

Influence of Oak Chips Geographical Origin, Toast Level, Dosage and Aging Time on Volatile Compounds of Apple Cider

Wenlai Fan¹, Yan Xu^{1,2} and Aimei Yu¹

ABSTRACT

J. Inst. Brew. 112(3), 255–263, 2006

The effects of different geographical origin, levels of toasting, dosage and the aging time of oak chips on volatile compounds released into ciders were studied. The oak chips tested were the same size and with three different toast levels (light, medium and heavy) from French, American and Chinese oak. The oak wood chips were immersed in identical ciders. Higher alcohols, acids and esters were determined by headspace (HS)–solid phase microextraction (SPME) and gas chromatography (GC)–mass spectrometry (MS), while oak-related aroma compounds including *trans*- and *cis*-oak lactones, guaiacol, 4-methylguaiacol, furfural, 5-methylfurfural, vanillin, eugenol and isoeugenol, were determined by liquid-liquid extraction by means of ultrasound and GC/MS selective ion monitoring (SIM). The results showed that there was little difference between the oak-related volatile compositions of ciders aged with French oak chips and those aged with American oak chips, but that there were obvious differences with Chinese oak chips. It was observed that oak chips, at medium toasting levels, released the highest concentrations of volatile components into the ciders. Most of the oak-related volatile aroma compounds extracted had an increase that depended on the oak chip dosage with the exception of guaiacol and furfural.

Key words: Aged, cider, oak chips, oak lactone, volatile compounds.

INTRODUCTION

Cider generally refers to a fermented beverage obtained wholly or partly from apples¹⁵. It is a popular drink in many western countries, especially in the UK where much commercial cider is produced (ca. 90 million gallons annually). Recently, there has been a great interest in cider drink production in China. The main reason for the rapid development of the cider industry in China is the overproduction of apples. China has the largest world output of apples at 2200 million tons in 2005. Cider in China is usually produced from apple cultivars that include *Fuji*,

Starking, *Gala*, and *Ralls*. The apples are harvested, milled, pressed, clarified, and SO₂ is added to the apple juice. The juice is fermented by a selected culture. After finishing, the apple wine is racked and supplemented with SO₂. Like other spirit beverages, aging in oak barrels is a very old tradition and is used to improve the quality and the sensory characteristics of wine. When aging in oak barrels, red wine undergoes a series of processes that result in important improvements of wine aroma, colour and taste^{5,14}.

The oak composition and the conditions under which wine maturation takes place are of primary importance to the impact of oak on wine and brandy quality^{17,27,30,31}. Several aroma compounds identified in wine include *cis*- and *trans*-oak lactones (*cis*- and *trans*- β -methyl- γ -octalactone), vanillin (4-hydroxy-3-methoxybenzaldehyde), eugenol (4-allyl-2-methoxyphenol) and guaiacyl derivatives (Fig. 1) and these are derived principally from the oak barrels during the process of oak barrel maturation of the wine. Some volatile oak-derived compounds are formed during the charring or toasting of the oak barrels from the thermal degradation of lignin, cellulose and hemicellulose^{3,11,21}.

Few studies have been carried out to investigate the effect of fermentation conditions and oak chips on cider. Xu et al.³⁴ studied the control and formation of volatile components in cider by using a combination of *Saccharomyces cerevisiae* and *Hanseniaspora valbyensis* yeast species. Wang et al.³² investigated the fermentation kinetics of different sugars using the apple wine yeast *Saccharomyces cerevisiae*. Yu et al.³⁵ analyzed the influence of different raw materials on the volatile aroma compounds of ciders. Mangas et al.¹⁷ studied the volatiles in distillates of cider aged in American oak wood, and found that significant increases were detected in the concentration of diethyl butanedioate, ethyl 3-methylbutanoate, esters of long-chain fatty acids and 1-hexanol. In contrast, acetate esters and long-chain fatty acids decreased during cider aging.

The addition of oak chips, as a more rapid and economical method of oak treatment, allows the incorporation of oak flavors and interaction of wood and cider constituents without traditional barrel maturation^{13,21}. Moreover, the cost of the oak barrels is the second greatest expense followed by the expense of wine²⁴. Floating oak chips, or larger pieces of wood in wine, could give similar flavors to those obtained through storing in the much more expensive barrels. The use of oak chips, although a contro-

¹Laboratory of Brewing Microbiology and Applied Enzymology, School of Biotechnology and Key Laboratory of Industrial Biotechnology, Ministry of Education, School of Biotechnology, Southern Yangtze University, Wuxi, China, 214036.

²Corresponding author. E-mail: yxu@sytu.edu.cn

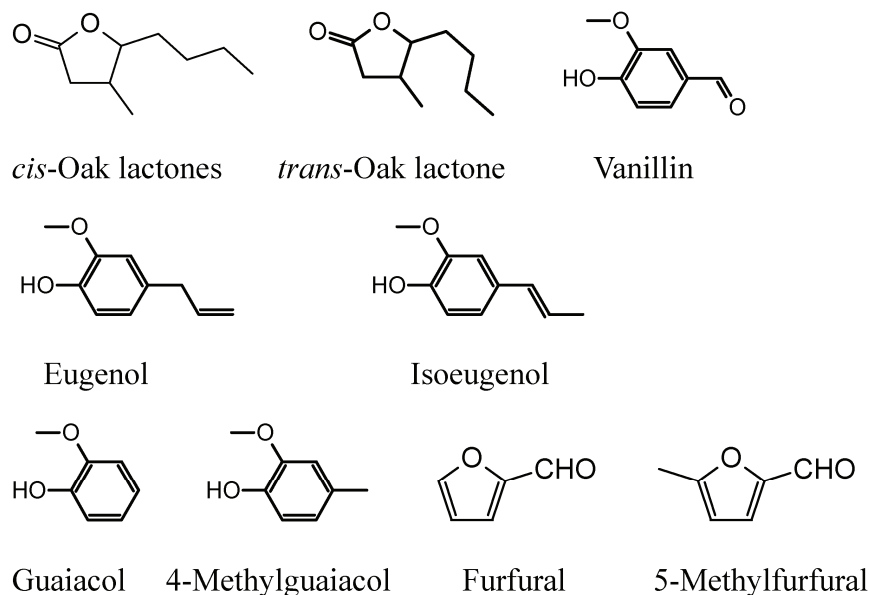


Fig. 1. Structure of some oak-related compounds of cider.

versial technique, may be a shortcut in modern winemaking. The use of oak chips to accelerate the aging of wine has been reported in the literature¹¹ and oak chips have successfully been used to shorten aging time in wine vinegar^{21,29}. The main aim of this work was to quantify the volatile aroma compounds of cider aged with oak chips and to explore that the effects of different geographical origin, levels of toasting, dosage and the aging time of oak chips on the volatile compounds released into cider.

