

Identification and Synthesis of 2-Heptanethiol, a New Flavor
Compound Found in Bell Peppers[‡]HERVÉ SIMIAN,[†] FABIEN ROBERT, AND IMRE BLANK*

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2-Heptanethiol was identified for the first time as a constituent of red and green bell pepper extracts. The chemical structure of this new aroma compound was proposed on the basis of mass spectra and retention indices and confirmed by chemical synthesis and nuclear magnetic resonance spectroscopy measurements. Its aroma properties were described as sulfury, onion-like, and vegetable-like, reminiscent of bell pepper at lower concentrations, with an orthonasal detection threshold of 10 $\mu\text{g/L}$ of water. No differences in odor note and threshold value were observed for the enantiomeric forms, which were prepared from enantiopure 2-heptanol by tosylation, followed by thioacetylation and reduction, giving the target thiol enantiomers.

KEYWORDS: Bell peppers; 2-heptanethiol; identification; GC–MS; NMR; synthesis; odor thresholds

INTRODUCTION

The study of bell pepper's volatile constituents has been the subject of numerous publications. Up to now almost 200 volatiles have been reported (1), of which only a few are reminiscent of bell pepper aroma, such as 3-isobutyl-2-methoxy-pyrazine first identified by Buttery and co-workers (2). This odorant has a characteristic green, bell pepper-like note and a very low detection threshold of 2 ng/L water (2). Additional odor-active compounds have been reported in fresh green bell pepper on the basis of gas chromatography/olfactometry (GC/O), e.g. 2-methylpropanal, 2- and 3-methylbutanal, 2,3-butanedione, 1-penten-3-one, hexanal, heptanal, β -ocimene, *trans*-3-hepten-2-one, dimethyl trisulfide, and β -cyclocitral (3). More recently, a systematic work characterized odor-active compounds of sweet bell pepper powder of different origins (4). The authors stressed the importance of β -ionone, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone, and 2- and 3-methylbutanoic acid among more than 30 odorants identified.

Changes during drying of bell pepper have been studied by Luning and co-workers (5). These authors reported on additional bell pepper-like smelling compounds such as the monoterpene Δ -3-carene, which was particularly abundant in red bell pepper. This typical bell pepper note had an increasing impact in turning and mature samples, particularly in fresh and dried red, yellow, and white bell peppers (6). In addition, 2-heptanone/heptanal has been suggested to elicit bell pepper and cooked vegetable notes in rehydrated bell peppers (7). Moreover, correlation of

GC and sensory data revealed that green bell peppers were characterized by the sensory attributes grassy, green bell pepper, and fruity, which were closely related to 1-penten-3-one, (*Z*)-3-hexanal, (*Z*)-3-hexanol, 3-isobutyl-2-methoxypyrazine, and linalool (8).

Volatile organic sulfur compounds obtained by enzymatic and chemical reactions contribute to the aroma of many vegetables, fruits, and food products (9, 10). In general, thiols and sulfides belong to the most intense and characteristic aroma substances with sulfury, vegetable-like, fruity notes perceived at low concentrations. For example, (2*R*,3*S*)-3-mercapto-2-methyl-1-pentanol found in fresh onions and dimethyl sulfide found in cooked tomatoes show low odor thresholds of 0.03 and 0.3 $\mu\text{g/kg}$ of water, respectively (11, 12), and are character-impact constituents of the respective vegetable. In bell peppers, only a few odor-active sulfur compounds have been identified, such as methional (4) and dimethyl trisulfide (3, 5). However, no thiols have so far been reported as odorants of bell peppers.

In our work on the natural constituents of vegetables, we investigated the odor-active compounds of red bell pepper. This paper deals with the identification of a secondary alkanethiol, a new odorant found in red bell pepper extracts, as well as its sensory properties and synthesis.

