

Distribution and Organoleptic Impact of Sotolon Enantiomers in Dry White Wines

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The enantiomers of sotolon, a flavor compound typical of oxidized white wines, were separated by preparative HPLC to determine their perception thresholds and distribution in wines. The enantiomeric ratios of chiral sotolon were evaluated in several dry white wines using gas chromatography and a chiral column (β -cyclodextrin) connected to a 2 m precolumn (BP20). The perception threshold of (*S*)-sotolon (0.8 $\mu\text{g/L}$) in model wine solution was 100 times lower than that of the (*R*) form (89 $\mu\text{g/L}$), indicating that (*S*)-sotolon contributes to the characteristic aroma of prematurely aged dry white wines. Both enantiomers are detected in white wines. Analysis of commercial dry white wines from various vintages and origins revealed three types of distribution patterns: the racemic form, an excess of *R*, and an excess of *S*. The proportions found in these wines may be partially explained by the slow racemization kinetics (20 months) of optically active sotolon.

KEYWORDS: Sotolon; enantiomers; wine; racemization; chiral GC

INTRODUCTION

Sotolon [3-hydroxy-4,5-dimethyl-2(5*H*)-furanone] is a chiral lactone with an intense curry odor. This volatile compound is known to impact flavor in many foodstuffs and wines. It contributes significantly to the burnt note of cane sugar (1) and aged sake (2), as well as the curry odor of fenugreek seeds (3). Sotolon contributes to the aromas of “vins jaunes” from the Jura and sherries (4, 5), as well the “dried fig” and “rancio” nuances in French fortified wines [Vins doux Naturels (VDN)] and port (6, 7). Concentrations of sotolon found in these types of wines are generally $>10 \mu\text{g/L}$. Sotolon has also been detected in white wines made from botrytized grapes (8, 9). The contribution of this powerful flavor compound to the aroma of prematurely aged dry white wines has now also been clearly established (10–12). Concentrations in prematurely aged dry white wines are generally $<10 \mu\text{g/L}$ (10, 13). The perception threshold is 2 $\mu\text{g/L}$ in model solution and 8 $\mu\text{g/L}$ in dry white wine. All of these analyses were obtained using a synthetic racemate molecule.

The perception threshold and descriptors of an odoriferous compound may differ according to the stereoisomer considered (14, 15). It was, therefore, important to separate the two

enantiomers of sotolon and determine the perception thresholds and distribution of the *R* and *S* forms in wine to obtain an accurate assessment of their organoleptic impact. These data may also contribute to our understanding of the origins of the chemical formation of this compound during the oxidative aging of white wines.

The stereoisomer distribution of sotolon in sherry and *vin jaune* has already been analyzed by two-dimensional gas-phase chromatography coupled with an FID detector (16). However, to our knowledge, their distribution in dry white wines aged under reducing conditions has not previously been reported.

MATERIALS AND METHODS

Reagents. 4,5-Dimethyl-3-hydroxy-2(5*H*)-furanone ($>99\%$), dichloromethane (Chromasolv grade), ethyl acetate (HPLC grade), isopropanol (HPLC grade), and heptane (HPLC grade) were obtained from Sigma-Aldrich (St Quentin Fallavier, France). Anhydrous sodium sulfate (99%) was supplied by Prolabo (France). L-(+)-Tartaric acid (99.5%) was supplied by Fluka (France) and sodium hydroxide (99%) by Riedel de Haen. Ethanol (Lichrosolv grade) was supplied by Merck (France).

Wine Samples. White wines from several vintages and origins were all analyzed in 2005. The composition of the model wine solution was as follows: L-(+)-tartaric acid (5 g/L), ethanol (12% vol.), adjusted with NaOH (M) to pH 3.5.

Sotolon Extraction from Wine. The extraction procedure was based on the method described by Cutzach (7). Wine samples (100 mL) were spiked with 100 μL of 3-octanol (100 mg/L solution in ethanol), as an internal standard, and 15 g of anhydrous sodium sulfate (to increase ionic strength and extractability). Wines were extracted three times with 10, 5, and 5 mL of CH_2Cl_2 (magnetic stirring for 10, 5, and 5 min at

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750 rpm). The resulting organic phases were mixed and dried over anhydrous sodium sulfate. The organic extract was then concentrated to 0.5 mL under a nitrogen stream (100 mL/min). Two microliters of the extract was injected into a gas chromatograph (GC) with a mass spectrometer (MS) detector.

