

# Identification of Volatile Compounds with a “Toasty” Aroma in Heated Oak Used in Barrelmaking

Isabelle Cutzach,<sup>\*,†</sup> Pascal Chatonnet,<sup>‡</sup> Robert Henry,<sup>§</sup> and Denis Dubourdieu<sup>||</sup>

Groupement Interproducteurs Collioure-Banyuls, GICB, F-66650 Banyuls/Mer, France, Seguin-Moreau Cooperage, Merpins, F-16103 Cognac, France, INSA—Lyon, Organic Chemistry Laboratory, F-69621 Villeurbanne Cedex, France, and Faculty of Enology, Bordeaux II University, 351 Cours de la Libération, F-33405 Talence Cedex, France

Toasting wood to be used in barrels for aging wine and brandy produces a great number of volatile and odiferous compounds. Some of these have a “toasty caramel” aroma. Analysis by high-performance gas chromatography of toasted oak extracts, combined with olfactory detection, enabled various chromatographic peaks with these specific aromas to be isolated. These same odors were simultaneously studied by heating glucose both with and without proline. Aromatic compounds of interest were identified thanks to a combination of gas chromatography and both mass and infrared spectrometry. In addition to already-known substances such as 2-hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene) (**1**) and 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol) (**2**), we identified, for the first time, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (DDMP) (**3**), 4-hydroxy-2,5-dimethyl-3(2*H*)-furan-3-one (furaneol) (**4**), and 2,3-dihydro-5-hydroxy-6-methyl-4*H*-pyran-4-one (dihydromaltol) (**5**) as compounds which actively contribute to the “toasty caramel” aroma of heated oak. Their role in the aroma of wines and spirits is thus well worth studying. These molecules were absent from the glucose pyrolysis but were relatively plentiful after heating in the presence of proline. Therefore, Maillard reactions were seen to be the cause of these substances in the heated oak wood.

**Keywords:** Oak; thermal degradation; volatile compounds; “toasty” aroma; Maillard reactions

## INTRODUCTION

Oak (*Quercus* sp.) is currently the only wood used in making barrels for fermenting and aging quality wines and spirits. During heating, there is a change in oak's chemical composition that affects the organoleptic properties of wine (Singleton, 1974; Marche *et al.*, 1975; Ribereau-Gayon *et al.*, 1976; Nishimura *et al.*, 1983; Dubois, 1989; Nomdedeu, 1987; Chatonnet and Boidron, 1990; Chatonnet *et al.*, 1989b, 1990a; Puech and Vissokis, 1986; Rabier and Moutounet, 1991; Sarni *et al.*, 1991; Chatonnet, 1991; Puech, 1987; Puech *et al.*, 1993).

Phenolic and furanic aldehydes are the most abundant of the numerous compounds identified in heated wood (Nishimura *et al.*, 1983). However, with regard to perception thresholds, only vanillin (4-hydroxy-3-methoxybenzaldehyde) actively contributes to aroma (Boidron *et al.*, 1988). A number of other volatile phenols are also formed during heating and are responsible for the “spicy” and “smoky” character of heated oak (Chatonnet *et al.*, 1990). Nevertheless, not a great deal is known about “toasty” and “caramel-like” odors. Both 2-hydroxy-3-methyl-2-cyclopenten-1-one (**1**) (Meyerfeld, 1912) and 3-hydroxy-2-methyl-4*H*-pyran-4-one (**2**) (Nishimura *et al.*, 1983) are present in oak after heating, and

these substances have a “toasty” aroma. However, the role of these molecules in the aroma of wine is somewhat limited with regard to their perception thresholds and extractable quantities (Chatonnet, 1995).

Analysis by gas chromatography, combined with olfactory detection, enabled us to locate new aromatic zones with these same types of odors in oak wood extracts after heating. In this study, we sought to identify the probable origin of the molecules responsible for these odors.

## MATERIALS AND METHODS

**Chemical Products Used.** The following reference compounds were used: L-Proline, 99+% (Aldrich, cat. no. 13,154-7); D-(+)-glucose *anhidra purissimo*, (PRS, cat. no. 141341); silica gel (grade 60, 230–400 mesh, 60 Å, Aldrich, cat. no.: 22,719-6); piperidine, 99% (Sigma, cat. no.: P-5881); 2-hydroxy-3-methyl-2-cyclopenten-1-one 99% (Aldrich, cat. no. 17,-850-0); 3-hydroxy-2-methyl-4*H*-pyran-4-one, 99% (Aldrich, cat. no. H4,340-7); 4-hydroxy-2,5-dimethyl-3(2*H*)-furan-3-one, 95% (Aldrich, cat. no. 32,248-2); 2,3-dihydro-5-hydroxy-6-methyl-4*H*-pyran-4-one (synthesized by Firmenich SA, Geneva).

**Heated Wood Extracts.** The oak used in the study came from the center of France and is the type most often used for aging fine wines (*Quercus petraea*). Oak sawdust was toasted at various intensities (low, medium, and high) for 5, 15, and 20 min (Chatonnet and Boidron, 1989). Samples of heated wood (50 g/L) were directly extracted by dichloromethane (24 h at 20 °C with 700 rpm magnetic agitation). The organic phase thus obtained was dried on anhydrous sodium sulfate and then cold-concentrated with nitrogen gas to 2 mL.