MATERIALS AND METHODS

Chemicals. Ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, ethyl dodecanoate, hexyl acetate, 3-methylbutyl acetate, 2-phenylethyl acetate, 2-phenylethanol, 1-propanol, 1-butanol, 2-methylpropanol, 3-methylbutanol, 1-hexanol, isoeugenol, 5-methylfurfural, vanillin, 4-methylguaiacol and 2-octanol were obtained from Sigma-Aldrich (St. Louis, MO, USA). Butyl acetate, furfural, guaiacol, eugenol, hexanoic acid, octanoic acid and decanoic acid were from Shanghai Reagent Co. (Shanghai, China). The *cis*-oak lactone and *trans*-oak lactone were a gift from the Dalian Jinju Perfume Co. Ltd. (Dalian, Liaoning, China). Dichloromethane, NaCl and anhydrous sodium sulfate were from the Shanghai Reagent Co. (Shanghai, China). Solid phase microextraction (SPME) fibers, 75 μ m Carboxen-PDMS [poly (dimethylsiloxane)], were purchased from Supelco Inc. (Bellafonte, PA, USA).

Oak chips. Three kinds of oak chips from different geographical origins were used in this work. They were American white oak (*Quercus alba*), French oak (*Quercus petraea* from the Allier forest in France) and Chinese oak (northeast of China). The chips were sourced from the Changyu Pioneer Wine Company Ltd. (Yantai, Shandong, China). Oak chips with different levels of toasting (light, medium and heavy) were also obtained from the Changyu Pioneer Wine Company Ltd.

Cider. Apple juice concentrates (diluted to 14° Brix with distilled water) were inoculated with *Saccharomyces cerevisiae* strain CCTCC M201022 (a winery yeast coded M201022 sourced from the China Center for Type Culture Collection (CCTCC) Wuhan, China). Fermentations were carried out at 15°C and monitored by weight loss (CO₂ evolution) every 24 h until the weight stabilized. Apple cider was then racked and provided with SO₂ to a final concentration of 25 mg/L (determined as free), resulting in apple wine with an 8% (v/v) alcohol content after 15 days of fermentation. The apple wine was aged and soaked with the different oak chips.

Ciders immersed with oak chips. Oak chips (4 g/L) were immersed in 740 mL apple cider in 750 mL new bottles at 15°C for 30 days. The ciders were shaken once for 3–5 min daily during the aging period. To study the effect of the geographical origin, three types of oak chips (sized 1 cm \times 0.5 cm \times 1 cm) were tested in triplicate. Medium toasting levels from Chinese, French and American oak chips were used. Chips from French oak, light, medium and heavy, were studied in triplicate to determine the effect of the different toast levels. In the aging experiments, chips with medium toasting levels from French and American oak chips were used.

Maceration was stopped after 3, 6, 12, 18, 24 and 30 days from the beginning of the process. Ciders were filtered and filtrates were stored at –4°C prior to analysis.

Determination of alcohols, acids and esters by headspace (HS)–solid phase microextraction (SPME) and gas chromatography (GC)–mass spectrometry (MS)

HS-SPME conditions. The analysis method described by Wang et al.³³ was used for the determination of alcohols, esters and acids. The extraction procedure of the cider was as follows.

A 10 mL sample of each apple cider was transferred to a 15 mL vial containing a small magnetic stirrer. After

Table I. Calibration data for the 9 oak-related compounds and their recovery in cider.

Compounds	Slope	Intercept	r^2	n	Linear range ($\mu\text{g/L}$)	Recovery (%)	
						Synthesis cider	Cider
Furfural	0.0009	0.0023	0.9999	7	50–4000	93	89
5-Methylfurfural	0.0019	-0.0219	0.9978	7	12–1200	99	93
Guaiacol	0.0068	0.0155	0.9983	6	0.75–50	101	85
4-Methylguaiacol	0.0617	0.0012	0.9994	7	0.4–40	95	92
<i>cis</i> -Oak lactone	0.0854	0.0476	0.9999	8	0.6–360	99	90
<i>trans</i> -Oak lactone	0.0741	0.0127	0.9999	6	3–300	93	90
Eugenol	0.0470	0.0251	0.9999	5	3.5–60	102	98
Isoeugenol	0.0322	0.0522	0.9987	5	3–150	94	89
Vanillin	0.0038	0.0641	0.9969	8	10–1600	96	95

addition of 0.1 mL aliquots of internal standard (IS, 2-octanol, 2.00 mg/L in methanol) and 3.0 g NaCl, the vial was tightly capped with a silicon septum. Each sample was extracted by HS-SPME fiber at 45°C for 40 min with stirring. After extraction, the fiber was immediately injected into the injection port to desorb the analytes for 3 min. All tests were conducted in triplicate.

GC-MS analysis. Identifications and quantitations were carried out using a Finnigan TRACE GC-MS. Each sample was analyzed on a DB-Wax column (30 m \times 0.25 mm \times 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA). The oven temperature was held at 45°C for 1 min, and raised to 100°C at a rate of 4°C/min, followed by an increase of temperature to 190°C at a rate of 5°C/min, and held at 190°C for 10 min. The temperature of the injection port was 250°C. The carrier was helium and the flow rate was 1.1 mL/min. Splitless injections were taken. The electron impact energy was 70 eV, and the ion source temperature was set at 230°C. Mass spectra of unknown compounds were compared with those in the Wiley and NIST library in the Xcalibur Database (Finnigan).

