Research Note

# Aroma Components in Freon Extracts of Wine

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**The utility of a standard analysis technique for wine volatiles was expanded by the identification of eleven new components in the standard chromatogram. Acetoin was identified as the component interfering with the determination of hexyl acetate, whilst ethyl 3-hydroxybutyrate was positively identified as a constituent of Cabernet Sauvignon wine aroma.**

The freon extration technique described by Marais & Houtman (1979) has proved its reliability over the last number of years. Of the 42 peaks that normally appear in the standard chromatogram only 16 had, however, been identified at the time of publication.

In a recent publication Marais, Van Rooyen & Du Plessis (1981) differentiated between cultivar wines from different localities by the application of stepwise discriminant analysis to results obtained by the abovementioned extraction technique. Successful classifications of different Pinotage and Cabernet Sauvignon wines were made by using only 4 variables viz., ethyl caprate, ethyl acetate, isoamyl acetate and a compound tentatively identified as isovaleric acid. Hexyl acetate was also indicated as a useful variable but had to be discarded, as its peak was often obscured by an unknown component in red wine analyses. This study was undertaken to determine the identity of this unknown component. During the investigation the identity of eleven other components appearing in the standard chromatogram was also determined.

## MATERIALS AND METHODS

Ten commercial and experimental red wines were extracted, and the extracts analysed according to the technique of Marais & Houtman (1979). A 1976 vintage commercial Cabernet Sauvignon wine containing most of the unknown component was selected for further analysis. The concentrated extract of 1,5 litres of wine was subjected to gas chromatographic-mass spectrometric analysis. Gas chromatographic analysis was performed on a HP 5840A instrument, whilst mass spectra were recorded on a Varian MAT 311A instrument coupled to a Varian 2700 gas chromatograph using helium as carrier gas.

Components were identified by comparison of mass spectra with spectra of authentic reference compounds recorded under identical conditions.

All but two reference compounds were obtained from reliable commercial suppliers. Methionol (3-methylthio-1-propanol) was synthesized from methional according to the technique of Muller, Kepner & Webb (1971). 9-Decenoic acid was synthesized from 9-decenol by oxidation of the latter with pyridinium dichromate in dimethylformamide according to the technique of Corey & Schmidt (1979). The purified acid was esterified with ethanol according to the standard technique described by Vogel (1951).

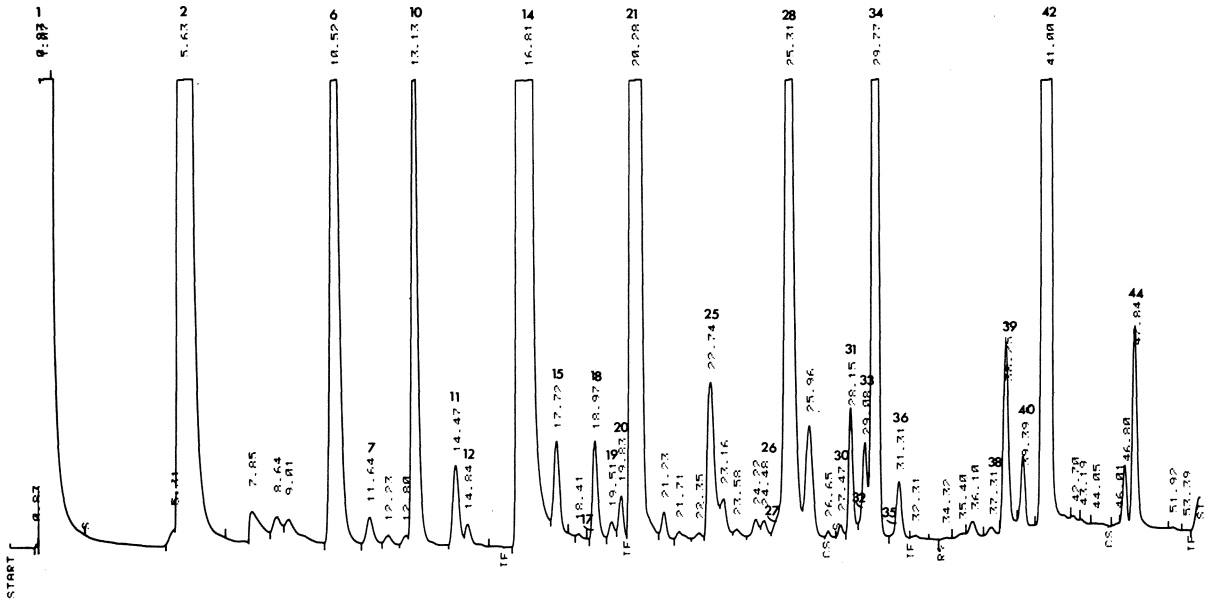


FIG. 1
Chromatogram of Freon 11 extract of Cabernet Sauvignon wine. Peak numbers correspond to those in table 1.

## RESULTS AND DISCUSSION

All the compounds identified in the standard chromatogram of a freon extract of Cabernet Sauvignon wine are listed in Table 1, whilst the standard chromatogram is depicted in Fig. 1. The compound interfering with the determination of hexyl acetate (peak 17) was identified as acetoin (peak 18). Acetoin concentration in wine varies from 2 mg/l to 53 mg/l (Ronkainen, Brummer & Suomalainen, 1970), while the hexyl acetate concentration varies between 0,1 mg/l and 1,00 mg/l (A. C. Houtman, 1981 personal communication). To determine the hexyl acetate concentration in the presence of substantial amounts of acetoin, more efficient Carbowax 4 000 M columns will have to be prepared or, alternatively, a more efficient stationary phase will have to be used.

