

# Analytical and Sensory Characterization of $\gamma$ - and $\delta$ -Thiolactones

Irmgard Roling,<sup>†</sup> Hans-Georg Schmarr,<sup>†</sup> Wolfgang Eisenreich,<sup>‡</sup> and Karl-Heinz Engel<sup>\*†</sup>

Technische Universität München, Lehrstuhl für Allgemeine Lebensmitteltechnologie, Am Forum 2, D-85350 Freising-Weihenstephan, Germany, and Technische Universität München, Lehrstuhl für Organische Chemie und Biochemie, Lichtenbergstrasse 4, D-85748 Garching, Germany

$\gamma$ -Thiolactones [5-alkyldihydro-2(3*H*)-thiophenones] and  $\delta$ -thiolactones (6-alkyltetrahydro-2*H*-thiopyran-2-ones) were synthesized via isothiuronium salts by reaction of the corresponding oxygen-containing lactones with thiourea and hydrobromic acid. The identity of the compounds was confirmed by means of IR, MS, and <sup>1</sup>H and <sup>13</sup>C NMR. Separation of the enantiomers of the thiolactones was achieved by capillary GC using heptakis(2,3-di-*O*-methyl-6-*O*-TBDMS)- $\beta$ -cyclodextrin as stationary phase. The substitution of oxygen by sulfur induces tropical fruit notes, which are more pronounced for the  $\delta$ -thiolactones. Odor thresholds are dependent on ring size and chain length.

**Keywords:**  $\gamma$ -Thiolactone;  $\delta$ -thiolactone; capillary GC; spectroscopic data; GC enantioseparation; odor threshold

## INTRODUCTION

Sulfur-containing compounds play an important role in flavor chemistry (Boelens, 1993; Mussinan and Keelan, 1994). Thermally generated flavors (Güntert et al., 1993) as well as the biogenetically derived aroma patterns of some fruits, e.g. passion fruit (Engel and Tressl, 1991) or Durian fruit (Fischer, 1996), are markedly determined by sulfur-containing volatiles. Another outstanding class of substances known to contribute significantly to many flavors comprises aliphatic  $\gamma$ - and  $\delta$ -lactones (Maga, 1976). Typical examples of "lactone-type" fruits are nectarines (Engel et al., 1988), apricots (Takeoka et al., 1990), and peaches (Horvat et al., 1990).

Having these two phenomena in mind, the objective of our studies was to investigate the effect of a substitution of the oxygen in the lactone ring by sulfur.  $\gamma$ -Thiovalerolactone, a short-chain example for such compounds, has been detected after heating of cysteine or cystine-containing model mixtures (Mussinan and Katz, 1973; Shu and Ho, 1989). However, systematic studies on this class of volatiles are missing. This paper presents the synthesis, provides analytical data, and evaluates sensory properties of a series of  $\gamma$ - and  $\delta$ -thiolactones.

## MATERIALS AND METHODS

**Reagents.**  $\gamma$ - and  $\delta$ -lactones were obtained as gifts from Haarmann & Reimer, Holzminden, Germany, and Frey & Lau, Henstedt-Ulzburg, Germany.  $\gamma$ -Thiobutyrolactone was purchased from Aldrich, Steinheim, Germany.

**Synthesis of  $\gamma$ - and  $\delta$ -Thiolactones.** In analogy to the procedure described by Kharasch and Langford (1963) a mixture of lactone (15 mmol), 1.1 g of thiourea (15 mmol), and 2 mL of hydrobromic acid (48%) was refluxed with stirring ( $\gamma$ -lactones, 8 h;  $\delta$ -lactones, 10 h). After cooling, 2 g of sodium hydroxide in 2 mL of water was added and the mixture was

refluxed again under nitrogen without stirring for 2 h. The cooled solution was extracted with ether (50 mL), and the ether extract was discarded. The aqueous residue was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether (3  $\times$  50 mL). The extract was dried over sodium sulfate, and the ether was removed under aspirator vacuum. The residual oil was heated slowly in a distilling apparatus at atmospheric pressure until the removal of water was complete (105 °C) and the temperature rose to 200 °C. At this point, the residue was allowed to cool, and after the apparatus was dried, the distillation was continued under reduced pressure. Boiling points (0.5–1 mmHg): **1a**, 55–65 °C; **2a**, 55–65 °C; **1b**, 80–90 °C; **2b**, 80–90 °C; **1c**, 105–120 °C; **2c**, 105–115 °C; **1d**, 125–135 °C; **2d**, 130–140 °C.

