Note

Gas Chromatographic Analysis of Volatile Esters in Wines*

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Volatile esters in alcoholic beverages, such as ethyl esters of fatty acids and acetate esters of higher alcohols, have pleasant, fresh and fruitlike odors.^{1,2)} Analyses of volatile esters in wines have been also reported by several workers^{3~7)} and a significance of volatile esters to wine quality was suggested by the investigators.^{8,9)} This paper deals with the rapid gas chromatographic analysis of the volatile esters with use of a simple extraction method to clarify the ester contents in various wines and the contribution of the esters to wine bouquet. The volatile esters concerned in this work are ethyl esters of caproic, caprylic and capric acids, acetate esters of isoamyl, *n*-hexyl and 2-phenylethyl alcohols and diethyl succinate, which are generally found relatively large amounts in wines and likely to relate to wine odor.

The analyses were performed using a Jeol gas chromatograph model JGC-1100 (Japan Electron Optics Laboratory Co., Ltd.) with dual columns and dual hydrogen flame ionization detectors. Preparation of samples. Method A: Volatiles in 10 ml of wine were extracted with 1.5 ml of *n*-pentane after addition of internal standard (*n*-butyl and *n*-octyl alcohols) by shaking for ten minutes and the solvent layer was used for gas chromatographic analysis. Method B: Volatiles in 5 ml of wine were extracted with 2 ml of ethyl acetate-*n*-pentane mixture (2:1, v/v) by shaking for ten minutes after addition of 2 ml of water and internal standard (3-phenylpropyl alcohol) and the solvent layer was used for determination of 2-phenylethyl acetate.

Gas chromatographic conditions. Two to three microliters of the solvent layer (extract of wine) were injected on to the stainless steel column (2 m × 3 mm i.d.) packed with Chromosorb W (AW, 60~80 mesh) as solid support and stationary phases and column temperatures were as follows (1) Ethyl caproate (Et-C6): 15% PEG (polyethylene glycol)-600, 75°C. (2) Ethyl caprylate (Et-C8), ethyl caprate (Et-C10), *n*-hexyl acetate (HxOAc) and diethyl suc-

cinatate (DES): 15% PEG-1000, 125°C. (3) *iso*-Amyl acetate (AmOAc): 15% PEG-1000, 75°C. (4) 2-Phenylethyl acetate (PhEtOAc): 10% EGSP (ethylene glycol succinate polyester), 125°C.

Since the coefficients of variation in sixfold analyses of a white wine were 6.3 to 9.7% for Et-C6, Et-C8, Et-C10 and AmOAc, and 11.5 to 16.1% for HxOAc, PhEtOAc and DES,¹⁰⁾ esters in wine were rapidly determined by this method with satisfactory accuracy.

Table I shows analytical results of volatile esters in commercial wines of various types. White and rose wines were generally contained more Et-C6, Et-C8 and AmOAc (mean values: 0.2~1.1 mg/liter) than red table wines (mean values: 0.2~0.3 mg/liter). A small amount (mean values: 0~0.1 mg/liter) of Et-C10, HxOAc and PhEtOAc were found in all the wines. DES content was apparently larger (mean values: 11~20 mg/liter) than the other esters. Sparkling wines contained similar concentrations of these esters to table wines, while lower levels of the esters except DES than table wines were found in sherries.

As shown in Table II, the ester contents of new wines are generally larger than those of matured wines (Table I), especially the contents of AmOAc which seems to give more fruity and esteric odor.

The contents of volatile esters in wines as shown in Tables I and II are in fair agreement with ordinary concentrations of those reported in the literatures.^{3~11)} However, there were some differences in the ester contents among wine-types. These results suggest that various ester contents resulted from alcoholic fermentation and aging process reflect the odor characteristic and the quality of wines.

Therefore, the contribution of each ester to wine odor was examined with threshold^{11~14)} and odor values (Table III). As the concentrations of Et-C6, Et-C8 and AmOAc in some wines were fairly exceeded the threshold values, these esters were considered to participate in wine odor more than Et-C10, HxOAc, PhEtOAc and DES in which the concentrations were lower than the threshold values. The results on the odor values and the additive effect of aroma compounds (data are not shown) indicate that these volatile esters clearly contributed to wine bouquet.

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REFERENCES

- 1) H. Suomalainen and M. Lehtonen, *J. Inst. Brew.*, **85**, 149 (1979).
- 2) K. Yoshizawa, *J. Brew. Soc. Jpn.*, **61**, 629 (1966); **67**, 936 (1972).
- 3) H. Komoda and M. Yamada, *Nippon Nôgeikagaku Kaishi*, **42**, 406 (1968).