Quantitation method. The quantitation method was described by Wang et al.³³ The standard curves for analytes were built up by plotting the response ratio of analytes to 2-octanol (IS) against the concentration ratio. Each cider analyzed (10 mL) was placed into a 15 mL vial with Teflon-faced silicone septa, and was spiked with 2-octanol solution to give a final concentration of 0.02 mg/L. The spiked cider sample was analyzed with the HS-SPME and GC-MS methods described before. Each sample was analysed in triplicate.

Determination of the oak-derived aroma compounds by GC/MS selective ion monitoring (SIM)

Liquid-liquid extraction (LLE). A total of 100 mL of each cider, spiked with 2-octanol (IS) to a final concentration of 0.02 mg/L, in a 250 mL spherical flask with 20 mL of freshly redistilled dichloromethane, was extracted by means of ultrasound over 20 min at 20°C²⁴. The organic phase was saved in a flask. The second and third extractions were performed with 15 mL of dichloromethane, and all the organic phases were collected in the same flask. After separation using a separatory funnel, the organic layer was dried overnight with anhydrous sodium sulfate. The extracts were filtered, and then slowly concentrated to a final volume of 0.5 mL under a gentle stream of nitrogen for GC-MS analysis.

GC-MS analysis. Each extract were analyzed with the GC-MS described above. The GC was fitted with a DB-Wax column (30 m \times 0.25 mm \times 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA). The carrier was helium and the flow rate was 1.1 mL/min. The oven temperature was started at 60°C and then increased to 240°C at 10°C/min. The injector temperature was 250°C. The injection volume was 1 μL , and the splitless mode was used.

Quantitation of the oak-related aroma compounds. For quantification of the oak-related compounds, the ions monitored in the SIM runs were as follows: (1) m/z 109 and 124 for guaiacol; (2) m/z 123 and 138 for 4-methylguaiacol; (3) m/z 99 for *cis*- and *trans*-oak lactones; (4) m/z 96 for furfural; (5) m/z 53 and 110 for 5-methylfurfural; (6) m/z 151 and 152 for vanillin; (7) m/z 164 for eugenol; and (8) m/z 164 for isoeugenol. 2-Octanol was used as the internal standard and the quantitative method is described above. Equations, regression coefficients and recovery are shown in Table I.

Statistical analysis. The data were processed using the SPSS version 11.0 statistical package for windows (SPSS Inc., Chicago, Illinois). Significant differences among wines and for each variable were assessed using analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Effect of the geographical origin of oak chips

Three kinds of oak chips (Chinese oak, American white oak and French oak) with the same size and toast level (medium) were studied. The results showed that the total concentration of esters of ciders aging in oak chips increased by 0.837, 5.012 and 2.512 $\mu\text{g/L}$ respectively, and the concentration of acids increased by 1.089, 0.763 and 2.918 $\mu\text{g/L}$ respectively (Table II), while the concentration of alcohols decreased by 32.096, 18.758 and 32.394 $\mu\text{g/L}$ in the three treatments, respectively, in comparison to the cider without soaked oak chips (control cider). Specifically, almost all the ester levels increased in each treatment, except for ethyl octanoate and ethyl dodecanoate, and all the acid levels increased. In contrast, the alcohol levels fell except for 1-hexanol. This was different from the results reported by Mangas et al.¹⁷ for distillates of cider.

The ciders immersed with oak chips had higher concentrations of oak-related aroma compounds than the control ciders (Table III). 5-Methylfurfural, guaiacol, *trans*-

Table II. Concentration of alcohols, acids and esters in ciders aged with oak chips ($\mu\text{g/L}$).

Volatile compounds	Control ^a	Ciders aged with oak chips			Ciders aged with French oak chips			Ciders aged with American oak chips		
		Chinese	American	French	Light	Medium	Heavy	2 g/L	4 g/L	8 g/L
Ethyl acetate	23.400	23.800	27.800	25.100	23.730	25.100	24.100	22.000	27.800	25.300
Ethyl butanoate	0.130	0.180	0.214	0.192	0.172	0.192	0.268	0.173	0.214	0.138
3-Methylbutyl acetate	0.917	1.360	1.650	1.280	1.750	1.280	2.250	4.760	1.650	4.260
Butyl acetate	0.209	0.057	0.018	0.717	0.301	0.717	0.290	ND	0.018	0.008
Ethyl hexanoate	0.436	0.430	0.458	0.501	0.600	0.501	0.906	0.290	0.458	0.323
Hexyl acetate	0.009	0.012	0.011	0.032	0.009	0.032	0.011	0.021	0.011	0.012
Ethyl heptanoate	0.003	0.006	0.006	0.041	0.004	0.041	0.002	0.004	0.006	0.029
Ethyl octanoate	0.508	0.302	0.378	0.299	0.547	0.299	0.897	0.657	0.378	0.713
Ethyl dodecanoate	0.100	0.068	0.063	0.063	0.111	0.063	0.136	0.071	0.063	0.117
2-Phenylethyl acetate	0.234	0.567	0.361	0.233	0.241	0.233	0.291	0.184	0.361	0.161
Σ Esters	25.946	26.783	30.958	28.458	27.465	28.458	29.151	28.159	30.958	31.061
1-Propanol	94.500	82.100	90.400	82.800	67.400	82.800	128.000	73.800	90.400	71.500
2-Methylpropanol	60.300	50.800	49.700	47.000	59.700	47.000	42.400	61.600	49.700	68.400
1-Butanol	0.339	ND	ND	0.280	0.228	0.280	0.528	ND	ND	0.260
3-Methylbutanol	117.000	106.000	113.000	104.000	109.000	104.000	92.000	94.800	113.000	114.200
1-Hexanol	0.055	0.128	0.116	0.120	0.076	0.120	0.061	0.038	0.116	0.027
2-Phenylethanol	6.900	7.970	7.120	12.500	6.300	12.500	4.890	20.900	7.120	16.000
Σ Alcohols	279.094	246.998	260.336	246.700	242.704	246.700	267.879	251.138	260.336	270.387
Hexanoic acid	0.987	1.760	1.675	1.860	1.940	1.860	1.762	2.210	1.675	1.080
Octanoic acid	2.370	2.610	2.375	4.230	3.050	4.230	1.390	2.310	2.375	2.871
Decanoic acid	0.198	0.274	0.268	0.382	0.206	0.382	0.430	0.089	0.268	0.200
Σ Acids	3.555	4.644	4.318	6.472	5.196	6.472	3.582	4.609	4.318	4.150

