirmed by retention data), benzaldehyde (peak 34), and nonanal (peak 47) were found. Two acetals were identified, 2,4,5-trimethyl-1,3-dioxolane (peak 13) and 1,1-diethoxyethane (peak 14). Authentic dioxolane was synthesized from optically active 2,3-butandiol and acetaldehyde which gave a single dioxolane with the same mass spectral pattern and gas chromatographic retention time as peak 13. Flath *et al.* (1967) reported it in Delicious apple essence.

In contrast to the Muscat of Alexandria, Grenache grape oil contains a higher percentage of esters—e.g., *n*-pentyl acetate (peak 24), *cis*-3-hexenyl-1-acetate (peak 37), *n*-hexyl acetate (peak 39), and *trans*-2-hexenyl-1-acetate (peak 40). Smaller quantities of ethyl acetate, ethyl propionate, ethyl butanoate, benzyl acetate, and 2-phenylethyl acetate have been found.

The ketones represent only a very small quantity of the oil, a situation also found in the Muscat oil. Acetone (peak 2) may be a laboratory contaminant, but 2-pentanone (peak 11), 2- and 3-heptanone (peaks 27 and 26, respectively), acetophenone (peak 44), and 2-nonanone (peak 46) are presumably from the grape.

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Received for review November 14, 1966. Accepted March 13, 1967. Presented at Western Regional Meeting, ACS, San Francisco, Calif., October 1966. Reference to a company or product name does not imply approval or recommendation of the product by the USDA to the exclusion of others that may be suitable.