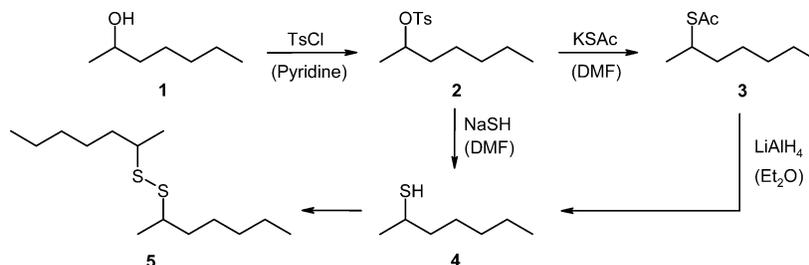
EXPERIMENTAL PROCEDURES

Materials. The following chemicals were commercially available: 2-heptanol (>99%), *p*-toluenesulfonyl chloride (>99%), sodium hydrogen sulfide monohydrate (NaSH, 97%), potassium thioacetate (97%), lithium aluminum hydride (>99%) (Fluka, Buchs, Switzerland); (*R*)-2-heptanol (>99%), (*S*)-2-heptanol (>99%), deuteriochloroform ($\text{C}^2\text{-HCl}_3$, >99%) (Aldrich, Buchs, Switzerland); ammonium chloride (98%), hydrochloric acid (HCl, 37%), magnesium sulfate (98%), sodium sulfate, silica gel 60 (Merck, Darmstadt, Germany). The solvents pentane, ethyl acetate (EtOAc), methylene chloride, ethanol (EtOH), toluene, pyridine, dimethylformamide (DMF), and diethyl ether (Et_2O) were from Merck and were freshly distilled prior to use.

[‡] Dedicated to Professor Dr. Werner Grosch on the occasion of his 70th birthday.

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Scheme 1. Synthesis of 2-Heptanethiol and Its Dimerization upon Heat Treatment^a

^a See the text for abbreviations and an explanation.

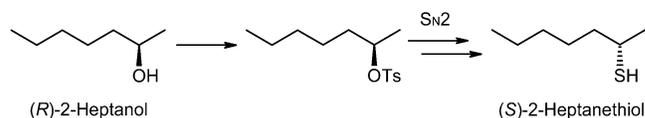
Syntheses. The target compound was synthesized from 2-heptanol **1** as starting material using classical approaches (13) and two methods to transform the intermediary tosylate **2** into the target thiol **4** (Scheme 1).

2-(*p*-Toluenesulfonyl)heptane (2). 2-Heptanol (**1**; 28 mL, 200 mmol, 1.0 equiv) dissolved in pyridine (135 mL) was placed in a 500-mL flask and cooled to 0 °C. *p*-Toluenesulfonyl chloride (41.8 g, 220 mmol, 1.1 equiv) was slowly added and the mixture was stirred at room temperature overnight. Toluene was added (200 mL), the reaction mixture filtered, and the filtrate washed with toluene (200 mL). The mother liquor was washed twice with an aqueous HCl solution (5 N, 200 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. After dry chromatography on silica gel (eluent pentane/EtOAc, 9:1, v/v), 2-(*p*-toluenesulfonyl)heptane (**2**) was obtained as a colorless oil (40.8 g, 76% yield). ¹H NMR (360 MHz, C²HCl₃, δ/ppm): 0.82 (t, 3H, CH₃, ³J = 7.2 Hz), 1.12–1.23 (m, 6H, 3 CH₂), 1.26 (d, 3H, CH₃, ³J = 6.3 Hz), 1.42–1.63 (m, 2H, CH₂), 2.44 (s, 3H, CH₃), 4.59 (qt, 1H, CH, ³J = 6.1 Hz, ³J = 6.35 Hz), 7.33 (d, 2H, ³J = 8.3 Hz), 7.79 (d, 2H, ³J = 8.3 Hz). ¹³C NMR (90 MHz, C²HCl₃, δ/ppm): 14.3 (CH₃), 21.3 (CH₃), 22.1 (CH₃), 22.8 (CH₂), 24.9 (CH₂), 31.7 (CH₂), 36.8 (CH₂), 81.1 (O–CH), 128.1 (C=CH), 130.1 (C=CH), 135.0 (C=C), 144.8 (C=C).