^a Control – ciders not soaked in oak chips. ND: not detected.

and *cis*-oak lactones, eugenol and isoeugenol showed significant differences among the three treatments ($\alpha = 0.05$). The oak lactones were affected by the oak geographical origin, and they gave the aromas described as oaky, coconut, or vanilla at a low concentration²⁴. The threshold values are 67 and 790 $\mu\text{g/L}$ for *cis*- and *trans*-isomers, respectively^{6,22}. The main differences were observed in *trans*-oak lactone (see Table III). These values were almost 3.5 times higher in ciders aged with French oak chips than with American oak chips. But the isomer *cis*-oak lactone was higher in cider aged with American oak chips compared to French oak chips. It has been reported that the *cis*-isomer has a more powerful aroma than the *trans*-isomer, and that American white oak is richer in the *cis*-isomer compared to other oak species^{14,16,24}. The *cis*-oak lactone was detected at a higher concentration than the *trans*-oak lactone (Table III), and this has been previously reported by other authors for most oak species^{11,19,23,30}.

Vanillin gives sweet, spicy and candy aromas, and has a relatively low flavour threshold of 200 $\mu\text{g/L}$ as determined in water/ethanol (10%, w/w) by Guth¹². According to Culleré et al.⁶ its threshold was 60 $\mu\text{g/L}$ in a 10% water/ethanol mixture containing 5 g/L tartaric acid at pH 3.2. The cider aged with the American oak chips had the highest concentration of vanillin among the three treatments (Table III). Similar results have been reported by other authors^{18,20}, although some researcher found that vanillin levels were higher in the wines matured in French oak barrels^{24,28}.

Furfural and 5-methylfurfural had a higher concentration in the ciders matured with oak chips than in the control cider (Table III). Furfural gives sweet and almond aromas, and it has a high threshold of 14100 $\mu\text{g/L}$ ⁹. 5-Methylfurfural contributes to green and roasted odors, and

has an odor threshold of 20000 $\mu\text{g/L}$ ^{7,9}. These two compounds are produced during the fermentation of cider²⁴, and their concentrations increased in the cider aged with the oak chips (Table III). The two compounds had a higher concentration in the cider matured with French oak chips than with American and Chinese oak chips. The ciders matured with Chinese oak chips had the lowest levels of these two compounds.

Phenolic compounds had a relatively low concentration in the ciders immersed with oak chips. Among these compounds, guaiacol (2-methoxyphenol) has a smoky, phenolic, aromatic, burnt, and burnt bacon aroma, while 4-methylguaiacol (4-methyl-2-methoxyphenol) has a smoky aroma^{6-8,25}. Eugenol contributes to clove and balsamic aromas, and it has a sensory threshold of 6 $\mu\text{g/L}$ ⁹, while isoeugenol gives a floral aroma, and its threshold is 6 $\mu\text{g/L}$ in a 10% water/ethanol mixture⁶. The results showed that the cider matured with French oak chips had the highest concentration of phenolic compounds among the three treatments, except for eugenol (Table III). Because of the very low flavour thresholds of eugenol and isoeugenol, these two compounds could play a very important role in the aroma compounds of cider. Table III also shows that Chinese oak chips were not superior to American or French oak chips.

Fig. 2 shows the diagram obtained by representing the first two functions. It can be seen that function 1 and 2 are clearly differentiated (between aged ciders in oak chips). While the distances between the control ciders and the cider matured in Chinese oak chips are near.

Effect of the toast levels of the French oak chips

Toasted oak chips impart an intense flavour and aroma to the cider in the form of volatile aroma compounds¹¹. Ciders matured with different toasting levels of the

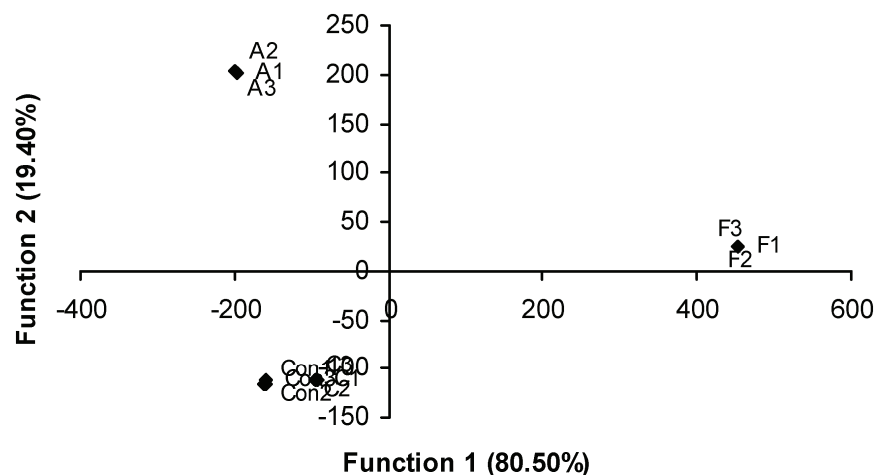


Fig. 2. Discriminant analysis according to oak chips in the ciders. Con: control is ciders not soaked in oak chips. C: Chinese oak chips. A: American oak chips. F: French oak chips. Number 1, 2 and 3: means the number of the bottles.

Table III. Concentration of the oak-related compounds in ciders aged with Chinese, French and American oak chips ($\mu\text{g/L}$)^a.