**Fractionation by Adsorption Chromatography on Silica Gel.** The extracts obtained by direct dichloromethane extraction were fractionated on silica gel. The silica (Aldrich silica gel, 70–230 mesh, 60 Å) was activated 12 h beforehand at 120 °C. After being cooled in a dehumidifier, the silica was deactivated by adding 5 g of distilled water per 15 g of silica. Fractionation of the volatile compounds in oak was obtained by an elutrope serie of solvents using 0.5 bar of pressure of

\* Corresponding author (telephone +33 56 84 64 90; fax +33 56 84 64 68; e-mail oenogene@oenologie.u-bordeaux2.fr).

† GICB, F-66650 Banyuls/Mer, in conjunction with the Comité Interprofessionnel des Vins Doux Naturels, CIVDN, F-66300 Tresserres, at the Bordeaux Faculty of Enology.

‡ Seguin-Moreau at Faculty of Enology, Bordeaux II University, F-33405 Talence Cedex, France.

§ INSA—Lyon.

|| Faculty of Enology, Bordeaux II University.

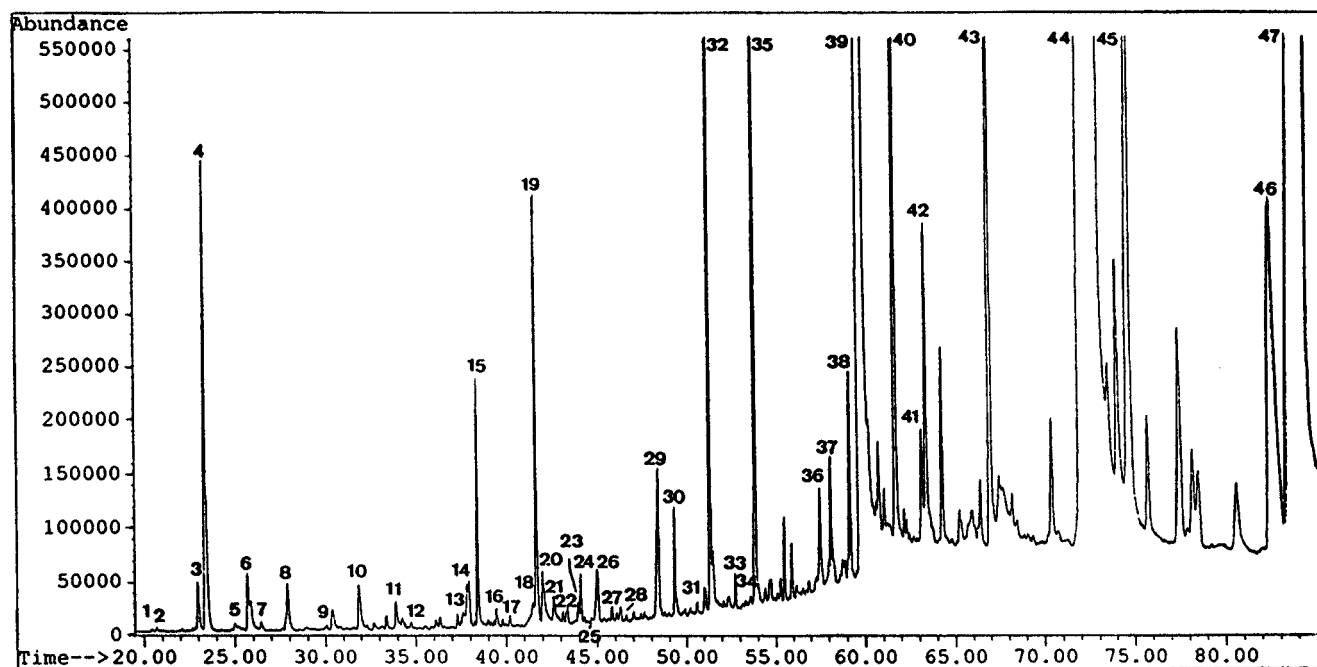


Figure 1. Gas chromatogram of volatile compounds identified from toasted oak wood (BP-20 column).

Table 1. Identification of Aromatic Compounds in Toasted Oak Wood

compounds	OZ <sup>a</sup>	peak no. <sup>b</sup>	sensory description <sup>c</sup>	compounds	OZ <sup>a</sup>	peak no. <sup>b</sup>	sensory description <sup>c</sup>
2,5-dimethylpyrazine		1		<b>1H-pyrrole-2-carboxaldehyde + furaneol</b>	OZ4	25	caramel-like
2,6-dimethylpyrazine		2		octanoic acid		26	
acetic acid		3		<i>m</i> -cresol		27	
furfural		4		<i>p</i> -cresol + 4-propylguaiaicol		28	
acetyl furan		5		eugenol		29	
benzaldehyde		6		isomaltol		30	
propionic acid		7		4-vinylguaiaicol		31	
5-methylfurfural		8		<b>syringol + 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (m/z 144)</b>	OZ5	32	toasty caramel
butyrolactone		9		decanoic acid		33	
hydroxybenzaldehyde		10		isoeugenol		34	
3,4-dimethyl-2(5H)-furan		11		4-methylsyringol		35	
2(3H)-furanone		12		dodecanoic acid		36	
<b>cyclotene</b>	OZ1	13	caramel-like	5-hydroxymethylfurfural		37	
hexanoic acid		14		4-allylsyringol		38	
<b>guaiaicol + dihydromaltol (m/z 128)</b>	OZ2	15	toasty caramel	vanillin		39	
<i>trans</i> -methyloctalactone		16		acetovanillone		40	
2-phenylethanol		17		tetradecanoic acid		41	
benzothiazole		18		propiovanillone		42	
<i>cis</i> -methyloctalactone		19		butyrovannillone		43	
<b>maltol</b>	OZ3	20	caramel-like	syringaldehyde		44	
2,5-diformylfuran		21		acetosyringone		45	
<i>o</i> -cresol		22		propiosyringone		46	
phenol		23		coniferaldehyde		47	
4-ethylguaiaicol		24					