Racemization Studies in Wine Model Solution. Samples (500 μ L) were extracted twice with 200 μ L of ethyl acetate (vortex 2, 2 min). Organic phases were mixed and dried over anhydrous sodium sulfate. Two microliters of the extract was injected into a GC with an MS detector.

Gas Chromatography–Mass Spectrometry (GC-MS) Conditions.

A Star 3400CX gas chromatograph (Varian) fitted to a Saturn 2000 electronic ion trap mass spectrometer from Varian was used to analyze the wine extracts. The precolumn was a fused silica column coated with polar phase (BP20; 2 m \times 0.25 mm i.d. internal diameter; 0.25 μ m film thickness) (SGE, France) followed by a 30 m \times 0.25 mm i.d. fused silica column coated with a 0.25 μ m film of a solution of 20% β -cyclodextrin in (35% phenyl)-methylpolysiloxane (HPchiral) from J&W (France). The carrier gas was He (Linde gas, Bordeaux), 5.3 grade, with a flow rate of 1 mL/min. A Varian 1078 temperature-programmable injector was used to inject the 2 μ L sample. The injector was initially set at 180 $^{\circ}$ C for 0.3 min, and then the temperature was raised to 230 at 180 $^{\circ}$ C/min for 30 min. Oven temperature was initially set at 50 $^{\circ}$ C for 0.1 min, raised to 110 at 1 $^{\circ}$ C/min, held at that temperature for 20 min, then raised to 210 at 3 $^{\circ}$ C/min, and held at that temperature for a further 20 min.

The transfer line and manifold were maintained at 210 and 80 $^{\circ}$ C, respectively. Trap temperature was maintained at 170 $^{\circ}$ C. Axial modulation was 3.5 V. Injection (2 μ L) was in splitless mode (closure time = 0.75 min). For the sotolon detection segment, 55–80 min after the beginning of the GC run (Tr = 55–80 min), current intensity was 20 μ amp and the offset multiplier for the voltage value was at 100 V. The mass spectra were acquired in electron impact mode (ionization energy = 70 eV), limiting the mass range between 81 and 130 (SIS mode). Ion 83 was used to quantify sotolon, and ion 128 confirmed its presence.

Racemization studies were carried out with a GC HP-5890 (Agilent, France) coupled to MS HP-5972, fitted with the capillary column previously described. The operating parameters were as follows: isothermal injection temperature, 180 $^{\circ}$ C; transfer line temperature, 230 $^{\circ}$ C. The GC temperature program was the same as for Varian GC.

Impact of Injection Temperature on Sotolon Racemization. A model solution (12% vol EtOH; 5 g/L tartaric acid, pH 3.5) supplemented with (*R*)-sotolon (10 μ g/L) was extracted, as previously described. The resulting organic extract was analyzed by GC-MS (Varian), varying the injector temperature from 150 to 230 $^{\circ}$ C. Injection was repeated three times at each temperature. The programmable injector temperature settings and chromatographic conditions were as described above.

Separation of (*R*)-Sotolon and (*S*)-Sotolon from a Commercial Racemic Mixture. *HPLC Separation.* HPLC was performed on a Merck L-7100 pump connected to a Merck variable-wavelength UV detector. The preparative column was a Chiralpak AS-H model (250 \times 20, 5 μ m). The eluent consisted of 10% isopropanol in *n*-heptane with a flow rate of 20 mL/min at a constant temperature of 25 $^{\circ}$ C. When the two compounds were collected after HPLC purification, 50 mg of each sotolon enantiomer was obtained.

Purity Control. The purity of each enantiomer was assessed by HPLC fitted with a Chiralpak AS-H 5 μ m (250 \times 4.6 mm). Detection wavelength was 250 nm. Enantiomeric excesses were 99.5 and 98.5% for the first and second eluting peaks, respectively.