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TABLE I. CONTENTS OF VOLATILE ESTERS IN JAPANESE AND FOREIGN WINES

Wines	Samples	Et-C6 ^a			Et-C8			Et-C10			AmOAc			HxOAc			PhEtOAc			DES		
		R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$	R	$\bar{X}$	$\bar{X}$
		(milligrams per liter) ^b																				
Table wines Japanese	white 10	t ^c ~0.7	0.4	0.4	t ^c ~1.0	0.4	0.4	0~0.5	0.1	t ^c ~1.2	0.4	0.4	0~t ^c	0~0.2	0	0	0~0.2	0	0	4~17	9	
	rose 4	0.2~0.6	0.3	0.3	0.1~0.5	0.2	0.2	0~0.3	0.1	0.1~0.8	0.3	0.3	0~0.1	0	0	0	0~0.1	0	0	8~14	11	
	red 10	t ~0.6	0.2	0.2	0.1~0.4	0.3	0.3	0~0.5	0.1	t ~0.5	0.2	0.2	0~t	0~t ^c	0	0	0~t	0~t ^c	0	14~26	20	
Foreign ^d	white 10	0.1~1.0	0.3	0.3	0.1~1.6	0.6	0.6	0~0.6	0.1	t ~3.8	0.8	0.8	0~0.3	0~1.1	0	0	0~0.3	0~1.1	0	0~52	12	
	rose 3	0.3~0.4	0.3	0.3	0.2~0.8	0.5	0.5	0~0.4	0.1	0.1~3.1	1.1	1.1	0~0.2	t ~1.1	0	0	0~0.2	t ~1.1	0	6~27	14	
	red 7	0.1~0.6	0.3	0.3	0.1~0.6	0.3	0.3	0~0.4	0.1	0.1~0.4	0.2	0.2	0~t	0~0.1	0	0	0~t	0~0.1	0	3~28	17	
Sparkling wines ^e	4	0.1~0.4	0.3	0.3	0.1~1.2	0.4	0.4	0~0.3	0.1	t ~0.2	0.1	0.1	0	0	0	0	0	0	8~23	13		
Sherries ^f	5	0.2~0.3	0.2	0.2	0.1~0.3	0.2	0.2	0	0	t	t	t	0	0	0	0	0	0	49~66	55		

^a Et-C6, ethyl caproate; Et-C8, ethyl caprylate; Et-C10, ethyl caprate; AmOAc, *iso*-amyl acetate; HxOAc, *n*-hexyl acetate; PhEtOAc, 2-phenylethyl acetate; DES, diethyl succinate.

^b R, range; $\bar{X}$, mean value.

^c t, traces, less than 0.1 mg/liter.

^d White wines, French 3, German 5, South African 1 and American 1 samples; Rose wines, French 1, German 1 and American 1 samples; Red wines, French 4, German 2 and American 1 samples.

^e Japanese 1, French 1, German 1 and American 1 samples.

^f Spanish sherries, fino 2, medium 2 and cream 1 samples.

TABLE II. CONTENTS OF VOLATILE ESTERS IN NEW WINES^a

	Et-C6	Et-C8	Et-C10	AmOAc	HxOAc	PhEtOAc	DES
	(milligrams per liter)						
Commercial table wines ^b							
No. 1 white wine 1978	0.8	1.0	0.3	1.0	t	t	4
2 white wine 1978	0.4	1.1	0.4	0.6	0.1	0.1	4
3 white wine 1978	1.0	0.9	0.3	1.9	0.2	0.1	3
Wines in a cellar ^c							
4 Koshu	0.4	0.6	0.3	2.3	0.2	0.1	0
5 Zenkoji	0.5	0.6	0.5	2.7	0.4	0.2	0
6 Muscat Bailey A	0.2	0.2	0	0.8	0	0	2
7 Cabernet-Sauvignon	0.2	0.2	0	1.0	t	0	3

^a Wines were analyzed after aging for one year (1979).^b Japanese wines.^c Wines were produced in 1978 and aged in vessels in a cellar.
White wines, Nos. 4 and 5; red wines, Nos. 6 and 7.

TABLE III. THRESHOLD AND ODOR VALUES OF VOLATILE ESTERS IN WINE

Esters	Concentration in wines ^a (mg/liter)	Threshold value (mg/liter)	Odor value ^e
Ethyl caproate (Et-C6)	0.1 ~ 1.0	0.5 ^b	0.2 ~ 2.0
Ethyl caprylate (Et-C8)	0.1 ~ 1.6	1.0 ^b	0.1 ~ 1.6
Ethyl caprate (Et-C10)	0 ~ 0.6	2.0 ^b	0 ~ 0.3
iso-Amyl acetate (AmOAc)	0.1 ~ 3.8	1.0 ^c	0.1 ~ 3.8
n-Hexyl acetate (HxOAc)	0 ~ 0.4	3.0 ^c	0 ~ 0.1
2-Phenylethyl acetate (PhEtOAc)	0 ~ 1.1	3.0 ^b	0 ~ 0.3
Diethyl succinate (DES)	0 ~ 66	75 ^d	0 ~ 0.8

^a All the commercial wines analyzed (Tables I and II).^b Estimated values by the reported data.¹¹⁻¹³⁾^c R. F. Simpson (1978)¹⁴⁾^d Determined in our laboratory.^e Concentration/threshold value.

- 4) A. Bertrand, Thèse 3ème cycle, Faculté des Sciences de l'Université de Bordeaux, France (1968).
- 5) C. E. Daudt and C. S. Ough, *Am. J. Enol. Viticult.*, **24**, 125, 130 (1973).
- 6) J. P. Snyman, *Vitis*, **16**, 295 (1977).
- 7) J. Marais and A. C. Houtman, *Am. J. Enol. Viticult.*, **30**, 250 (1979).
- 8) C. J. Van Wyk, O. P. H. Augustyn, P. de Wet and W. A. Joubert, *Am. J. Enol. Viticult.*, **30**, 167 (1979).
- 9) J. Marais, P. C. Van Rooyen and C. S. du Plessis, *Vitis*, **18**, 31 (1979).
- 10) T. Shinohara, J. Shimizu and Y. Shimazu, *Agric. Biol. Chem.*, **43**, 2351 (1979).
- 11) R. F. Simpson, *Food Tech. Australia*, **31**, 516 (1979).
- 12) G. A. Harrison, *J. Inst. Brew.*, **76**, 486 (1970).
- 13) A. A. Williams, *J. Inst. Brew.*, **80**, 455 (1974).
- 14) R. F. Simpson, *Vitis*, **17**, 274 (1978); **18**, 148 (1979).