Purification of the distilled thiolactones was achieved by column chromatography on silica gel (11 g; Merck, 7734). The  $\gamma$ -lactones elute in the last 90 mL of fraction I (250 mL of pentane/ethyl acetate, 90:1), whereas the  $\delta$ -lactones are obtained by subsequent elution with fraction II (125 mL of pentane/ethyl acetate, 97:3). Overall yields (purity determined by GC): **1a**, 15% (92%); **2a**, 45% (>99%); **1b**, 10% (94%); **2b**, 23% (>99%); **1c**, 6% (94%); **2c**, 15% (>99%); **1d**, 1% (75%); **2d**, 19% (96%).

**Capillary Gas Chromatography.** Purity control of the synthesized compounds was performed by gas chromatography (GC) on two systems: (a) A Carlo Erba Mega II 8575 (Rodano, Italy) was equipped with a flame ionization detector (FID) and a flame photometric detector (FPD; FPD 80, Carlo Erba Instruments). Parallel detection was achieved by dividing the effluent of the column (DB-Wax, J&W, Folsom, CA; 60 m  $\times$  0.32 mm i.d., 0.25  $\mu$ m film thickness) via press-fit splitter and short pieces of deactivated fused silica capillaries to the two detectors. Split injection was performed at 220 °C, and column temperature was programmed from 40 °C (5 min hold) to 235 °C (5 min hold) at 4 °C/min. Hydrogen was used as carrier gas at a constant inlet pressure of 105 kPa. (b) A Carlo Erba Fractovap 4160 gas chromatograph was equipped with FID and split injector; the column was a 30 m  $\times$  0.32 mm i.d. fused silica capillary column coated with a dimethylsiloxane stationary phase (PS-255, ABCR, Karlsruhe, Germany) providing a film thickness of 1.0  $\mu$ m. Column temperature was programmed from 40 °C (10 min hold) to 300 °C (5 min hold) at 4 °C/min; carrier gas was hydrogen (inlet pressure 50 kPa).

Separation of the enantiomers of the thiolactones was achieved on a fused silica column (30 m  $\times$  0.25 mm i.d.) coated

\* Author to whom correspondence should be addressed (telephone +49 8161 714250; fax +49 8161 714259).

<sup>†</sup> Lehrstuhl für Allgemeine Lebensmitteltechnologie.

<sup>‡</sup> Lehrstuhl für Organische Chemie und Biochemie.

in the laboratory with 25% of heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- $\beta$ -cyclodextrin in SE 54 to provide a film thickness of 0.25  $\mu$ m. Deactivation with Carbowax 4000 and static coating were accomplished according to standard procedures as reported by Grob (1986). Synthesis and purification of the cyclodextrin derivative was performed according to described procedures (Dietrich et al., 1992; Schmarr, 1992). The column was installed in a gas chromatograph (Carlo Erba, Mega 5160) with an FID detector, and split injection was performed at 210 °C. Hydrogen was used as carrier gas at a constant inlet pressure of 100 kPa. To separate the enantiomers of the thiolactones, the oven temperature was programmed from 100 °C (2 min hold) to 125 °C (10 min hold) at a rate of 3 °C/min and then to 205 °C at a rate of 1.5 °C/min. Conditions for the determination of the chromatographic data shown in Table 3 were the same as mentioned above, except that the runs were performed isothermally at the cited temperatures. Data acquisition was with the Chrom-Card system (Carlo Erba Instruments).

**Gas Chromatography/Mass Spectrometry (GC/MS).** Mass spectral data were acquired on an HP 5890 gas chromatograph coupled to an HP 5970 mass selective detector (Hewlett-Packard, Palo Alto, CA). The mass spectrometer interface temperature was set to 250 °C, and the electron energy was 70 eV. The column used for GC/MS was a 50 m  $\times$  0.2 mm i.d. FFAP fused silica capillary with a film thickness of 0.33  $\mu$ m (Hewlett-Packard). Split injection was performed at 230 °C, and oven temperature was programmed from 70 °C (5 min hold) to 235 °C (10 min hold) at 5 °C/min. Helium was used as carrier gas at a constant inlet pressure of 175 kPa.

**Infrared Spectroscopy.** Infrared spectra (film) were recorded from 4000 to 500  $\text{cm}^{-1}$  (resolution = 4  $\text{cm}^{-1}$ ) on a Nicolet 320 FT-IR.