2-Heptanethiol (4). In a 50-mL flask equipped with a reflux condenser, 2-(*p*-toluenesulfonyl)heptane (**2**; 10.0 g, 37 mmol, 1.0 equiv) and sodium hydrogen sulfide monohydrate (7.0 g, 94 mmol, 2.5 equiv) were stirred in dimethylformamide (25 mL) at 80 °C for 2 h. The reaction mixture was diluted in brine (200 mL) and the aqueous layer was extracted with diethyl ether (3 × 200 mL). The organic layers were combined and washed with brine (5 × 200 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The racemic target compound **4** was obtained after distillation (143 mbar, 120 °C) as a colorless oil (1.82 g, 40% yield). ¹H NMR (360 MHz, C²HCl₃, δ/ppm): 0.82 (t, 3H, CH₃, ³J = 7.2 Hz), 1.27–1.38 (m, 6H, 3 CH₂), 1.36 (d, 3H, CH₃, ³J = 6.7 Hz), 1.49–1.62 (m, 2H, CH₂), 2.96 (tq, 1H, ³J = 6.5 Hz, ³J = 6.1 Hz). ¹³C NMR (90 MHz, C²HCl₃, δ/ppm): 14.5 (CH₃), 23.0 (CH₂), 26.0 (CH₃), 27.5 (CH₂), 31.9 (CH₂), 36.0 (CH₃), 41.3 (CH).

2-(Acetylthio)heptane (3). In a 50-mL flask equipped with a reflux condenser, 2-(*p*-toluenesulfonyl)heptane (**2**; 4.0 g, 15 mmol, 1.0 equiv) and potassium thioacetate (4.3 g, 38 mmol, 2.5 equiv) were stirred in dimethylformamide (15 mL) at 80 °C for 2 h. The reaction mixture was diluted in brine (100 mL) and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The organic layers were combined and washed with brine (5 × 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure. Distillation (0.16 mbar, 35 °C) gave **3** as a colorless oil (2.2 g, 84% yield). ¹H NMR (360 MHz, C²HCl₃, δ/ppm): 0.89 (t, 3H, CH₃, ³J = 6.5 Hz), 1.27–1.41 (m, 6H, 3 CH₂), 1.30 (d, 3H, CH₃, ³J = 6.8 Hz), 1.51–1.56 (m, 2H, CH₂), 2.31 (s, 3H, CH₃), 3.55 (tq, 1H, SCH, ³J = 6.8 Hz, ³J = 7.0 Hz). ¹³C NMR (90 MHz, C²HCl₃, δ/ppm): 14.4 (CH₃), 21.7 (CH₃), 22.9 (CH₂), 27.1 (CH₂), 31.2 (CH₃), 31.9 (CH₂), 36.7 (CH₂), 40.0 (CH), 196.6 (S–C=O).

2-Heptanethiol via 2-(Acetylthio)heptane. 2-(Acetylthio)heptane (**3**; 0.146 g, 0.84 mmol) was diluted in dry diethyl ether (3 mL) and added slowly (1.5 h) at –10 °C under nitrogen to a suspension of lithium aluminum hydride (0.144 g) dissolved in dry diethyl ether (2 mL). The temperature inside the flask did not exceed 5 °C. After

Scheme 2. Synthesis of Enantiopure (*S*)-2-Heptanethiol

the addition, stirring was continued for another 0.5 h at room temperature. First a saturated ammonium chloride solution (2 mL) and then hydrochloric acid (2 N, 2 mL) were added at –10 °C for hydrolysis. The organic phase was separated and the aqueous phase extracted with diethyl ether (2 × 20 mL). The combined organic phases were dried over sodium sulfate. The solvent was evaporated to furnish the racemic target product **4** (91 mg, 82% yield).

(*R*)- and (*S*)-2-Heptanethiol. Optically active 2-heptanethiols were prepared from (*S*)- and (*R*)-2-heptanol using the reductive approach (Scheme 2). The optical rotation of the target compounds, measured in ethanol at 25 °C, was +33.7° (*c* = 0.96) and –33.2° (*c* = 0.83) for (*R*)- and (*S*)-2-heptanethiol, respectively.