Chiral Identity. The absolute configuration of sotolon was elucidated by measuring the specific rotation values of this optically active furanone. For the first eluting peak: $[\alpha]_D^{20} = -10.2^{\circ}$ (*c* 0.45; CHCl₃) and for the second eluting peak: $[\alpha]_D^{20} = +14.4^{\circ}$ (*c* 0.5; CHCl₃). These values are close to those obtained by Guichard (16) for the optical rotation of (*R*) and (*S*)-sotolon: $[\alpha]_D^{20} = -19.3$ (*c* 1.15; CHCl₃) and $[\alpha]_D^{20} = +16.5^{\circ}$ (*c* 1.2; CHCl₃), respectively.

Optical Rotation. Optical rotation was determined on a Perkin-Elmer 341 polarimeter using a 1 dm cell.

Table 1. Impact of Injector Temperature on the Racemization of Sotolon in GC-MS

injector temp ($^{\circ}$ C)	(<i>R</i>)-enantiomeric excess (%) (<i>R</i> – <i>S</i>)/(<i>R</i> + <i>S</i>)
150	99
180	98
190	97
200	92
210	79
230	65

Odor Thresholds. The sotolon enantiomer perception thresholds were determined using the method described by Boidron (9). The sensory panel consisted of 60 persons from 20 to 40 years old, who received weekly training sessions. Tests were performed at a controlled room temperature of 20 $^{\circ}$ C, in individual booths, using covered AFNOR glasses containing about 40 mL of liquid. Olfactory thresholds were measured using ranking tests, with five series of triangular tests, presented with increasing sotolon content. The perception threshold corresponded to the minimum concentration recognized by 50% of the tasters. The neutral white wine used to determine olfactory thresholds was previously extracted and analyzed and then supplemented with sotolon.

Racemization of (*R*)-Sotolon. A 40 mL sample of a model wine solution was supplemented with (*R*)-sotolon (100 mg/L) [enantiomeric excess (ee) = 99.5%] and divided among four 10 mL flasks. To study the influence of the model wine solution's pH on the racemization of (*R*)-sotolon, NaOH was added to obtain pH values of 3.0 and 3.5 (WTW 720 pH-meter; VWR, France). Samples (in duplicate) were kept in the dark, at room temperature (20 $^{\circ}$ C). Every 15 days in the first month, then once per month, an aliquot of each sample (500 μ L) was extracted with ethyl acetate and injected into the GC-MS. The sotolon extraction procedure and chromatographic conditions were as described above.

RESULTS AND DISCUSSION

Impact of Temperature Injection by GC on Racemization of the Sotolon Enantiomer in White Wine Extract.

Many optically active compounds are racemized simply by heating them (17). For example, Marriot (18) demonstrated partial racemization of linalool during the distillation (*T* = 100 $^{\circ}$ C) of a lavender extract. The thermodegradation of sotolon is one of the known properties applied in this GC-MS on-column assay mode (13, 19). In a previous work, sotolon degradation was shown to occur in the gas chromatograph injector at temperatures above 180 $^{\circ}$ C (20), suggesting that it could be linked with the racemization phenomenon. However, to our knowledge, examples of partial or total racemization of volatile compounds in the chromatograph injector have not been widely reported.

We determined the optimum injector temperature, under our assay conditions. A model dry white wine solution supplemented with 10 μ g/L sotolon was extracted, as previously described. The organic extract obtained was analyzed repeatedly by GC-MS, varying the injector temperature from 150 to 230 $^{\circ}$ C. The results obtained are shown in **Table 1**. Partial racemization was observed at high temperature (230 $^{\circ}$ C), with a decrease in the enantiomeric excess (ee) value from 99 to 65%. Therefore, lower temperatures (180 $^{\circ}$ C) would be more appropriate for studying the distribution of sotolon enantiomers in wine.

Distribution of the Sotolon Enantiomers in Dry White Wine. The optical isomers of sotolon in the dry white wines were separated by chiral GC analysis on a β -cyclodextrin phase with a polar precolumn. Each enantiomer had previously been injected separately to identify its retention time (**Figure 1**). The commercial dry white wines were tasted by a panel of well-trained jury prior to analysis. All of the wines were systematically found to be strongly oxidized with odors reminiscent of honey.