<sup>a</sup> OZ, odorant zone. <sup>b</sup> Numbers correspond to chromatogram in Figure 1. <sup>c</sup> Description of sensory impression perceived at the GC-sniffing.

nitrogen (Tressl *et al.*, 1975). Fraction I was eluted by 60 mL of pentane; fraction II was eluted by 60 mL of a mixture of pentane-dichloromethane (9:1); fraction III was eluted by 60 mL of a mixture of pentane-dichloromethane (2:1); fraction IV was eluted by 60 mL of a mixture of pentane-dichloromethane (1:9); fraction V was eluted by 60 mL of a mixture of pentane-ether (9:1); fraction VI was eluted by 60 mL of a mixture of pentane-ether (1:1); fraction VII was eluted by 60 mL of ether, and fraction VIII was eluted by 60 mL of a mixture of ether-methanol. Each fraction was concentrated with nitrogen gas to 500  $\mu$ L. Those with the most sensory activity were analyzed by gas chromatography in combination with olfactory detection and mass spectrometry.

**Gas Chromatography and Olfactory Detection.** Sensory analysis of the extracts thus obtained was carried out through a combination of gas chromatography and olfactory detection (GC-OD). Samples of 3  $\mu$ L were injected in splitless

mode (division quotient = 70, closing time = 30 s; injector temperature = 230 °C) on a poly(ethylene glycol) capillary column chemically grafted made of fused silica (Carbowax 20M, 50 m  $\times$  0.25 mm; 0.25  $\mu$ ; BP-20, SGE). The vector gas was helium N55 (18 psi). The chromatographic temperature was programmed from 45 to 230 °C, at a rate of 3 °C/min, with a final isotherm of 30 min. An SGE ODO-1TM system connected to a HP5890 chromatograph was used.

**Gas Chromatography and Mass Spectrometry.** Volatile extracts were identified with a combination of gas chromatography and mass spectrometry (GC-MS) under the following operating conditions. We used a Carbowax 20M column (50 m  $\times$  0.25 mm, 0.25  $\mu$ , BP-20, SGE) installed on an HP5890 chromatograph connected to a quadrupole mass spectrometer (MSD HP5970b and 5972) running in the electron impact mode (EI) (ionization energy = 70 eV; source temperature = 250 °C). The extracts were injected under the

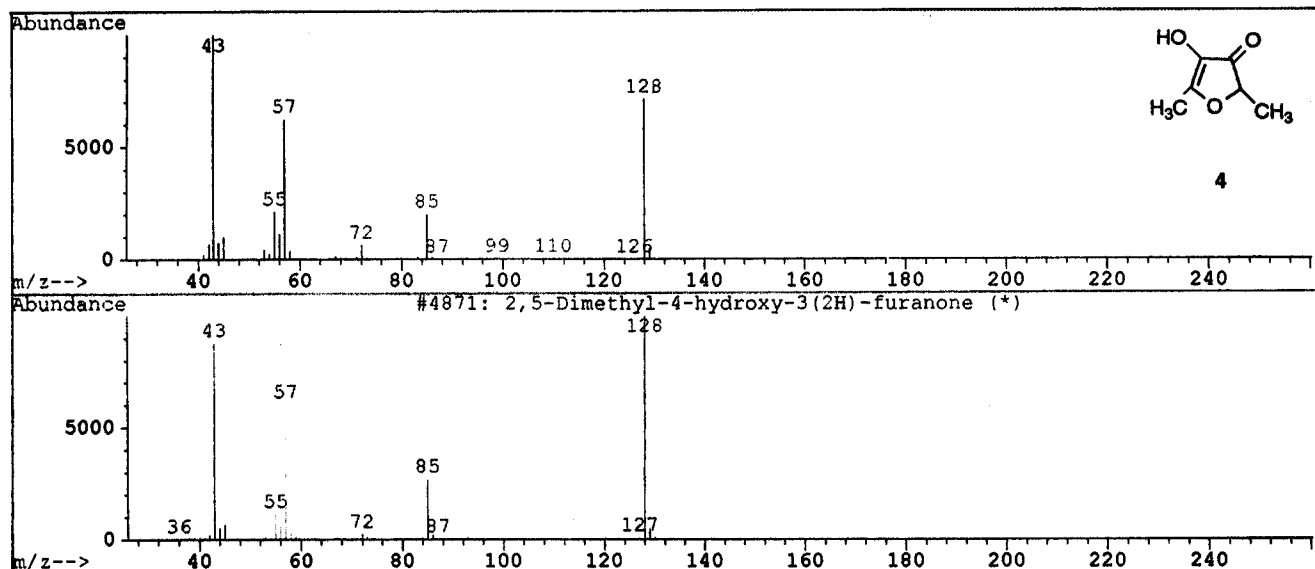


Figure 2. Mass spectra of 4-hydroxy-2,5-dimethylfuran-3(2H)-one (4).