**NMR Spectroscopy.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 22 °C using DRX 500 and AC 200 spectrometers, respectively, from Bruker, Karlsruhe, Germany.  $^1\text{H}$ -detected experiments were performed using an inverse broadband probehead, and  $^{13}\text{C}$ -detected experiments were performed using a dual  $^{13}\text{C}/^1\text{H}$  probehead. The parameters of  $^1\text{H}$  spectra were as follows: transmitter frequency, 500.13 MHz; 45° pulse, 3  $\mu$ s; repetition time, 3 s; spectral width, 8.0 kHz; 32K data set, zero-filled to 64K prior to Fourier transformation; Gaussian apodization. The parameters of  $^{13}\text{C}$  NMR spectra were as follows: transmitter frequency, 125.77 MHz; 30° pulse, 3  $\mu$ s; repetition time, 2 s; spectral width, 28.9 kHz; 64K data set, zero-filled to 128K;  $^1\text{H}$  composite pulse decoupling (Waltz 16) during relaxation and acquisition; Gaussian apodization. DEPT and two-dimensional double-quantum filtered COSY and HMQC experiments were performed according to standard Bruker software.

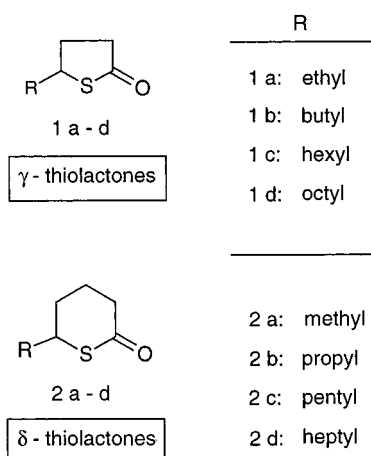
**Odor Thresholds.** Odor thresholds in water were determined in Teflon squeeze bottles according to the procedure described by Guadagni and Buttery (1978). Odor thresholds in air were determined by gas chromatography-olfactometry according to the method reported by Schieberle (1991).

## RESULTS AND DISCUSSION

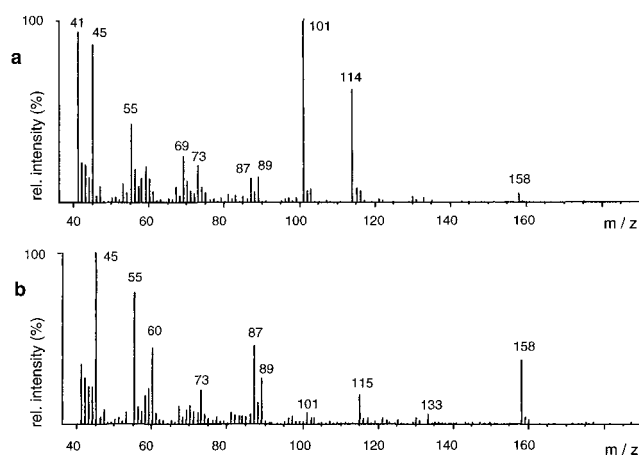
5-Alkyldihydro-2(3*H*)-thiophenones (Figure 1, **1a-d**) and 6-alkyltetrahydro-2*H*-thiopyran-2-ones (Figure 1, **2a-d**) were synthesized by the reaction of the corresponding oxygen-containing  $\gamma$ - and  $\delta$ -lactones with thiourea and hydrobromic acid. The method involving isothiuronium bromide as an intermediate (Frank and Smith, 1946) was applied according to the procedure described for the conversion of  $\gamma$ -butyrolactone to dihydro-2(3*H*)-thiophenone by Kharasch and Langford (1963).

**Identity of Synthesized Compounds.** The identity of the synthesized  $\gamma$ - and  $\delta$ -thiolactones was established by means of IR, MS, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

In agreement with the reference compound  $\gamma$ -thiobutylactone, the synthesized  $\gamma$ -thiolactones showed a



**Figure 1.** Structures of the synthesized 5-alkyldihydro-2(3*H*)-thiophenones ( $\gamma$ -thiolactones, **1a-d**) and 6-alkyltetrahydro-2*H*-thiopyran-2-ones ( $\delta$ -thiolactones, **2a-d**).



**Figure 2.** Mass spectra of  $\gamma$ -thiooctalactone (a) and  $\delta$ -thiooctalactone (b).

strong carbonyl absorption signal at 1711  $\text{cm}^{-1}$  in IR; the oxygen-containing  $\gamma$ -lactones, on the other hand, exhibited the corresponding band at 1777  $\text{cm}^{-1}$ . Analogously, a strong signal at 1670  $\text{cm}^{-1}$  was observed for the  $\delta$ -thiolactones, in contrast to 1730  $\text{cm}^{-1}$  for the oxygen-containing  $\delta$ -lactones.

