Note

Gas Chromatographic Analysis of Furfural and Hydroxymethylfurfural in Wine

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Recent progress on gas chromatography made possible to determine rapidly and accurately trace volatile components in wine.

The occurrence of furfural in processed beverages is known as indication of deterioration in quality. The methods of quantitative analysis of furfural have been studied with reference to the changes during storage in citrus juice¹⁻³⁾ and wine.⁶⁾ The assay methods of hydroxymethylfurfural (HMF) have also been developed in regard to the formation in wine,⁶⁻⁹⁾ brandy,¹⁰⁾ grape concentrate,^{11,12)} beer¹³⁾ and others.^{14,15)} However, only one paper⁶⁾ was reported on determination of these carbonyl compounds in wine by the use of a gas chromatographic technique.

The present communication deals with gas chromatographic determination of furfural and HMF in various types of wines.

Table I shows the samples analysed. All reagents used in the experiments are special grade and redistilled solvent was employed for the extraction of trace volatile compounds in wine. The analyses were performed with a Shimadzu gas chromatograph (model GC-6A) with dual hydrogen flame ionizing detectors.

Calibration curves were obtained with standard reagents of furfural and HMF diluted to 2, 5, 10, 15 and 20 $\mu\text{g}/\text{ml}$ each with ordinary table wine which contained no detectable amount of these compounds. To 1 ml of the above standard solution or sample, 10 μg of *n*-octanol as the internal standard and 20 μg of methyl heptadecanoate as the supplementary internal standard, 30 ml of deionized water and 30 ml of dichloromethane were added. After the mixture was mechanically stirred for 15 minutes, solvent layer was separated and concentrated with a rotary evaporator. A portion of the concentrate was injected on the glass column (2 m $\times$ 3 mm i.d.) peaked with 20% diethylene glycol succinate (DEGS) on chromosorb W (AW-DMCS), 60~80 mesh. Oven temperature was programmed from 100 to 210°C at a rate of 4°C/min. Both injection and detection temperatures were set at 300°C and flow rate of carrier gas (N_2) was 30 ml/min.

FIG. 1. Calibration Curves for Furfural and HMF. Working method, see the text. The ordinate shows the ratio of the peak height on the gas chromatogram of furfural or HMF to that of the internal standard (10 μg of *n*-octanol).

FIG. 2. Gas Chromatogram of the Extract from Sherry.

Peaks: 1, *n*-octanol (internal standard); 2, furfural; 3, diethyl succinate; 4, diethyl malate; 5, methyl heptadecanoate (internal standard); 6, diethyl tartrate; 7, hydroxymethylfurfural. Operating condition, Apparatus: Model GC-6A (Shimadzu Seisakusho Co., Ltd. Japan); column, 2 m $\times$ 3 mm i.d. glass column; packing, 20% diethylene glycol succinate on chromosorb W (AW-DMCS), 60~80 mesh (Nippon Chromato Kogyo, Japan); detector, hydrogen flame ionizing detector (FID); injection and detection temp., 300°C; column temp., 100°C to 210°C, programmed at 4°C/min; carrier gas flow rate, N_2 , 30 ml/min.

A plot of the ratio of peak height on the chromatogram of furfural or HMF to that of the internal standard (*n*-octanol) versus concentration was linear up to 20 μg of each carbonyl compound (Fig. 1).

Figure 2 shows a typical gas chromatogram of sherry wine. Diethylesters could also simultaneously be determined from the same chromatogram as previously reported.¹⁶⁾

As shown in Table I, Japanese wines were found to contain trace (less than 0.1 mg) to 1.2 mg of furfural and trace (less than 0.1 mg) to 24.3 mg of HMF each per liter. On the other hand, trace to 4.5 mg of furfural and trace to 93.2 mg of HMF each per liter were found

TABLE I. ANALYSES OF FURFURAL AND
HYDROXYMETHYLFURFURAL IN DOMESTIC
AND FOREIGN WINES

Wines	Furfural	HMF	No. of samples
	(mg/liter)		
I. Japanese			
White	tr ~1.2	0.6~24.3	19
Red	0.1~0.5	tr	5
II. German			
White	tr ~4.2	tr ~27.3	8
III. French			
Red	0.2~0.4	tr	5
IV. American			
White	tr ~2.1	tr ~ 0.3	5
Fruit ^a	0.2~4.5	0.6~24.3	6
V. Spanish sherries			
Fino type	tr ~0.4	1.4~ 8.2	6
Amontillado type	1.4~2.0	23.5~80.2	4
Oloroso type	3.1	93.2	1

^a These wines are commercial fruit wines.

Others are commercial grape wines. Abbreviation:
tr, trace; <0.1 mg/liter.

in foreign wines. Large amounts of furfural (0.2~4.5 mg per liter) in American fruit wines and of HMF (1.4~93.2 mg per liter) in Spanish sherries were noteworthy.

In general, these carbonyl compounds in red wines were found less than those in white wines. Contents of HMF varied over wide ranges in both Japanese and foreign wines, particularly Spanish sherries. The wines containing more residual sugars showed a tendency to have more HMF.

The present investigation confirmed that the wines with abundant residual sugars stored for a long period under the oxidized condition showed high levels of furfural and HMF. These carbonyl compounds seemed to cause characteristic flavor (Rancio flavor) of sherries and such wines as described above.

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