Compounds	Control ^b	Ciders aged with oak chips		
		Chinese	French	American
Furfural	204.42 \pm 4.28	325.03 \pm 10.36 ^c	578.40 \pm 15.78 ^c	569.52 \pm 11.93 ^c
5-Methylfurfural	40.19 \pm 1.63	24.27 \pm 1.62 ^d	383.83 \pm 17.10 ^d	250.41 \pm 14.05 ^d
4-Methylguaiacol	1.48 \pm 0.20	2.61 \pm 0.22 ^d	17.60 \pm 1.99 ^d	13.76 \pm 1.12 ^d
Guaiacol	0.93 \pm 0.07	2.48 \pm 0.19 ^e	2.68 \pm 0.36 ^e	1.74 \pm 0.22 ^e
<i>cis</i> -Oak lactone	1.61 \pm 0.22	13.98 \pm 1.00 ^d	63.81 \pm 3.93 ^d	90.01 \pm 4.06 ^d
<i>trans</i> -Oak lactone	4.83 \pm 0.71	11.66 \pm 1.32 ^d	143.61 \pm 6.35 ^d	39.27 \pm 2.62 ^d
Eugenol	9.07 \pm 1.21	28.49 \pm 2.21 ^d	11.20 \pm 1.15 ^d	15.50 \pm 1.61 ^d
Isoeugenol	6.08 \pm 0.84	12.29 \pm 1.05 ^d	52.56 \pm 3.54 ^d	46.05 \pm 3.06 ^d
Vanillin	19.59 \pm 1.23	75.32 \pm 4.86 ^c	271.16 \pm 16.68 ^c	291.17 \pm 16.67 ^c

^a Average and standard deviation ($x \pm \text{SD}$) were calculated for three samples in ciders soaked with Chinese, French and American oak chips.

^b Control – ciders not soaked in oak chips.

^c Means between the treatment with Chinese oak chips and the one with French or American oak chips within the same row are significantly different by one-way ANOVA analysis, but between the treatments with French and American chips, the means are not significantly different ($\alpha = 0.05$).

^d Means among three treatments within the same row are significantly different ($\alpha = 0.05$).

^e Means between the treatment with American oak chips and the one with Chinese or French oak chips within the same row are significantly different, but between the treatment with Chinese and French chips, the means are not significantly different ($\alpha = 0.05$).

French oak chips were studied. The total of the alcohols and esters showed little change among ciders aged with different toasting levels (Table II), while the total acids of cider showed an increase in comparison to the control cider. The cider soaked with medium toast level chips had the highest concentration of acids. It was clear that guaiacol and 4-methylguaiacol were significantly different in the three treatments ($\alpha = 0.05$). The oak chips at the medium toasting levels released the highest concentrations of 5-methylfurfural, guaiacol, isoeugenol and *cis*- and *trans*-oak lactones into the ciders (Table IV), while the heavy toasting levels released the highest concentrations of vanillin, furfural and eugenol into the ciders. Chatonnet and Dubourdieu⁴ studied oak chips of three different toasting intensities, and found that the medium toasted oak chips contained the highest concentration of the oak-derived volatile aroma compounds. But, Guchu et al.¹¹ found that

non-toasted oak chips released more oak lactone to wines than did toasted chips. The two isomers of oak lactones were thought to be formed during the toasting of the barrels through dehydration of 2-methyl-3-(3,4-dihydroxy-5-methoxybenzo)-octanoic acid (a minor component with a tannin-like structure) present in oak wood².

Effect of the dosage of the American oak chips

The dosage of oak chips also affects the flavour and aroma of cider in the form of the volatile compounds. The extraction rates of furfural, 5-methylfurfural, guaiacol, 4-methylguaiacol, *cis*- and *trans*-oak lactones, eugenol, isoeugenol and vanillin was studied in ciders matured with different dosages of the same medium toasting level of American oak chips (2 g/L, 4 g/L and 8 g/L). Most of the oak-related volatile aroma compounds extracted had an

Table IV. Concentration of the oak-related compounds in ciders aged with French oak chips of different toast levels ($\mu\text{g/L}$)^a.

Compounds	Control ^b	Ciders aged with oak chips		
		Light	Medium	Heavy
Furfural	204.42 \pm 4.28	457.77 \pm 9.13 ^c	578.40 \pm 15.78 ^c	1079.56 \pm 48.80 ^c
5-Methylfurfural	40.19 \pm 1.63	181.25 \pm 3.65 ^c	383.83 \pm 17.10 ^c	294.39 \pm 12.82 ^c
4-Methylguaiacol	1.48 \pm 0.20	12.48 \pm 1.07 ^d	17.60 \pm 1.99 ^d	11.54 \pm 1.10 ^d
Guaiacol	0.93 \pm 0.07	1.79 \pm 0.18 ^c	2.68 \pm 0.36 ^c	1.13 \pm 0.13 ^c
<i>cis</i> -Oak lactone	1.61 \pm 0.22	38.33 \pm 2.00 ^c	63.81 \pm 3.93 ^c	28.83 \pm 2.22 ^c
<i>trans</i> -Oak lactone	4.83 \pm 0.71	84.60 \pm 5.50 ^c	143.61 \pm 6.35 ^c	129.00 \pm 5.66 ^c
Eugenol	9.07 \pm 1.21	14.53 \pm 1.48 ^c	11.20 \pm 1.15 ^c	22.20 \pm 2.12 ^c
Isoeugenol	6.08 \pm 0.84	41.67 \pm 3.09 ^c	52.56 \pm 3.54 ^c	13.30 \pm 1.29 ^c
Vanillin	19.59 \pm 1.23	147.20 \pm 7.80 ^c	271.16 \pm 16.68 ^c	882.17 \pm 61.79 ^c

^a Average and standard deviation ($x \pm \text{SD}$) were calculated for three samples in ciders soaked with light, medium and heavy toast level oak chips.

^b Control – ciders not soaked in oak chips.

^c Means among three treatments within the same row are significantly different ($\alpha = 0.05$).

^d Means between the treatment with medium toast and the one with light or heavy toast within the same row are significantly different by one-way ANOVA analysis, but the means between the treatment with light and heavy toast are not significantly different ($\alpha = 0.05$).