In analogy to the characteristic ions  $m/z$  85 and 99 for  $\gamma$ - and  $\delta$ -lactones, the mass spectra of the thio compounds exhibited the expected fragments at  $m/z$  101 and 115, respectively. As examples, the fragmentation patterns of  $\gamma$ - and  $\delta$ -thiooctalactone are shown in Figure 2. Mass spectral and chromatographic data of the synthesized compounds are summarized in Table 1. The retention indices on polar and apolar stationary phases demonstrate that the chromatographic behavior of the thiolactones is comparable to that of their oxygen-containing counterparts.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are compiled in Table 2. Comparison of the spectra and assignment of the signals of the reference compounds  $\gamma$ -butyrolactone and  $\gamma$ -thiobutylactone allowed the differentiation of the two classes. As shown in Table 2, the substitution of oxygen by sulfur in the lactone ring is reflected by a significant upfield shift of the signals obtained for the proton as well as for the carbon in position 4 (position 5 for  $\delta$ -lactones). In contrast, the  $^{13}\text{C}$  NMR signal assigned to the carbon in position 1 is markedly shifted downfield ( $\sim$ 30 ppm) in the sulfur-containing compound. These differences could consistently be observed by

**Table 1. Chromatographic and Mass Spectral Data of  $\gamma$ - and  $\delta$ -Thiolactones**

compd	KI		MW	fragmentation <i>m/z</i> (rel intensity, %)
	DB-Wax	PS-255		
<b>1a</b>	1697	1094	130	41 (100), 130 (76), 45 (66), 42 (59), 55 (52), 101 (49), 73 (20), 58 (14), 88 (13), 75 (12)
<b>1b</b>	1909	1312	158	101 (100), 41 (92), 45 (86), 114 (61), 55 (44), 69 (25), 42 (22), 43 (21), 73 (19), 89 (14), 87 (13)
<b>1c</b>	2142	1534	186	45 (100), 41 (66), 142 (48), 101 (41), 43 (41), 55 (37), 129 (32), 115 (29), 73 (26), 89 (25)
<b>1d</b>	2382	1754	214	45 (100), 89 (28), 73 (25), 87 (23), 101 (19), 115 (18), 55 (17), 59 (15), 170 (16), 157 (10)
<b>2a</b>	1791	1124	130	60 (100), 42 (79), 130 (66), 41 (56), 55 (51), 45 (50), 59 (33), 87 (27), 61 (24), 102 (15)
<b>2b</b>	2004	1344	158	45 (100), 55 (72), 87 (44), 60 (42), 158 (35), 41 (33), 89 (26), 59 (21), 73 (19), 115 (16)
<b>2c</b>	2233	1565	186	45 (100), 55 (35), 87 (30), 115 (25), 41 (27), 89 (25), 73 (21), 59 (19), 60 (17), 186 (11)
<b>2d</b>	2473	1789	214	55 (100), 41 (69), 87 (54), 143 (44), 60 (42), 129 (40), 45 (39), 115 (21), 67 (19), 214 (15)