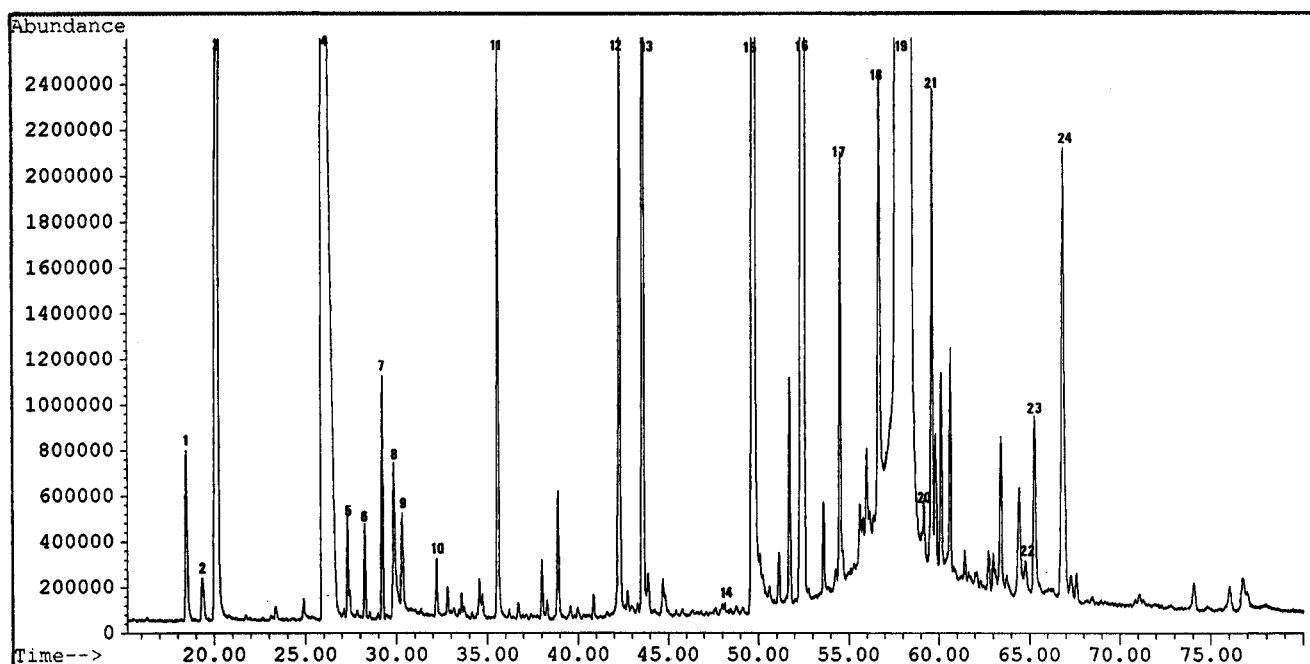


Figure 3. Gas chromatogram of volatile compounds identified from proline-glucose at 180 °C.

previously described chromatographic conditions. Identification was carried out after the mass spectra, and retention indices were compared to those of control compounds, when available, or to data from previously published scientific literature when they were not.

**Gas Chromatography and Infrared Spectrophotometry.** The organic extracts of volatile compounds were analyzed through a combination of gas chromatography and infrared spectrophotometry with a Fourier electron density map (GC-IRFT) HP5965B. The chromatographic conditions were identical to those previously described.

**Experimental Production of "Toasty" Aroma Compounds.** In an SVL stoppered glass test tube, 180 mg of glucose (1 mmol) and 90 mg of proline (0.78 mmol) were heated in a 180 °C oil bath for 10 min. In addition, direct pyrolysis was achieved by directly heating 100 mg of glucose under the same conditions.

**Synthesis of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (DDMP) (3).** Synthesis of 3 was carried out by the method described by Kim and Baltes (1996). A mixture of 0.2 mol of  $\alpha$ -D-glucose and 0.2 mol of piperidine in 150 mL

of ethanol was brought to reflux for one and a half hours. At this point, 0.2 mol of acetic acid in 30 mL of ethanol was very carefully added to the initial mixture and brought up to a temperature of 90 °C for 22 h. The ethanol was then evaporated to one-third of its initial volume. The insoluble piperiductone thus obtained was filtered and washed with isopropyl alcohol. The resulting residue was dissolved in 40 mL of water and extracted by ethyl acetate using magnetic agitation (600 rpm) for 3 h. The extract was then distilled at 120–140 °C under vacuum (0.1 torr). The oily residue was analyzed by GC-MS. The yield of the synthesis did not exceed 3%, and the oily residue in vacuum contained 48% of 3. Chromatography is then used in order to purify the product: 1 g of product was fractionated on a polyamide column ( $l = 60$  cm;  $\phi = 1$  cm; Macherey and Nagel SC6 polyamide, 12 g); elution is made by a mixture of ether-pentane (50:50). The fractions obtained were then analyzed by CCM, eluted by a mixture of ether-methanol (97:3), and revealed with UV or  $\text{FeCl}_3$  (color blue). The result is a solid, which is recrystallized in a mixture of ether-pentane. The mass obtained is 336 mg with a purity of 68% and boiling point of 67–68 °C.