Table V. Concentration of the oak-related compounds in ciders aged with American oak chips of different dosage^a.

Compounds	Control ^b	Ciders aged with oak chips		
		2 g/L	4 g/L	8 g/L
Furfural	204.42 \pm 4.28	364.11 \pm 9.37	569.52 \pm 11.93	483.34 \pm 15.05
5-Methylfurfural	40.19 \pm 1.63	132.69 \pm 6.76	250.41 \pm 14.05	297.49 \pm 12.97
4-Methylguaiacol	1.48 \pm 0.20	5.61 \pm 0.38	13.76 \pm 1.12	22.92 \pm 1.88
Guaiacol	0.93 \pm 0.07	3.20 \pm 0.45	1.74 \pm 0.22	1.57 \pm 0.23
<i>cis</i> -Oak lactone	1.61 \pm 0.22	40.34 \pm 4.54	90.01 \pm 4.06	185.82 \pm 15.21
<i>trans</i> -Oak lactone	4.83 \pm 0.71	29.41 \pm 3.22	39.27 \pm 2.62	52.15 \pm 5.05
Eugenol	9.07 \pm 1.21	10.13 \pm 0.93	15.50 \pm 1.61	27.88 \pm 1.84
Isoeugenol	6.08 \pm 0.84	25.71 \pm 2.87	46.05 \pm 3.06	89.30 \pm 8.32
Vanillin	19.59 \pm 1.23	85.60 \pm 5.42	291.17 \pm 16.67	373.71 \pm 22.27

^a Average and standard deviation ($x \pm \text{SD}$) were calculated for three samples in ciders soaked with American oak chips at different dosages.

^b Control – ciders not soaked in oak chips.

increase that depended on the dosage of oak chips (Table V). The amount of oak chips recommended would be 4 g per liter of apple cider, because this dosage of chips avoids both excessive and too little impact of wood character in ciders.

Effect of the aging time with the American and French oak chips

The effects of the aging time with the oak chips on the oak-derived volatile aroma compounds in the ciders were studied. It was found that the levels of *cis*- and *trans*-oak lactones in American and French oak increased with the time aged in wood (Fig. 3a). The *cis/trans* ratio in the case of French oak ranges around 0.25, while in the case of American oak it ranges around 2.50 (Fig. 3b). Morales et al.²¹ researched wine vinegar aged with oak chips, and they found that the *cis/trans* ratios were 2 to 5 in American oak chips samples and 9 to 12 in American oak barrels. But Towey and Waterhouse³¹ found that the *cis/trans* ratios in American oak barrels were always greater than 5, while the ratios in European oak-aged wines were always 2 or less. Some authors suggest that this ratio could be used as an index for identifying woods of different species and different geographical origins^{21,23}.

The evolution of phenolic alcohols with aging time can be seen in Fig. 3c and 3d. The phenolic alcohols are mainly from the thermal degradation of lignin at high temperature²¹. The content of isoeugenol increased with aging times, while the level of eugenol descended with aging times. The concentrations of guaiacol and 4-methylguaiacol lingered at the same levels after 6 days (Fig. 3d). These results differ from other authors^{1,2,11,21}.

The concentration of furfural was reduced after 6 days in the French oak sample, while the concentration of 5-methylfurfural was reduced after 12 days (Fig. 3e). Furfural and 5-methylfurfural appeared to have a very fast and progressive extraction rate, and this has also been reported by Arapitsas et al.¹ The compounds related to oak toasting, including *trans*- and *cis*-oak lactones, isoeugenol, 4-methylguaiacol, furfural, 5-methylfurfural and vanillin, appear to be extracted faster during the beginning of oak maturation with the exception of guaiacol. A recent report supports this observation¹⁰.

Vanillin emanates from lignin degradation and can be synthetically produced from eugenol or guaiacol²⁶. It influences wine aroma directly and pleasantly by attributing a vanilla character. The concentration of vanillin in American oak chip ciders was higher than in French oak chip

ciders during the first days, but the extraction rate of French oak chips was higher than that of American oak chip samples (Fig. 3f).

CONCLUSIONS

The effects of different geographical origins, levels of toasting, dosage and the aging times of oak chips on volatile compounds released into ciders were studied. The results showed that there was little difference between the volatile compositions of ciders aged with French oak chips

and of those aged with American oak chips, but that there were obvious differences from those aged with Chinese oak chips. It was also observed that the oak chips at medium toasting levels released the highest concentrations of volatile components into the ciders. Most of the oak-related volatile aromatic compounds extracted had an increase that depended on the dosage of oak chips with the exception of guaiacol and furfural. The accelerated aging of cider using oak chips appears to be an adequate practice, especially using medium toasted French and American oak chips. The optimal amount of oak chips in this