**Table 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Assignments by Two-Dimensional COSY and HMQC Experiments**

position	chemical shifts			
	$^1\text{H}^a$	$^{13}\text{C}^a$	$^1\text{H}$	$^{13}\text{C}$
	$\gamma$ -Butyrolactone		$\gamma$ -Thiobutyrolactone	
1		177.8 (C)		209.2 (C) <sup>b</sup>
2	2.31 (t, <i>J</i> = 8.3 Hz, 2H)	27.6 (CH <sub>2</sub> )	2.41 (t, <i>J</i> = 7.3 Hz, 2H)	33.4 (CH <sub>2</sub> )
3	2.11 (qui, <i>J</i> = 7.6 Hz, 2H)	21.9 (CH <sub>2</sub> )	2.18 (qui, <i>J</i> = 6.9 Hz, 2H)	25.5 (CH <sub>2</sub> )
4	4.17 (t, <i>J</i> = 7.2 Hz, 2H)	68.5 (CH <sub>2</sub> )	3.32 (t, <i>J</i> = 6.5 Hz, 2H)	41.0 (CH <sub>2</sub> )
	$\gamma$ -Hexalactone		$\gamma$ -Thiohexalactone	
1		177.1 (C)		208.7 (C)
2	2.40 (m, 2H)	28.5 (CH <sub>2</sub> )	2.57 (m, 2H)	42.0 (CH <sub>2</sub> )
3	2.21 (m, 1H), 1.74 (m, 1H)	27.2 (CH <sub>2</sub> )	2.35 (m, 1H), 1.86 (m, 1H)	31.7 (CH <sub>2</sub> )
4	4.32 (qui, <i>J</i> = 6.9 Hz, 1H)	81.9 (CH)	3.77 (m, 1H)	53.0 (CH)
5	1.63 (m, 1H), 1.53 (m, 1H)	28.1 (CH <sub>2</sub> )	1.77 (m, 2H)	29.4 (CH <sub>2</sub> )
6	0.87 (t, <i>J</i> = 7.5 Hz, 3H)	9.1 (CH <sub>3</sub> )	1.01 (t, <i>J</i> = 7.4 Hz, 3H)	12.5 (CH <sub>3</sub> )
	$\delta$ -Hexalactone		$\delta$ -Thiohexalactone	
1		171.4 (C)		202.0 (C)
2	2.34 (m, 1H), 2.22 (m, 1H)	28.7 (CH <sub>2</sub> )	2.57 (dt, <i>J</i> = 17.5, 5.0 Hz, 1H), 2.42 (ddd, <i>J</i> = 17.5, 10.5, 5.4 Hz, 1H)	40.4 (CH <sub>2</sub> )
3	1.68 (m, 2H)	17.9 (CH <sub>2</sub> )	2.02 (m, 1H), 1.82 (m, 1H)	22.0 (CH <sub>2</sub> )
4	1.78 (m, 1H), 1.30 (m, 1H)	29.0 (CH <sub>2</sub> )	2.15 (m, 1H), 1.53 (m, 1H)	32.1 (CH <sub>2</sub> )
5	4.25 (m, 1H)	76.4 (CH)	3.54 (m, 1H)	40.8 (CH)
6	1.16 (d, <i>J</i> = 6.4 Hz, 3H)	21.1 (CH <sub>3</sub> )	1.31 (d, <i>J</i> = 6.7 Hz, 3H)	22.3 (CH <sub>3</sub> )
	$\gamma$ -Decalactone		$\gamma$ -Thiodecalactone	
1		177.3 (C)		208.7 (C)
2	2.45 (m, 2H)	28.7 (CH <sub>2</sub> )	2.60 (m, 1H), 2.54 (m, 1H)	42.1 (CH <sub>2</sub> )
3	2.26 (m, 1H), 1.79 (m, 1H)	27.8 (CH <sub>2</sub> )	2.35 (m, 1H), 1.86 (m, 1H)	32.2 (CH <sub>2</sub> )
4	4.42 (m, 1H)	81.0 (CH)	3.82 (m, 1H)	51.4 (CH)
5	1.66 (m, 1H), 1.54 (m, 1H)	35.4 (CH <sub>2</sub> )	1.73 (m, 2H)	36.5 (CH <sub>2</sub> )
6	1.37 (m, 1H), 1.30 (m, 1H)	25.0 (CH <sub>2</sub> )	1.37 (m, 2H)	28.2 (CH <sub>2</sub> )
7	1.25 (m, 2H)	28.8 (CH <sub>2</sub> ) <sup>c</sup>	1.27 (m, 2H)	29.0 (CH <sub>2</sub> ) <sup>c</sup>
8	1.25 (m, 2H)	31.5 (CH <sub>2</sub> ) <sup>c</sup>	1.27 (m, 2H)	31.6 (CH <sub>2</sub> ) <sup>c</sup>
9	1.22 (m, 2H)	22.4 (CH <sub>2</sub> ) <sup>c</sup>	1.27 (m, 2H)	22.5 (CH <sub>2</sub> ) <sup>c</sup>
10	0.81 (t, <i>J</i> = 6.8 Hz, 3H)	13.9 (CH <sub>3</sub> )	0.86 (t, <i>J</i> = 6.8 Hz, 3H)	14.0 (CH <sub>3</sub> )
	$\delta$ -Decalactone		$\delta$ -Thiodecalactone	
1		171.9 (C)		202.2 (C)
2	2.48 (dt, <i>J</i> = 17.7, 6.5 Hz, 1H), 2.35 (dt, <i>J</i> = 17.7, 7.5 Hz, 1H)	29.2 (CH <sub>2</sub> )	2.59 (dt, <i>J</i> = 17.4, 5.0 Hz, 1H), 2.43 (ddd, <i>J</i> = 17.4, 10.5, 5.4 Hz, 1H)	40.9 (CH <sub>2</sub> )
3	1.75 (m, 2H)	18.3 (CH <sub>2</sub> )	2.02 (m, 1H), 1.81 (m, 1H)	22.0 (CH <sub>2</sub> )
4	1.84 (m, 1H), 1.48 (m, 1H)	24.4 (CH <sub>2</sub> )	2.17 (m, 1H), 1.54 (m, 1H)	30.2 (CH <sub>2</sub> )
5	4.18 (m, 1H)	80.4 (CH)	3.43 (m, 1H)	46.2 (CH)
6	1.60 (m, 1H), 1.45 (m, 1H)	35.6 (CH <sub>2</sub> )	1.60 (m, 2H)	36.8 (CH <sub>2</sub> )
7	1.45 (m, 2H)	27.5 (CH <sub>2</sub> )	1.35 (m, 2H)	26.1 (CH <sub>2</sub> )
8	1.21 (m, 2H)	31.4 (CH <sub>2</sub> ) <sup>c</sup>	1.26 (m, 2H)	31.4 (CH <sub>2</sub> ) <sup>c</sup>
9	1.21 (m, 2H)	22.3 (CH <sub>2</sub> ) <sup>c</sup>	1.26 (m, 2H)	22.4 (CH <sub>2</sub> ) <sup>c</sup>
10	0.79 (t, <i>J</i> = 6.8 Hz, 3H)	13.8 (CH <sub>3</sub> )	0.85 (t, <i>J</i> = 7.0 Hz, 3H)	13.9 (CH <sub>3</sub> )