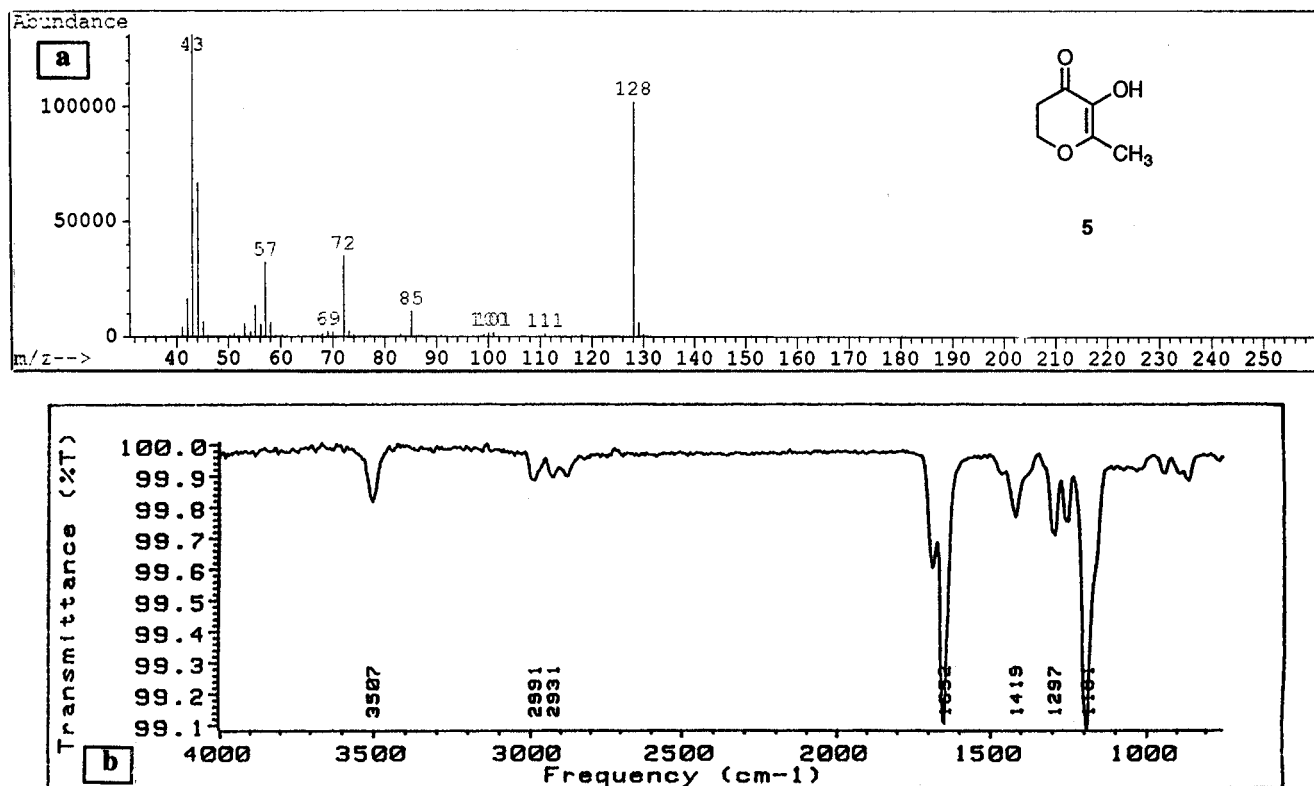


Figure 4. Mass (a) and infrared (b) spectra of 2,3-dihydro-5-hydroxy-6-methyl-4H-pyran-4-one (5).