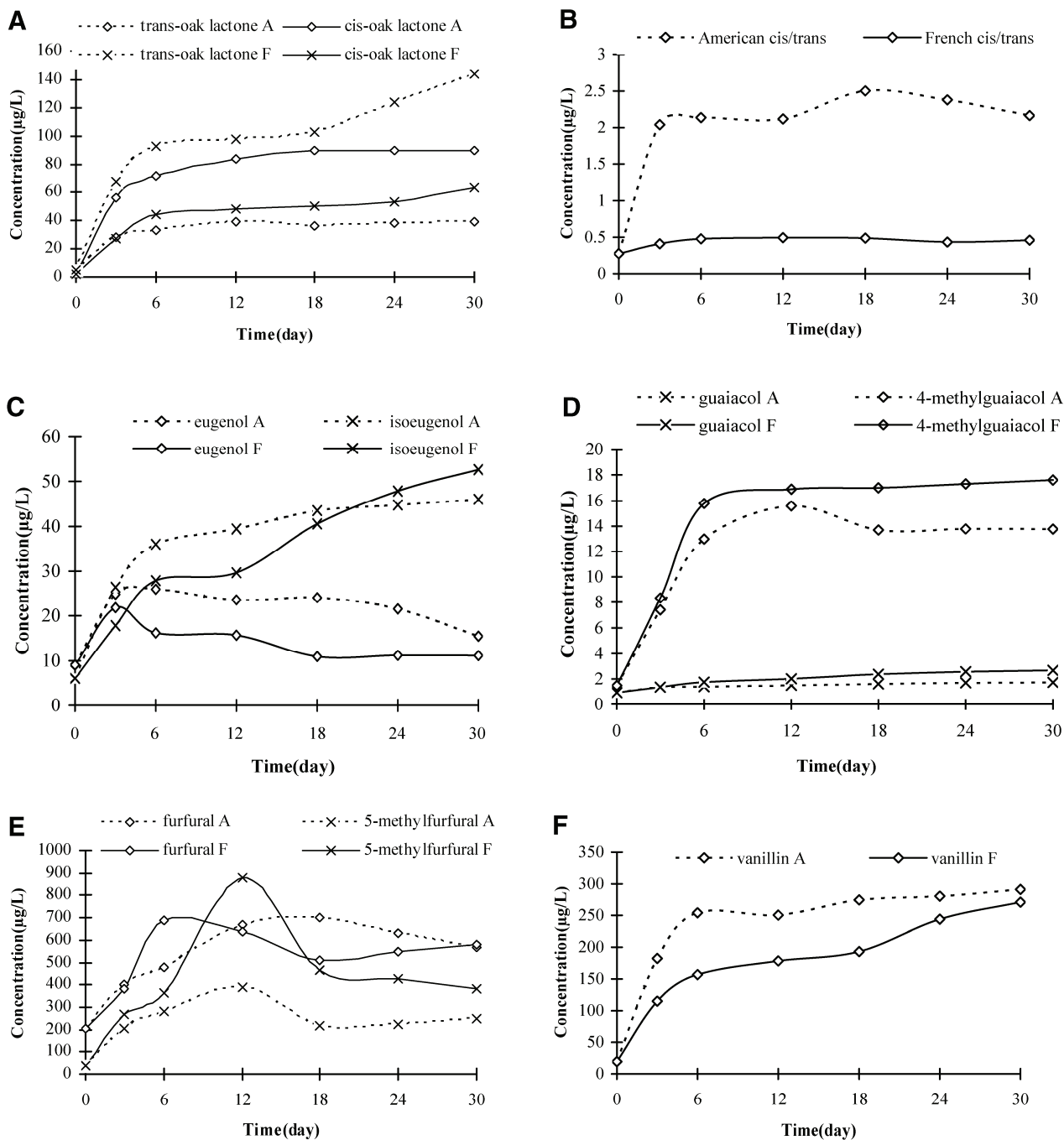


Fig. 3. Concentration of some oak-derived compounds vs. maturing time plots in two different ciders matured with American (A) or French (F) oak chips.

study appears to be 4 g per liter of cider for 30 days. The aroma compounds of cider can be increased by maturation with oak chips, but further research, including sensory evaluation and GC-olfactometry should be carried out.

ACKNOWLEDGEMENTS

Financial support from the Ministry of Science and Technology, P. R. China under No. 2001BA501B07 and from the Program for Changjiang Scholars and Innovative Research Team in the University (PCSIRT) under IRT0532 are gratefully acknowledged.