The two methyl pentanol isomers (peaks 19 & 20), as well as ethyl 3-hydroxybutyrate (peak 26), were first identified as wine aroma compounds by Van Wyk, Kepner & Webb (1967). According to Sakato *et al.* (1975), ethyl 3-hydroxybutyrate is only questionably present in Cabernet Sauvignon wines. The present results, however, leave no doubt that ethyl 3-hydroxybutyrate is indeed present in Cabernet Sauvignon wines. In a recent investigation of the volatile aroma compounds of Australian port wines the peak designated number 37b remained unidentified (Simpson, 1980). Comparison of the mass spectral results published in that report with those obtained during the present study, suggests that the unknown peak 37b is in fact ethyl 3-hydroxybutyrate.

Three isomers of 2,3-butanediol have been identified as wine aroma constituents, with the total butanediol concentration in wine ranging from 300 mg/ℓ to 1 300 mg/ℓ (Peynaud & Lafon, 1951; Ronkainen *et al.*, 1970; Schreier, 1979). From Fig. 1 it is evident that one of the butanediol isomers (peak 27) falls partially below the internal standard. Because of the high polarity of 2,3-butanediol and the non-polar nature of the Freon-11 extractant, it is unlikely that sufficient butanediol will be extracted from the wine to seriously affect quantitative results obtained by using this technique.

The identity of isovaleric acid (peak 33), tentatively identified by Marais *et al.* (1981) is confirmed. Methionol (3-Methylthio-1-propanol, peak 36) was first identified as a constituent of Cabernet Sauvignon wine aroma by Muller, *et al.* (1971). Some extracts analysed during the present study contained substantial amounts of this component. This is surprising, as previous studies (Muller, *et al.*, 1971; Schreier & Drawert, 1974) have indicated that methionol was present in wines at very low concentrations. Muller, *et al.* (1971), therefore, stated that this component, with its intense raw-potato odour, probably plays only a secondary role in the overall Cabernet Sauvignon aroma. Mass spectral scanning over the entire peak during this study, however, failed to indicate the presence of additional components in the peak. This observation will be the subject of further investigation.

The retention time of ethyl-9-decenoate in the standard chromatogram has become relevant in certain studies in progress at the OVRI (Houtman & Du Plessis, 1981). For this reason the ester was synthesized and its retention time determined. From Fig. 1 it is obvious that ethyl-9-decenoate has a retention time slightly shorter than that of methionol. Some of the extracts analysed during this study did in fact show small shoul-

TABLE 1
Compounds identified in a Freon 11 extract of Cabernet Sauvignon wine

| PEAK No. | COMPOUND | IDENTIFIED | |
|---|---|---|---|
| | | THIS STUDY | PREVIOUS STUDIES[1] |
| 2 | Ethyl acetate | | × |
| 6 | tert.-Amyl alcohol (int. std.) | | |
| 7 | Ethyl butyrate | | × |
| 10 | Isobutanol | | × |
| 11 | Isoamyl acetate | | × |
| 12 | Butanol | × | |
| 14 | Amyl alcohols | | × |
| 15 | Ethyl caproate | | × |
| 17 | Hexyl acetate | | × |
| 18 | Acetoin | × | |
| 19 | 4-Methyl-1-pentanol | × | |
| 20 | 3-Methyl-1-pentanol | × | |
| 21 | Ethyl lactate + hexanol | | × |
| 25 | Ethyl caprylate | | × |
| 26 | Ethyl 3-hydroxybutyrate | × | |
| 27 | 2, 3-Butanediol | × | |
| 28 | Ethyl nonanoate (int. std.) | | |
| 30 | Isobutyric acid | × | |
| 31 | δ- Butyrolactone | × | |
| 32 | Ethyl caprate | | × |
| 33 | Isovaleric acid | × | |
| 34 | Diethyl succinate | | × |
| 35[2] | Ethyl-9-decenoate | × | |
| 36 | Methionol | × | |
| 38 | 2-Phenethyl acetate | | × |
| 39 | Hexanoic acid | | × |
| 40 | Benzyl alcohol | × | |
| 42 | 2-Phenylethanol | | × |
| 44 | Octanoic acid | | × |

1. Marais & Houtman (1979). Numbers correspond to those in Marais *et al.* (1981)
2. Retention time determined – peak not identified – see text.

ders on the leading edge of the methionol peak. Because of the extremely small amount of material present, this microcomponent could not be identifed.

## CONCLUSIONS

In studies where it is necessary to quantitatively determine hexyl acetate (peak 17) in the presence of substantial amounts of acetoin (peak 18), and/or ethyl caprate (peak 32) in the presence of substantial amounts of isovaleric acid (peak 33), more efficient Carbowax 4 000 M columns will have to be prepared. If this is not possible, some other more efficient stationary phase capable of producing the desired separation will have to be found. Although large concentrations of 2,3-butanediol are usually found in wines, the amounts extracted by Freon 11 are small, so that reliable quantitative results are obtained even though this compound falls partially under the internal standard.

The identification of a further 11 compounds has increased the utility of this extraction technique.

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