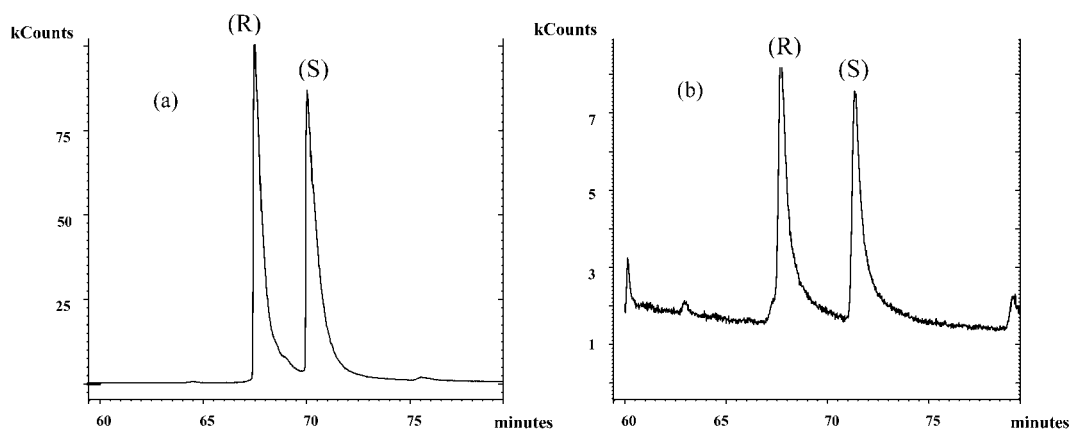


Figure 1. GC-MS (m/z 83) analysis of (a) a commercial racemic sotolon and (b) a dry white wine organic extract on a β -cyclodextrin column with a 2 m polar precolumn. The optical isomers were assigned as described under Materials and Methods.

Table 2. Examples of Enantiomer Distributions and Determination of the Enantiomeric Excess of Sotolon in Several Dry White Wines

	<i>R</i> (%)	<i>S</i> (%)	$(R - S)/(R + S)$ enantiomeric excess (%)
commercial sotolon	52	48	4
1980 Graves	52	48	4
1981 Graves	51	49	2
1981 Pessac Leognan	53	47	6
2003 Entre-Deux-Mers	52	48	4
1975 Pessac Leognan	49	51	2
1992 Pessac Leognan	47	53	6
2000 Entre-Deux-Mers	54	46	8
2000 Entre-Deux-Mers	45	55	10 (<i>S</i>)
1973 Pessac Leognan	23	77	54 (<i>S</i>)
1997 Pessac Leognan	38	62	24 (<i>S</i>)
1999 Bordeaux	22	78	56 (<i>S</i>)
1999 Bordeaux	22	78	56 (<i>S</i>)
1987 Pessac Leognan	71	29	42 (<i>R</i>)
1975 Pessac Leognan	60	40	20 (<i>R</i>)
2001 Entre-Deux-Mers	75	25	50 (<i>R</i>)

Chiral GC analysis of these white wines from several vintages and origins revealed three types of distribution patterns: the racemic form, an excess of (*R*), and an excess of (*S*). The vintage had no apparent impact on the ratio of the (*R*) and (*S*) forms of sotolon ($R^2 = 0.06$). The maximum enantiomeric excess was 50% for the (*R*) form and 56% for the (*S*) form.

Commercial sotolon, used as a benchmark, is a racemic mixture, so it does not correspond to the average distribution of the *R* and *S* forms in wine. The olfactory perception threshold determined using commercial racemic sotolon ($2 \mu\text{g/L}$ in dilute alcohol solution) was inadequate for assessing the real olfactory impact of this compound in wine. Moreover, the presence of enantio-enriched sotolon in wine was not systematic. This agrees with Guichard's findings (16) in a study of the enantiomeric distribution of sotolon in *vin jaune*. The racemization of sotolon in wine may provide a partial explanation of this enantiomeric distribution. (Table 2).