Isolation of Volatiles from Bell Peppers. Bell pepper (50 g, red or green) was cut in small pieces and stirred in methylene chloride (100 mL) overnight at room temperature. After removing the solids by filtration, crude extracts were obtained by high vacuum transfer using the SAFE apparatus (14). The resulting clear extracts were dried over sodium sulfate and concentrated on a Vigreux column (50 × 1 cm) and by microdistillation (15) to 0.6 mL.

Extracts of cooked bell pepper were obtained by the simultaneous distillation–extraction method (SDE) using methylene chloride as solvent (16). Crude bell pepper (50 g, red or green) was cut in small pieces and cooked in water (100 mL) for 2 h. The clear extracts (1.3 mL for the green and 2.5 mL for red bell pepper) were dried over sodium sulfate, and the resulting extracts were then concentrated to 0.7 mL on a Vigreux column and by microdistillation (15).

Gas Chromatography–Mass Spectrometry/Olfactometry (GC–MS/O). Mass spectra of the synthesized compounds and their retention indices were acquired using a gas chromatograph GC 5890 (Agilent, Geneva, Switzerland) equipped with two splitless injectors heated at 260 °C and coupled with a quadrupole mass spectrometer MS 5970 (Agilent, Geneva, Switzerland) operating in the electron impact ionization mode at 70 eV. Acquisitions were carried out over a mass range of 10–350 Da. Separations were performed on a 100% dimethyl polysiloxane apolar stationary phase (Ultra-1 PONA, 50 m × 0.20 mm i.d., 0.5 μm film thickness, Agilent) and on a poly(ethylene glycol) polar stationary phase (DB-Wax, 60 m × 0.25 mm i.d., 0.5 μm film thickness, J&W, Folsom, CA). Helium was used as the carrier gas with a constant flow rate of 0.6 and 1.0 mL/min, respectively. The oven was programmed as follows: 20 °C (0.5 min), 70 °C/min to 60 °C, 4 °C/min to 240 °C. The temperature of the transfer line was held at 280 °C during the chromatographic run. Sniffing detection was performed on both stationary phases. The same conditions were used for the GC–MS analysis of bell pepper extracts.

Nuclear Magnetic Resonance (NMR) Spectroscopy. The samples for NMR spectroscopy were prepared in Wilmad 528-PP 5 mm Pyrex NMR tubes using deuteriochloroform as solvent (0.7 mL). The NMR spectra were acquired on a Bruker AM-360 spectrometer equipped with a quadrinuclear 5 mm probe head, at 360.13 MHz for ¹H and at 90.03 MHz for ¹³C under standard conditions (17). All chemical shifts are cited in ppm relative to the solvent signal.

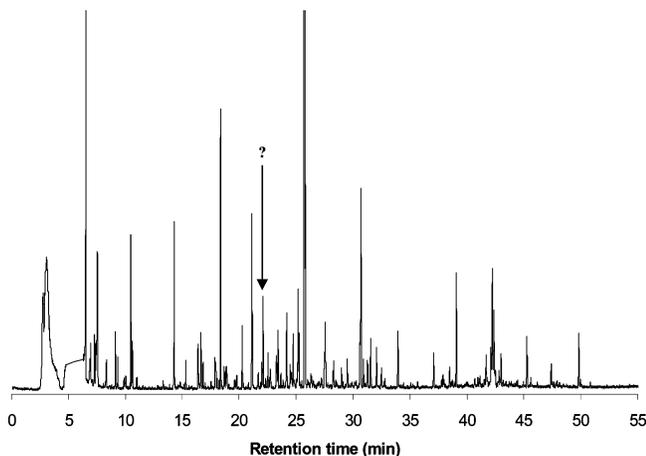


Figure 1. GC-MS profile of a cooked red bell pepper extract obtained on a nonpolar PONA capillary column. The unknown target compound is marked with an arrow.

Polarimetry. Optical activity was measured in ethanol at 25 °C using a Perkin-Elmer 241 polarimeter with a sodium lamp at 589 nm and a slit of 1 mm. The cuvette length was 100 mm.

Threshold Determination. Orthonasal detection thresholds were determined in water (Vittel) by seven panelists. Eight samples were presented in order of decreasing concentrations (a factor of 10 between samples) to estimate the range of threshold concentration. Threshold values were determined by a triangle test using a series of four concentrations (a factor of 2.5 between samples). Threshold values correspond to more than 70% of correct answers.