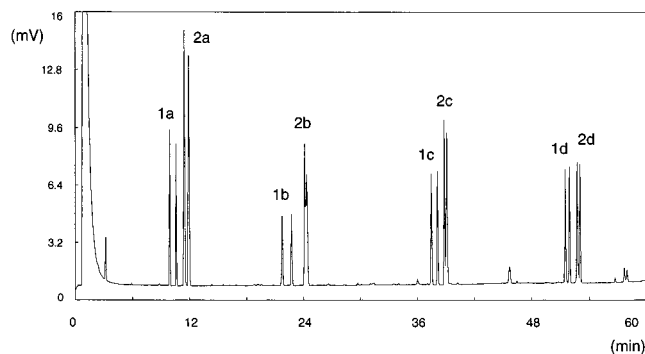
<sup>a</sup> Chemical shifts were referenced to solvent signals ( $^1\text{H}$ , 7.24 ppm;  $^{13}\text{C}$ , 77.0 ppm). <sup>b</sup> Carbon multiplicities as determined by DEPT experiments. <sup>c</sup> Assignments may be interchanged.

comparing the spectra of synthesized thiolactones to those of oxygen-containing reference compounds as shown in Table 2 for the C<sub>6</sub> and C<sub>10</sub> homologues.

**GC Enantioseparation.** The enantiomers of the  $\gamma$ - and  $\delta$ -thiolactones could be separated using heptakis-(2,3-di-*O*-methyl-6-*O*-TBDMS)- $\beta$ -cyclodextrin as chiral stationary phase (Figure 3). The chromatographic data are summarized in Table 3. The separation factors obtained for the  $\gamma$ -thiolactone enantiomers are consistently lower than those reported for the oxygen-contain-

ing counterparts on this modified cyclodextrin (Maas et al., 1994); they also decrease with increasing chain length. The  $\delta$ -thiolactones show a minimum discrimination of enantiomers for the C<sub>8</sub> homologue. The determination of the order of elution by means of optically pure compounds is the subject of ongoing studies.

**Sensory Evaluation.** Sensory characteristics of the thiolactones are summarized in Table 4. The odor thresholds (nanograms per liter) in air determined by



**Figure 3.** Capillary GC separation of the enantiomers of  $\gamma$ - and  $\delta$ -thiolactones using heptakis(2,3-di-*O*-methyl-6-*O*-TBDMS)- $\beta$ -cyclodextrin as stationary phase (for conditions see Materials and Methods).

**Table 3. Chromatographic Data for Enantioseparation of  $\gamma$ - and  $\delta$ -Thiolactones on Heptakis(2,3-di-*O*-methyl-6-*O*-TBDMS)- $\beta$ -cyclodextrin as Stationary Phase (for Conditions see Materials and Methods)**

thiolactone	$T$ ( $^{\circ}\text{C}$ )	$k_1^a$	$\alpha^b$	$R_s^c$
<b>1a</b>	130	5.0	1.088	3.92
<b>1b</b>	130	15.0	1.066	4.47
<b>1c</b>	130	49.4	1.060	4.27
<b>1d</b>	160	28.8	1.034	2.50
<b>2a</b>	130	6.8	1.051	2.58
<b>2b</b>	130	18.9	1.016	1.18
<b>2c</b>	130	56.8	1.023	1.68
<b>2d</b>	160	31.4	1.023	1.77

<sup>a</sup>  $k_1$ , capacity factor for the first eluting enantiomer. <sup>b</sup>  $\alpha$ , separation factors. <sup>c</sup>  $R_s$ , resolution of enantiomers.