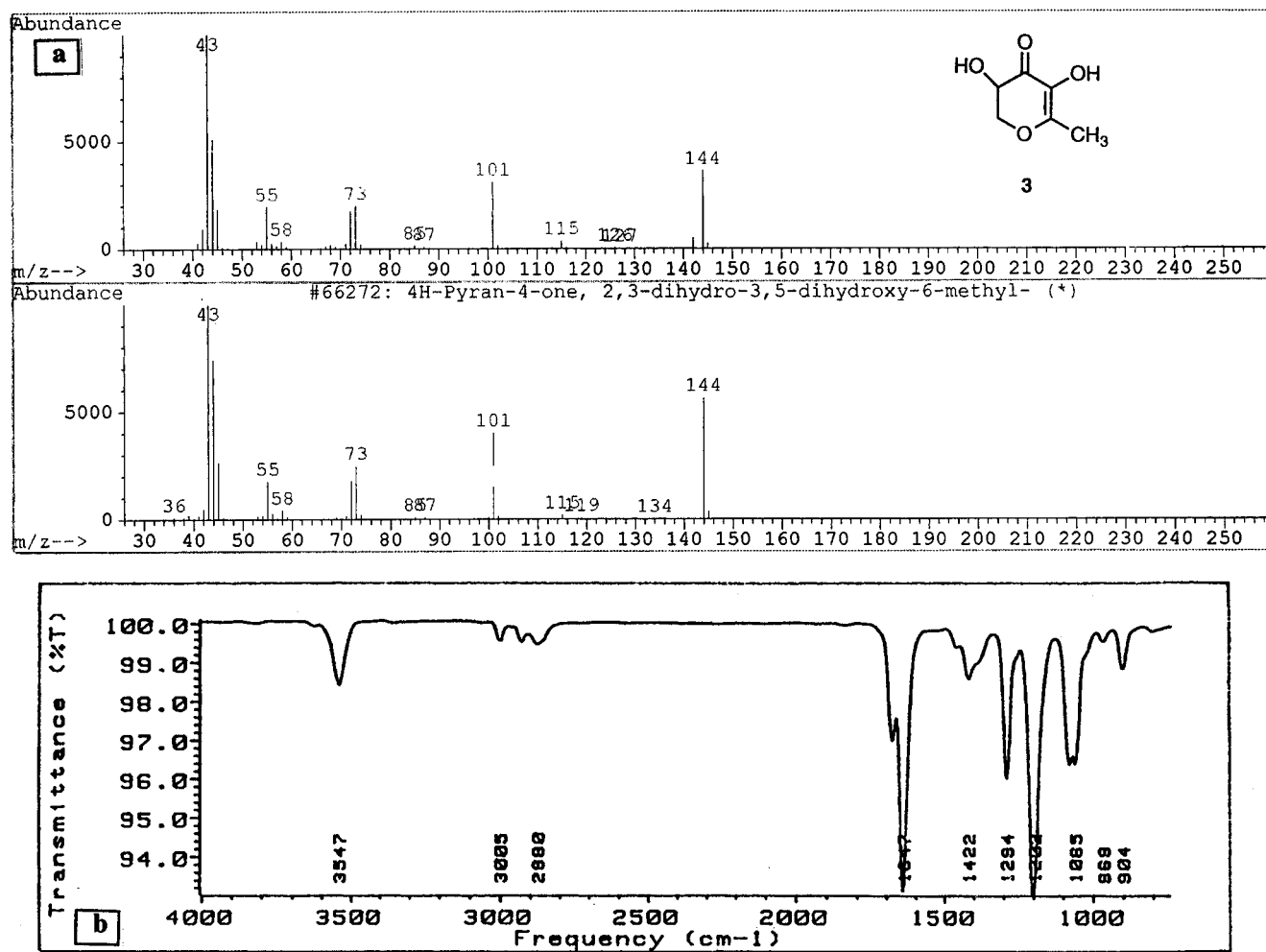


Figure 5. Mass (a) and infrared (b) spectra of 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (3).

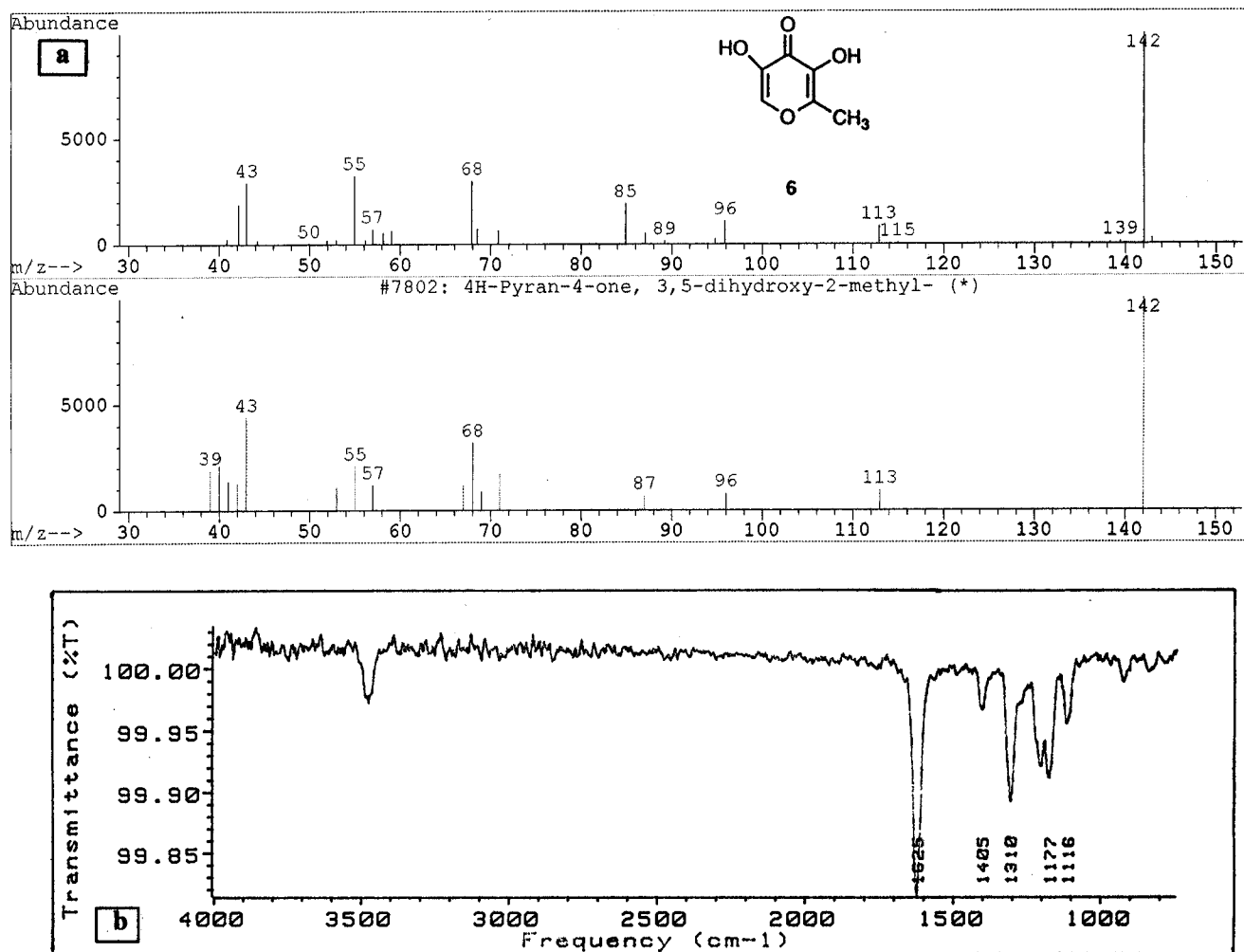


Figure 6. Mass (a) and infrared (b) spectra of 3,5-dihydroxy-2-methyl-4H-pyran-4-one (6).