RESULTS AND DISCUSSION

Investigation of Raw and Cooked Bell Peppers. In this work we focused on the volatile composition of red bell peppers. GC-O analysis performed on two capillary columns revealed a powerful and very typical red bell pepper-like note detected at RI(PONA) = 953 and RI(DB-Wax) = 1170. The compound was also described as sulfury and fruity. The abundance of this compound was relatively high, as shown in **Figure 1**, obtained by GC-MS of a cooked red bell pepper extract on the nonpolar capillary column. Luning and co-workers (5) also found a compound by GC-O having bell pepper-like notes at RI(CP-Wax 52CB) = 1152, which is close to the unknown compound found in this study. Surprisingly, the authors associated the strong red/green bell pepper-like, rubbery notes with Δ -3-carene, which has been described in the literature as terpene-like (18). Indeed, our panel used the descriptors terpenic, limonene-like, and slightly lemon-like for Δ -3-carene, which was baseline separated from the unknown bell pepper-like smelling odorant.

Therefore, additional experiments were performed to clarify the identity of the bell pepper-like odorant. **Figure 2** shows the GC-MS profiles of the raw (SAFE extraction) and cooked (SDE extraction) red and green bell peppers and confirms the presence of the unknown compound in all four extracts. Surprisingly, higher amounts of the thiol were found in cooked samples. It was about 4 times more concentrated in the red bell pepper than in the green variety. However, this compound was already detected at a low concentration level in raw red and green bell pepper.

Identification of 2-Heptanethiol. The corresponding peaks on polar and nonpolar capillary columns revealed identical mass spectra (**Figure 3**), thus confirming that only one specific molecule was imparting this typical note. Interpretation of the mass spectrum indicated the presence of an even fragment at m/z 98, which may stem from the mass at m/z 132 by loss of