**Table 4. Sensory Characteristics of Thiolactones**

thiolactone	odor quality <sup>a</sup>	odor threshold <sup>b</sup> (ng/L in air)
<b>1a</b>	sweet, sulfury, burnt	11
<b>2a</b>	slightly fruity, petroleum, sulfury	22
<b>1b</b>	mushroom homogenate, coconut, sweet, sulfury	0.3
<b>2b</b>	coconut, green, tropical fruit	0.7
<b>1c</b>	fruity, fatty, rancid	3
<b>2c</b>	tropical fruit, fresh	0.7
<b>1d</b>	slightly fruity, soapy	22
<b>2d</b>	sweet, soapy, apricot	5

<sup>a</sup> Determined in 0.004% solutions in water. <sup>b</sup> Determined by means of GC-olfactometry (Schieberle, 1991).

**Table 5. Influence of Oxygen/Sulfur on Odor Thresholds of Lactones in Water**

lactone	odor threshold ( $\text{H}_2\text{O}$ ), ppb
$\gamma$ -decalactone <sup>a</sup>	11
$\gamma$ -thiodecalactone	47
$\delta$ -decalactone <sup>a</sup>	100
$\delta$ -thiodecalactone	6

<sup>a</sup> Engel et al. (1988).

means of GC-olfactometry (Schieberle, 1991) show a relationship between chain length and sensory potency. Within the series of synthesized compounds, both  $\gamma$ - and  $\delta$ -thiolactones exhibit minimum odor thresholds for the  $\text{C}_8$  and  $\text{C}_{10}$  homologues. Table 5 lists odor thresholds (parts per billion) in water determined under the same conditions for oxygen- and sulfur-containing lactones. The replacement of oxygen by sulfur in the lactone ring leads to an increase of the threshold for  $\gamma$ -decalactone but to a drastic reduction for the corresponding

$\delta$ -lactone. Differences in the effects caused by the introduction of sulfur depending on the size of the lactone ring are also reflected in sensory descriptions obtained for solutions (0.004%) of the thiolactones in water (Table 4). Mushroom-like odors ( $\text{C}_8$ ) or fatty, rancid notes ( $\text{C}_{10}$ ) were perceived for the  $\gamma$ -thiolactones. The  $\delta$ -thiolactones, on the other hand, exhibit both the warm lactone aroma and the fresh, sharp tropical fruit character. This combination results in extremely pleasant notes for the  $\text{C}_8$  and  $\text{C}_{10}$  homologues.

The substitution of oxygen by sulfur in the ring moiety of  $\gamma$ - and  $\delta$ -lactones does not have the tremendous impact as reported for the replacement of a tertiary hydroxy group by a thiol group, e.g. from  $\alpha$ -terpineol to the extremely powerful 1-*p*-menthene-8-thiol (Demole et al., 1982). The effects are more comparable to those described for S-derivatives of maltol or rose oxide (Ohloff, 1990). The sensory evaluation of thiofuraneol also revealed a combination of the original strong burnt sugar note and caramel-like flavor of furaneol with the tropical fruit aroma induced by the sulfur exchange in the ring (Werkhoff et al., 1991).

**Outlook.** For a final evaluation of the sensory properties of the thiolactones, aroma profiles at various concentrations and the characterization of the resolved enantiomers will be required. The newly described sensorially interesting compounds call of course for a search in natural systems. Tropical fruits, many of them known for both lactone and sulfur metabolism, might be potential candidates.

#### ACKNOWLEDGMENT

We thank R. G. Buttery (Western Regional Research Center, U.S. Department of Agriculture) and P. Schieberle and T. Hofmann (Lehrstuhl für Lebensmittelchemie, Technische Universität München) for determining odor thresholds.