## RESULTS AND DISCUSSION

**Analysis and Identification of the Compounds Present in Heated Oak Wood Extracts.** Direct dichloromethane extraction and prefractionation on silica gel made it possible to obtain both a concentrated aromatic extract and to separate various odiferous substances in terms of their level of polarity. Fraction III, and also to some extent fraction IV, respectively eluted by a mixture of pentane-dichloromethane (2:1) and pentane-dichloromethane (1:9), contained most of the extractible odor active compounds of the heated wood.

In fraction III, we identified the majority of molecules already cited in previous scientific literature (Figure 1). Five odiferous zones (ZO) with "toasty" characteristics (Table 1) were defined by combined gas chromatography and olfactory detection. 1 and 2 were noted and identified as the compounds responsible for ZO 1 and 3. It is well-known that these compounds result from Maillard reactions (Patton, 1950; Hodge *et al.*, 1963). 2 is one of the major byproducts of heating maltose or lactose in the presence of glycine (Patton, 1950). According to a study by Hodge *et al.* (1967), heating glucose or galactose in the presence of an amino residue did not lead to the formation of maltol. This compound resulted only from the thermal degradation of substituted glucose-4-O structures.

The chromatographic peak corresponding to ZO 4 was identified by means of a mass spectrum and the co-injection of the reference substance, 4-hydroxy-2,5-

dimethylfuran-3(2H)-one (4) (HDMF) (Figure 2). 4 has been identified in several varieties of fruit such as pineapple (Rodin *et al.*, 1965) and raspberry (Ohloff, 1969), as well as in grilled meat (Tonsbeek *et al.*, 1968; Cerny and Grosch, 1992; Guth and Grosch, 1993), ground coffee (Tressl *et al.*, 1978), and roasted sesame seeds (Schieberle, 1993). This molecule abounds in grapes and wines made from American grape varieties and hybrids (Rapp *et al.*, 1980; Acree, 1981). The 4 that is present in heated wood must come from the thermal degradation of hexoses in the presence of amino residues (Hodge, 1963; Mills and Hodge, 1976). As opposed to certain authors (Fagerson, 1969), we did not obtain 4 in detectable quantities by simple glucose pyrolysis.

ZO 2 and 5 respectively correspond to a chromatographic peak identified with 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol). However, these two compounds, when pure, had a "smoky" and "phenolic" odor that was very different from those detected after combined gas chromatography and olfactory detection. A detailed analysis by electron impact mass spectrums, and using various background subtraction techniques, showed that both guaiacol and syringol peaks co-eluted with another compound. At the beginning of the chromatographic peak of guaiacol, we detected a mass fragment equal to 128 *m/z*. This was thought to correspond to the molecular ion of the co-eluted molecule. Similarly, a 144 *m/z* fragment disturbed the syringol spectrum. At this stage of the analysis it was not possible to identify these compounds.

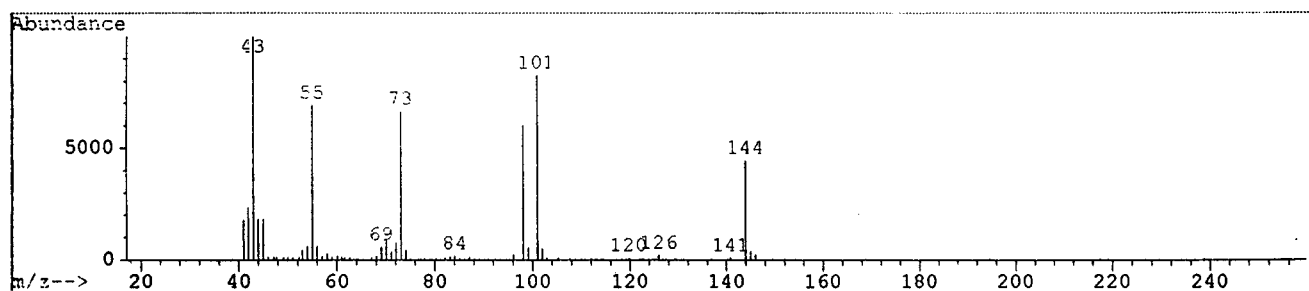


Figure 7. Mass spectra of unknown OZ7 ( $m/z$  144) (7). Identification tentative.

Table 2. Identification of Aromatic Compounds in the Reaction of Glucose and Proline

compounds	Kovats index <sup>a</sup>	OZ <sup>b</sup>	peak no. <sup>c</sup>
4,5-dihydro-2-methyl-3(2 <i>H</i> )-furan-3-one			1
3-hydroxybutan-2-one			2
propan-1-ol-2-one			3
acetic acid			4
furfural			5
2-ethylpyridine			6
ethanone 1-(2-furanyl)			7
unknown, $m/z$ 144	1542	OZ7	8
propionic acid			9
5-methylfurfural			10
furfurylic alcohol			11
<b>cyclotene</b>	1837	OZ1	12
<b>dihydromaltol or DHM</b>	1868	OZ2	13
<b>maltol</b>	1961	OZ3	14
<b>furaneol</b>	2013	OZ4	15
unknown, $m/z$ 149			16
unknown, $m/z$ 163			17
unknown, $m/z$ 137			18
<b>2,3-dihydro-3,5-dihydroxy-6-methyl-4(<i>H</i>)-pyran-4-one or DDMP</b>	2211	OZ5	19
<b>hydroxymaltol</b>	2233	OZ6	20
unknown, $m/z$ 162			21
5-(hydroxymethyl)furfural			22
5-acetylfuranemethanol			23
unknown, $m/z$ 179			24

<sup>a</sup> Kovats index on BP-20. <sup>b</sup> OZ, odorant zone. <sup>c</sup> Numbers correspond to chromatogram in Figure 3.