Perception Thresholds and Descriptors of the Sotolon Enantiomers. The sotolon optical isomers were separated by chiral phase HPLC analysis on a semipreparative Chiralpak AS-H column. HPLC analysis (using the same analytical column) of the collected fractions revealed enantiomeric excesses of up to 98%. The separate sotolon enantiomers were dissolved in ethanol and stored at low temperature (5°C) and then used to determine the perception threshold of sotolon

Table 3. Perception Thresholds and Olfactory Descriptors of the Sotolon Enantiomers

	perception threshold ($\mu\text{g/L}$)	descriptors ^a
(<i>R</i>)-sotolon	89^a – 121^b	walnut, rancid
(<i>S</i>)-sotolon	0.8^a – 5^b	curry, walnut
racemic	2^a – 8^b	curry, walnut

^a Wine model solution. ^b White wine.

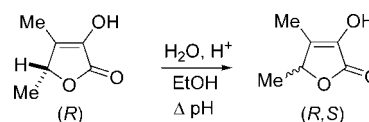


Figure 2. Sotolon racemization diagram.

enantiomers. Descriptors are given for an odor activity value (OAV) of 2. Although the aromatic nuances of both enantiomers were quite similar, the perception threshold of (*S*)-sotolon in dilute alcohol solution (12% vol) was >100 times lower than that of (*R*)-sotolon (Table 3). These results clearly demonstrated that the thresholds strongly depend on the stereochemistry of the odorant.

The perception threshold of (*S*)-sotolon was 10 times lower than the level determined by Guichard ($7 \mu\text{g/L}$) (14), whereas that of (*R*)-sotolon was quite similar ($89 \mu\text{g/L}$). Thresholds determined in white wine differed to a lesser extent. Indeed, the perception threshold of (*S*)-sotolon in wine was 20 times lower than that of (*R*)-sotolon (Table 3).

This demonstrated that the *S* form alone gives sotolon its odor and organoleptic properties. Only (*S*)-sotolon contributes to the characteristic aroma of prematurely aged dry white wines at the concentrations found, that is, generally $<10 \mu\text{g/L}$. Therefore, the aromatic impact of sotolon in dry white wines depends on the distribution of the (*R*) and (*S*) forms.

Racemization of (*R*)-Sotolon in Wine Model Solution. On the basis of our previous findings concerning the distribution of sotolon enantiomers in wine, we hypothesized that racemization (Figure 3) occurred during bottle aging.

The enantiomeric composition of an (*R*)-sotolon solution was analyzed over 4 months (Figure 2). We observed very slow racemization kinetics. This optically pure sotolon enantiomer was not stable in a model wine solution, resulting in 25% racemization within 4 months. In the pH range of white wine, between pH 3.0 and 3.5, racemization was apparently only slightly affected by variations in pH. Raab (21) found similar results concerning the racemization of enantiomers of Furanol [4-hydroxy-2,5-dimethyl-3(2*H*)-furanone], which is closely

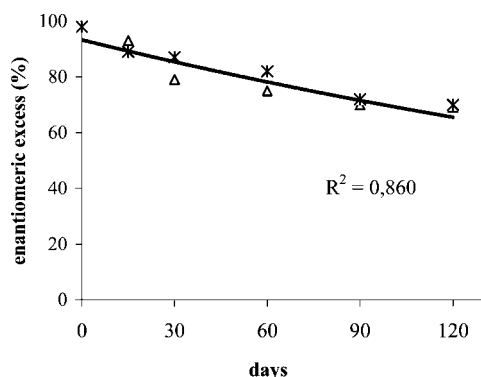


Figure 3. Racemization kinetics of sotolon at pH 3.0 (Δ) and 3.5 (*). A regression coefficient (first order) was calculated for the racemization experiment at pH 3.0.