#### LITERATURE CITED

- Boelens, H. M. Volatile Character-Impact Sulfur Compounds and their Sensory Properties. *Perfum. Flavor.* **1993**, *18*, 29–39.
- Demole, E.; Enggist, P.; Ohloff, G. 1-*p*-Menthene-8-thiol: A Powerful Impact Constituent of Grapefruit Juice (*Citrus paradisi* Macfayden) *Helv. Chim. Acta* **1982**, *65*, 1785–1794.
- Dietrich, A.; Maas, B.; Messer, W.; Bruche, G.; Karl, V.; Kaunzinger, A.; Mosandl, A. Stereoisomeric Flavor Compounds, Part LVIII: The Use of Heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- $\beta$ -cyclodextrin as a Chiral Stationary Phase in Flavor Analysis. *J. High Resolut. Chromatogr.* **1992**, *15*, 590–593.
- Engel, K.-H.; Tressl, R. Identification of New Sulfur-Containing Volatiles in Yellow Passion Fruits (*Passiflora edulis* f. *flavicarpa*). *J. Agric. Food Chem.* **1991**, *39*, 2249–2252.
- Engel, K.-H.; Flath, R. A.; Buttery, R. G.; Mon, T. R.; Ramming, D. W.; Teranishi, R. Investigation of Volatile Constituents in Nectarines. 1. Analytical and Sensory Characterization of Aroma Components in Some Nectarine Cultivars. *J. Agric. Food Chem.* **1988**, *36*, 549–553.
- Fischer, N. Flavor Components in Selected Exotic Fruits. *Dragoco Rep. (Flavor. Inf. Serv.)* **1996**, *41*, 137–147.
- Frank, R. L.; Smith, P. V. The Preparation of Mercaptans from Alcohols. *J. Am. Chem. Soc.* **1946**, *68*, 2103–2104.
- Grob, K. *Making and Manipulating Capillary Columns for Gas Chromatography*; Hüthig Verlag: Heidelberg, 1986.
- Guadagni, D. G.; Buttery, R. G. Odor Threshold of 2,3,6-Trichloroanisole in water. *J. Food Sci.* **1978**, *43*, 1346–1347.

- Güntert, M.; Bertram, H.-J.; Hopp, R.; Silberzahn, W.; Sommer, H.; Werkhoff, P. Thermal Generation of Flavor Compounds from Thiamin and Various Amino Acids. In *Recent Developments in Flavor and Fragrance Chemistry*; Hopp, R., Mori, K., Eds.; VCH: Weinheim, Germany, 1993; pp 215–240.
- Horvat, R. J.; Chapman, G. W., Jr.; Robertson, J. A.; Meredith, F. I.; Scorza, R.; Callahan, A. M.; Morgens, P. Comparison of the Volatile Compounds from Several Commercial Peach Cultivars. *J. Agric. Food Chem.* **1990**, *38*, 234–237.
- Kharasch, N.; Langford, R. B. Derivatives of Sulfenic Acids. XLII. 3-Chloroformylpropane-sulfonyl Chloride and 1,2-Thiazan-3-one. *J. Org. Chem.* **1963**, *28*, 1901–1903.
- Maas, B.; Dietrich, A.; Mosandl, A. Collection of Enantiomer Separation Factors Obtained by Capillary Gas Chromatography on Chiral Stationary Phases. *J. High Resolut. Chromatogr.* **1994**, *17*, 109–115.
- Maga, J. A. Lactones in Foods. *CRC Crit. Rev. Food Sci. Nutr.* **1976**, 1–56.
- Mussinan, C. J.; Katz, I. Isolation and Identification of Some Sulfur Chemicals Present in Two Model Systems Approximating Cooked Meat. *J. Agric. Food Chem.* **1973**, *21*, 43–45.
- Mussinan, C. J., Keelan, M. E., Eds.; *Sulfur Compounds in Foods*; ACS Symposium Series 564; American Chemical Society: Washington, DC, 1994.
- Ohloff, G. *Riechstoffe und Geruchssinn. Die molekulare Welt der Düfte*; Springer-Verlag: Berlin, 1990.
- Schieberle, P. J. Primary Odorants in Popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141–1144.
- Schmarr, H.-G. Doctoral Thesis, University of Frankfurt/Main, Germany, 1992.
- Shu, C.-K.; Ho, C.-T. Parameter Effects on the Thermal Reaction of Cystine and 2,5-Dimethyl-4-hydroxy-3(2H)-furanone. In *Thermal Generation of Aromas*; Parliment, T. H., McGorin, R. J., Ho, C. T., Eds.; ACS Symposium Series 564; American Chemical Society: Washington, DC, 1989; pp 229–241.
- Takeoka, G. R.; Flath, R. A.; Mon, R. T.; Teranishi, R.; Güntert, M. Volatile Constituents of Apricot (*Prunus armeniaca*). *J. Agric. Food Chem.* **1990**, *38*, 471–477.
- Werkhoff, P.; Bretschneider, W.; Emberger, R.; Güntert, M.; Hopp, R.; Köpsel, M. Recent Developments in the Sulfur Flavour Chemistry of Yeast Extracts. *Chem. Mikrobiol. Technol. Lebensm.* **1991**, *13*, 30–57.

Received for review September 2, 1997. Revised manuscript received November 24, 1997. Accepted November 25, 1997.

JF970748+