**Identification of Molecules with a "Toasty" Character Produced by Glucose Pyrolysis and Heating of a Proline–Glucose Mixture.** Glucose pyrolysis at 180 °C produced only furanic aldehydes. Heating the proline–glucose mixture (Figure 3) caused Maillard reactions, culminating in the formation of large quantities of furanic aldehydes (5-(hydroxymethyl)furfural, 5-methylfurfural, and furfural). In addition to these main substances, we also identified cyclotene, traces of maltol, and furaneol, as well as unknown compounds possessing the 128 and 144  $m/z$  molecular ion which had previously co-eluted with guaiacol and syringol. These compounds corresponded exactly with the five aromatic zones previously detected in the heated wood extract. In addition to these five zones, we detected two other zones (ZO 6 and 7) with a "toasty caramel" aroma (Table 2).

The chromatographic peak corresponding to ZO 2 possessed a 128  $m/z$  molecular ion and a fragmentation (Figure 4) which could correspond to either a furanone or pyranone structure. By means of gas chromatography coupled with infrared spectroscopy, we concluded that it was a pyranone structure, as the carbonyl frequency at 1652  $\text{cm}^{-1}$  was too low for a furanone structure. This substance was identified as 2,3-dihydro-5-hydroxy-6-methyl-4*H*-pyran-4-one (5) (DHM). Identifi-

cation was confirmed by co-injection of the reference molecule obtained by organic synthesis. This compound had already been identified as a byproduct of reaction cause by mixing glucose and proline during heating (see modification of T. H. Parliment in Nishibori and Bernhard, 1993).

The peak corresponding to ZO 5 possessed a 144  $m/z$  molecular ion and the fragmentation characteristic of a pyranon. By means of mass and infrared spectrometries, this compound was identified as 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (3) (Figure 5). Identification was confirmed by injection of a product synthesized according to the Kim and Baltes method (1996). This compound was identified for the first time by Mills *et al.* (1970). It is found in many heated foodstuffs (Ledl *et al.*, 1976) and results from the decomposition of Amadori compounds formed in Maillard reactions (Mills and Hodge, 1976; Nishibori *et al.*, 1993, 1994). Thermal degradation of DDMP (3) may lead to the formation of a large number of compounds, particularly 2, 4, 5, and 6 (Kim and Baltes, 1996).

As opposed to Hodge's results (1967), heating the glucose–proline mixture led to the formation of a very small amount of 2. Its odor was easily detected by combined gas chromatography and olfactory detection. It was highly likely that the traces of maltol (2) detected resulted from the thermal degradation of 3 during injection (Kim and Baltes, 1996) rather than from an artifact of the ionization of heterocycle of this same substance during electron impact (Yaylayan and Mandeville, 1991).

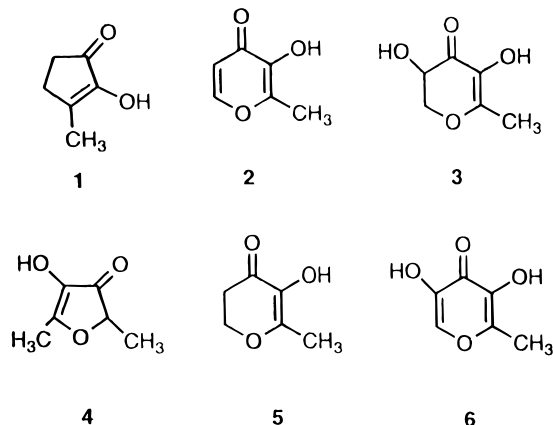
Using an electron impact mass spectrum and the infrared spectrum, we easily identified the peak corresponding to ZO 6 identified as 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one (6) (Figure 6).

The odiferous zone ZO 7 corresponded to the chromatographic peak with a molecular mass thought to be equal to 144 (Figure 7). In light of fragmentation upon electron impact and the odor of this molecule reminiscent of caramel, we conclude that the  $-\text{CH}_3-\text{C}=\text{C}(\text{OH})-\text{C}=\text{O}$  sequence was present in all of the compounds with this type of aroma (Hodge, 1967).

## CONCLUSIONS

Toasting the oak that is used in barrel making produces a great number of volatile and odiferous compounds. We noted the presence of cyclotene (1) and maltol (2) in heated wood. However, these molecules were responsible only to a small extent for the "toasty" aroma of wines aged in barrel.

DDMP (3), HDMF (4), and DHM (5) were identified for the first time in heated oak. These molecules were not formed by direct glucose pyrolysis. They were, on the other hand, produced in relatively large quantities when the glucose–proline mixture was heated. Thus,



**Figure 8.** Structures of volatile compounds identified with "toasty caramel" aroma.

Maillard reactions seemed to create these compounds. Perfecting a sufficiently sensitive method of measurement and determining perception thresholds in wine will make it possible to draw conclusions about the organoleptic role of these substances and the influence of toasting intensity.

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