LITERATURE CITED

1. Arapitsas, P., Antonopoulos, A., Stefanou, E. and Dourtoglou, V. G., Artificial aging of wines using oak chips. *Food Chem.*, 2004, **86**(4), 563–570.
2. Cerdán, T. G., Goñi, D. T. and Azpilicueta, C. A., Accumulation of volatile compounds during ageing of two red wines with different composition. *J. Food Eng.*, 2004, **65**(3), 349–356.
3. Cerdán, T. G., Mozaz, S. R. G. and Azpilicueta, C. A., Volatile composition of aged wine in used barrels of French oak and of American oak. *Food Res. Int.*, 2002, **35**(7), 603–610.
4. Chatonnet, P. and Dubourdieu, D., Comparative study of the characteristics of American white oak (*Quercus alba*) and European oak (*Quercus petraea* and *Q. robur*) for production of barrels used in barrel aging of wines. *Am. J. Enol. Vitic.*, 1998, **49**(1), 79–85.
5. Chatonnet, P., Cutzach, I., Pons, M. and Dubourdieu, D., Monitoring toasting intensity of barrels by chromatographic analysis of volatile compounds from toasted oak wood. *J. Agric. Food Chem.*, 1999, **47**(10), 4310–4318.
6. Culleré, L., Escudero, A., Cacho, J. F. and Ferreira, V., Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. *J. Agric. Food Chem.*, 2004, **52**(6), 1653–1660.
7. Fan, W. and Qian, M. C., Identification of aroma compounds in Chinese ‘Yanghe Daqu’ liquor by normal phase chromatography fractionation followed by gas chromatography/olfactometry. *Flavour and Fragrance J.*, 2005, **21**(2), 333–342.
8. Fan, W. and Qian, M. C., Characterization of aroma compounds of Chinese “Wuliangye” and “Jiannanchun” liquors by aroma extraction dilution analysis. *J. Agric. Food Chem.*, 2006, **54**(7), 2695–2704.
9. Ferreira, V., López, R. and Cacho, J. F., Quantitative determination of the odorants of young red wines from different grape varieties. *J. Sci. Food Agric.*, 2000, **80**(11), 1659–1667.
10. Guchu, E., Díaz-Maroto, M. C., Díaz-Maroto, I. J., Vila-Lameiro, P. and Pérez-Coello, M. S., Influence of the species and geographical location on volatile composition of Spanish oak wood (*Quercus petraea* Liebl. and *Quercus robur* L.). *J. Agric. Food Chem.*, 2006, **54**(8), 3062–3066.
11. Guchu, E., Díaz-Maroto, M. C., Pérez-Coello, M. S., González-Viñas, M. A. and Ibáñez, M. D. C., Volatile composition and sensory characteristics of Chardonnay wines treated with American and Hungarian oak chips. *Food Chem.*, 2006, **99**(2), 350–359.
12. Guth, H., Quantitation and sensory studies of character impact odorants of different white wine varieties. *J. Agric. Food Chem.*, 1997, **45**(8), 3027–3032.
13. Gutiérrez, V. L., Sensory descriptive analysis between white wines fermented with oak chips and in barrels. *J. Food Sci.*, 2002, **67**(6), 2415–2419.
14. Jarauta, I., Cacho, J. and Ferreira, V., Concurrent phenomena contributing to the formation of the aroma of wine during aging in oak wood: An analytical study. *J. Agric. Food Chem.*, 2005, **53**(10), 4166–4177.
15. Lea, A. G. H. Cidermaking. In: Fermented Beverage Production. A. G. H. Lea and J. R. Piggott, Eds., Blackie Academic & Professional: London, 1995, pp. 66–96.
16. Madrera, R. R., Gomis, D. B. and Alonso, J. J. M., Influence of distillation system, oak wood type, and aging time on volatile compounds of cider brandy. *J. Agric. Food Chem.*, 2003, **51**(19), 5709–5714.
17. Mangas, J., Rodríguez, R., Moreno, J. and Blanco, D., Volatiles in distillates of cider aged in American oak wood. *J. Agric. Food Chem.*, 1996, **44**(1), 268–273.
18. Marco, J., Artajona, J., Larrechi, M. S. and Rius, F. X., Relationship between geographical origin and chemical composition of wood for oak barrels. *Am. J. Enol. Vitic.*, 1994, **45**(2), 192–200.
19. Masson, G., Guichard, E., Fournier, N. and Puech, J.-L., Stereoisomers of β -methyl-octalactone. II. Contents in the wood of French (*Quercus robur* and *Quercus petraea*) and American (*Quercus alba*) oaks. *Am. J. Enol. Vitic.*, 1995, **46**(4), 424–428.
20. Miller, D. P., Howell, G. S., Michaelis, C. S. and Dickmann, D. I., The content of phenolic acid and aldehyde flavor components of white oak as affected by site and species. *Am. J. Enol. Vitic.*, 1992, **43**(4), 333–338.
21. Morales, M. L., Benitez, B. and Troncoso, A. M., Accelerated aging of wine vinegars with oak chips: evaluation of wood flavour compounds. *Food Chem.*, 2004, **88**(2), 305–315.
22. Otsuka, K., Zenibayashi, Y., Itoh, M. and Totsuka, A., Presence and significance of two diastereoisomers of β -methyl- γ -octalactone in aged distilled liquors. *Agric. Bio. Chem.*, 1974, **38**, 485–490.
23. Pérez-Coello, M. S., Sanzb, J. and Cabezudo, M. D., Analysis of volatile components of oak wood by solvent extraction and direct thermal desorption–gas chromatography–mass spectrometry. *J. Chromatogr. A.*, 1997, **778**(1–2), 427–434.
24. Pérez-Prieto, L. J., López-Roca, J. M., Martínez-Cutillas, A., Mínguez, F. P. and Gómez-Plaza, E., Maturing wines in oak barrels. Effects of origin, volume, and age of the barrel on the wine volatile composition. *J. Agric. Food Chem.*, 2002, **50**(11), 3272–3276.
25. Pollnitz, A. P., Pardon, K. H., Sykes, M. and Sefton, M. A., The effects of sample preparation and gas chromatograph injection techniques on the accuracy of measuring guaiacol, 4-methylguaiacol and other volatile oak compounds in oak extracts by stable isotope dilution analyses. *J. Agric. Food Chem.*, 2004, **52**(11), 3244–3252.
26. Puech, J.-L., Extraction of phenolic compounds from oak wood in model solution and evolution of aromatic aldehydes in wines aged in oak barrels. *Am. J. Enol. Vitic.*, 1987, **38**(3), 236–238.
27. Ramirez, G. R., Lubbers, S., Charpentier, C., Feuillat, M., Voilley, A. and Chassagne, D., Aroma compound sorption by oak wood in a model wine. *J. Agric. Food Chem.*, 2001, **49**(8), 3893–3897.
28. Spillman, P. J., Pollnitz, A. P., Liacopoulos, D., Pardon, K. H. and Sefton, M. A., Formation and degradation of furfuryl alcohol, 5-methylfurfuryl alcohol, vanillyl alcohol, and their ethyl ethers in barrel-aged wines. *J. Agric. Food Chem.*, 1998, **46**(2), 657–663.
29. Tesfaye, W., Morales, M. L., Benítez, B., García-Parrilla, M. C. and Troncoso, A. M., Evolution of wine vinegar composition during accelerated aging with oak chips. *Anal. Chim. Acta.*, 2004, **513**(1), 239–245.
30. Towey, J. P. and Waterhouse, A. L., Barrel-to-barrel variation of volatile oak extractives in barrel-fermented Chardonnay. *Am. J. Enol. Vitic.*, 1996, **47**(1), 17–20.
31. Towey, J. P. and Waterhouse, A. L., The extraction of volatile compounds from French and American oak barrels in Chardonnay during three successive vintages. *Am. J. Enol. Vitic.*, 1996, **47**(2), 163–172.

32. Wang, D., Xu, Y., Hu, J. and Zhao, G. A., Fermentation kinetics of different sugars by apple wine yeast *Saccharomyces cerevisiae*. *J. Inst. Brew.*, 2004, **110**(4), 340–346.
33. Wang, L., Xu, Y., Zhao, G. and Li, J., Rapid analysis of flavor volatiles in apple wine using headspace solid-phase micro-extraction. *J. Inst. Brew.*, 2004, **110**(1), 57–65.
34. Xu, Y., Zhao, G. and Wang, L., Controlled formation of volatile components in cider making using a combination of *Saccharomyces cerevisiae* and *Hanseniaspora valbyensis* yeast species. *J. Ind. Microbiol.*, 2006, **33**(3), 192–196.
35. Yu, A.-M., Xu, Y., Wang, D., Wang, L.-P., Liu, Y.-m. and Fei, X.-W., Analysis of influence on different raw materials on volatile aroma compounds of ciders. *Sci. Agric. Sinica*, 2006, **39**(4), 786–791.

(Manuscript accepted for publication October 2006)