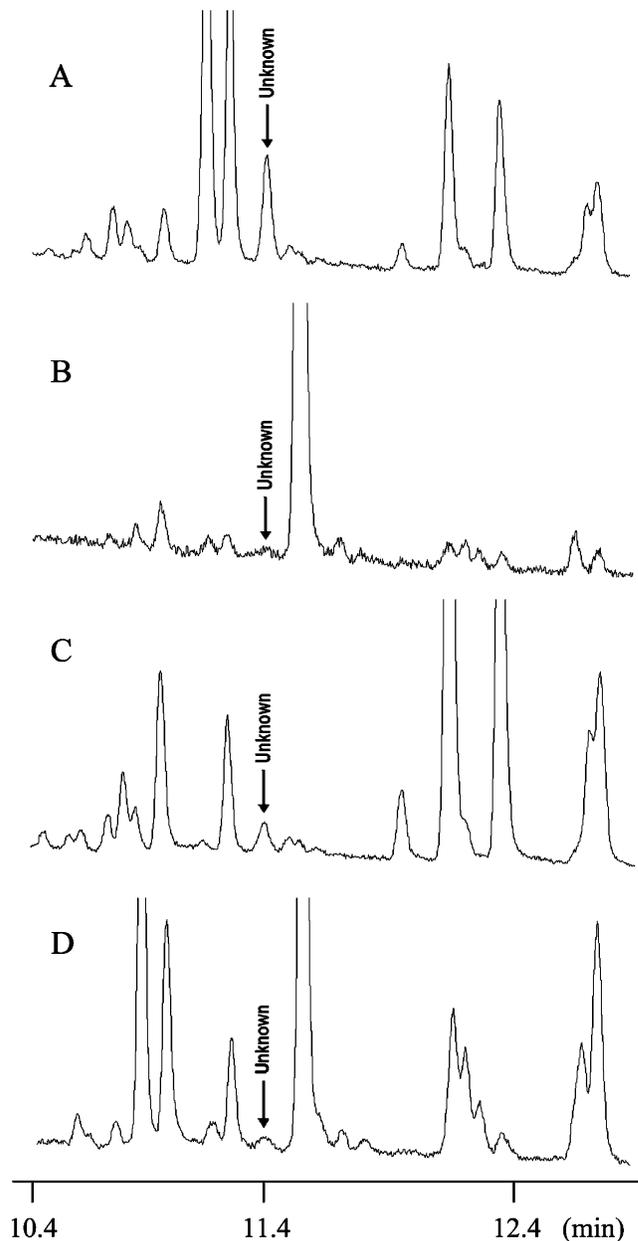


Figure 2. GC-MS profile of liquid bell pepper extracts obtained on a polar DB-Wax capillary column: **A**, cooked red bell pepper; **B**, raw red bell pepper; **C**, cooked green bell pepper; **D**, raw green bell pepper.

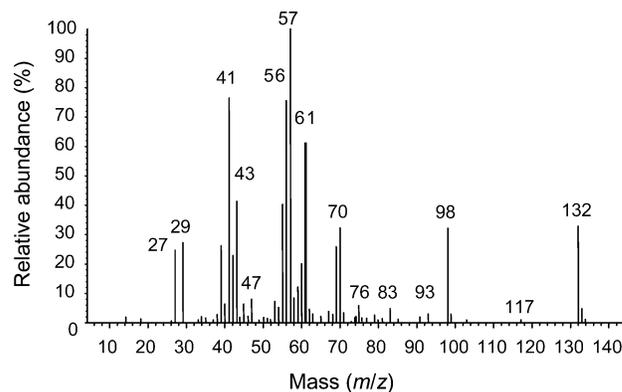


Figure 3. Mass spectrum of the unknown compound.

H_2S . Another main indication for a sulfur compound was the presence of an intense ion at m/z 61, generally associated with a C_2H_5S fragment. Assuming that 132 Da was the molecular

weight of the unknown compound, the isotopic distribution of the molecular peak was $M + 1$ (m/z 133) = 14.5% and $M + 2$ (m/z 134) = 3.6%. The value measured at $M + 2$ was close to the typical isotopic abundance of one sulfur atom (4.4%). This is consistent with the fragment at m/z 61 and a loss of 34 Da corresponding to H_2S . Consequently, the formulas $C_6H_{12}OS$ and $C_7H_{16}S$ were found to be coherent with the MS spectrum.

Moreover, the significant fragment at m/z 61 ($C_2H_5S^+$), as the result of an α -cleavage of the mercaptan, suggested a secondary thiol containing an adjacent methyl group, which is also indicated by m/z 117 ($[M - 15]^+$). The remaining part of the molecule was supposed to be a C_4H_7O or a C_5H_{11} with m/z 71. The base peak at m/z 57 is typical for an ethyl ketone ($MeCH_2COR'$) or an alkyl group with four carbons with or without ramifications (MeC_3H_6R') with $R' = C_3H_7S$ (due to the loss of 75 Da). After combining the two moieties of the molecule, a mass of 14 Da, corresponding to a methylene group, was still missing. Thus, the following hypothetical formulas can be proposed: $MeCH_2COCH_2CH(Me)SH$ or $MeC_4H_8CH(Me)SH$. The only way to associate a secondary thiol and an ethyl ketone with the formula $C_6H_{12}OS$ is 5-mercapto-3-hexanone. Concerning the secondary thiol with the formula $C_7H_{16}S$, five possible formulas were conceivable, but 2-methyl-2-hexanethiol could be excluded because the α -cleavage gives a strong peak at m/z 75 associated with the fragment $C_3H_7S^+$ (CMe_2SH^+).

Consequently, the four possible isomers were synthesized. Only the 2-heptanethiol showed exactly the same mass spectra and retention indices on both columns as the odorant isolated from bell peppers. The sensory properties of the synthetic compound were confirmed by GC-sniffing by three panelists with four repetitions each. 2-Heptanethiol is a new nature-identical component never described in food before. It has been cited as a constituent of crude oil distillate (19), natural gas (20), and in a Japanese patent focusing on asymmetric synthesis of optically active thioesters and thiols (21).