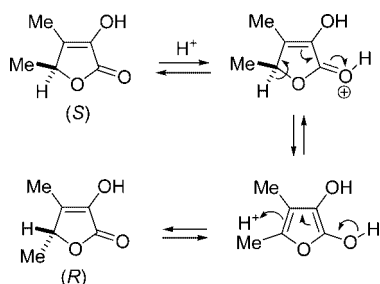


Figure 4. Sotolon racemization via enolization.

related to sotolon. These results are also consistent with data published for the pH dependency of 3-hydroxyfuranone formation, showing maximum stability for the keto form at pH 3.5–5.5 (22). Our initial results indicated, with a nonlinear first-order kinetic, that racemization of (*R*)-sotolon in a model wine solution at pH 3.0 occurred over 20 months. Further details concerning the determination of the racemization rate are published elsewhere (17). This result disagrees with the racemization kinetics calculated by Fronza (23). However, the experiments that led the author to conclude that this furanone was unstable were carried out under extreme conditions (12 N HCl, 100 °C), very different from those prevalent during wine aging.

We suggest that, in a mildly acidic medium (pH 3–3.5), racemization occurs via a keto–enol tautomerism, catalyzed by the presence of an acid (21). This may involve the formation and subsequent protonation of an aromatic furan-type intermediate, resulting in either enantiomeric form of sotolon, as illustrated in **Figure 4**. An alternative pathway, via the acid-mediated opening of a furanone ring, followed by a 1,4-addition of a molecule of water onto the corresponding α,β -unsaturated system and cyclization, as recently proposed (13), cannot be completely ruled out. However this mechanism appears less likely in our case, as that reaction took place in 5 M sulfuric acid at pH 1, much harsher conditions than those we chose to mimic natural wine aging.

Knowledge of the distribution of sotolon enantiomers in wine, associated with new data concerning the racemization kinetics of this lactone in wine model solution, are likely to shed light on the origins of sotolon formation in wine. The racemization of sotolon is a rapid process, compared to bottle aging. This provides a partial explanation for the presence of the racemic form in the wine analyzed. Production of racemic sotolon may also be related to a nonstereoselective mechanism, as suggested in the literature, such as the Maillard reaction (6, 24), chemical degradation of threonine in model wine solution (7), or the oxidative degradation of ascorbic acid (25). The formation of

the (*R*) and (*S*) enantiomers in various proportions, as revealed above in a wide range of white wines, is more difficult to rationalize. Two possible pathways have, as yet, received only limited attention. Sotolon may be generated in wine in enantiomerically pure form ($ee > 98\%$), via the transformation of natural enantiomerically pure chiral sources (possibly including amino acids, sugars, etc.). This was recently suggested to explain the formation of sotolon from 4-hydroxy-*L*-isoleucine (26) in fenugreek oleoresin. The enantiomerically pure isomer of sotolon then racemizes slowly over a period of time, depending on the aging conditions. A second route may also be envisioned, whereby sotolon is generated by a stereoselective (enantioselective) reaction, resulting in an enantio-enriched form (with ee varying from >0 to $>98\%$) (27). Sotolon generated via these processes may indeed present a wide range of enantiomeric purities, depending on the type of reaction. Sotolon formed in this way may also racemize over time, as described above. Whereas the first pathway has already been explored (26), the second route, involving stereoselective mechanisms, has yet to be investigated.

Conclusions. Understanding the mechanisms associated with the degradation of white wine flavor is an important field of research in wine chemistry. Several teams have made considerable efforts to identify and quantify the key odorants responsible for deteriorating wine flavor. However, from our point of view, the organoleptic role played by sotolon was previously underestimated, possibly due to the lack of information concerning its enantiomers in wine.

The separation of sotolon enantiomers in wines using chiral GC-MS clearly showed the presence of nonracemic forms. The organoleptic properties of the sotolon enantiomers were also studied. Compared to the (*R*) form, (*S*)-sotolon was found to possess, by far, the more intense organoleptic properties. Its perception thresholds in model wine solution and white wine were 0.8 and 5 $\mu\text{g/L}$, respectively. Consequently, the aromatic impact of sotolon in dry white wines depends on the distribution of the (*R*) and (*S*) forms.

Hence, knowledge of the olfactory properties of the sotolon enantiomers proved to be fundamental for assessing its olfactory impact on wine, as assaying overall concentrations produced inadequate results. The presence of nonracemic forms of sotolon in the wines analyzed suggested that stereoselective mechanisms were responsible for the excess of one of the enantiomers. It is now clear that the origin of sotolon is far more complex than expected, and further studies will be required to elucidate the formation of enantio-enriched sotolon during white wine aging.

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