Synthesis of 2-Heptanethiol. The target compound was synthesized from 2-heptanol **1** by activating the hydroxyl function with *p*-toluenesulfonyl chloride (TsCl), followed by two approaches to release the thiol from the intermediate tosylate **2** (Scheme 1). 2-Heptanethiol (**4**) was obtained either by a direct nucleophilic substitution of **2** with sodium hydrogen sulfide (NaSH) or with potassium thioacetate (KSAc) followed by reduction of the thioester **3**. With sodium hydrogen sulfide as nucleophile, the conversion was excellent, but the yield was not satisfactory, most likely due to the instability of the target thiol **4** that easily oxidized to the corresponding disulfide **5** upon distillation (Scheme 1). On the contrary, with potassium thioacetate as nucleophile, the nucleophilic substitution led to 2-(acetylthio)heptane **3** in good yields. Reduction with lithium aluminum hydride resulted in the target thiol.

The synthesis procedure chosen for secondary thiols and thioesters led to racemic mixtures. Both enantiomers of 2-heptanethiol were prepared to evaluate their sensory properties. The acetylthio approach was employed using commercially available pure (*R*)- and (*S*)-2-heptanol as starting materials. The two enantiomers were obtained in 56% and 45% overall yield, respectively. To keep the optical purity, the nucleophilic substitution should be an S_N2 reaction. Polarimetric measurements indicated that no racemization occurred during nucleophilic substitution. The optical rotation of the target compounds was $+33.7^\circ$ ($c = 0.96$, EtOH) and -33.2° ($c = 0.83$, EtOH) for (*R*)- and (*S*)-2-heptanethiol, respectively. Due to Walden inversion, (*S*)- and (*R*)-2-heptanethiol were obtained from (*R*)- and (*S*)-2-heptanol, respectively (Scheme 2).

Table 1. Thiols Synthesized and Their Sensory Properties

compound	odor description	threshold ^c
(<i>R,S</i>)-2-heptanethiol	bell pepper, fruity, vegetables (sulfury, onion, mushroom) ^b	10
2-heptanethiol ^a	fruity (4), sweet (4), tropical (4), fresh (2), floral (1)	nd
(<i>R</i>)-2-heptanethiol	bell pepper, fruity, vegetables (sulfury, onion, mushroom) ^b	10
(<i>S</i>)-2-heptanethiol	bell pepper, fruity, vegetables (sulfury, onion, mushroom) ^b	10

^a Odor description adapted from ref 22. The odor strength of each descriptor was scored from 0 (none) to 5 (strong). ^b Odor description at a higher concentration (about 1 mg/L). ^c Detection threshold in $\mu\text{g/L}$ of water was obtained by orthonasal measurements performed by seven panelists (nd = not determined).

Sensory Properties. The odor properties of 2-heptanethiol are summarized in Table 1. Racemic 2-heptanethiol showed a low orthonasal detection threshold value of 10 $\mu\text{g/L}$ of water. This threshold is similar to the well-known hydrogen sulfide, having a sulfury, egg-like note (9). In high dilution, i.e. about 10-times the threshold, racemic 2-heptanethiol was mainly described as bell pepper-like, fruity, and vegetable-like. At higher concentrations (100–1000 times the threshold), the odor description was completely different: sulfury, onion-like, with some mushroom note. However, no significant difference was observed between the two enantiomers (Table 1). In the literature, the odor of 2-heptanethiol has been described as sweet, fruity, tropical (sulfury), and floral, however, without indicating the threshold value (22). The authors stressed the unique odor of this compound and 2-octanethiol compared to other 1- and 2-alkylthiols.

The bell pepper-like note previously associated with 2-heptanone/heptanal and Δ -3-carene (5–7) was most likely provoked by 2-heptanethiol, considering its physical, chemical, and sensorial properties. On the other hand, 2-heptanol and 2-heptanone were detected in all extracts as possible precursors functionalized in position 2 and owning the same C_7 carbon chain. 2-Heptanone was present in higher amounts in raw green bell pepper than in red bell pepper (data not shown), which is in agreement with literature data (5). The same ratio was observed in cooked bell peppers but at higher concentrations. On the contrary, all samples contained the same low level of 2-heptanol. 2-Heptanethiol might be formed through the metabolism of the plant without any effect of the ripening because of the similar amounts found in raw green and red bell peppers. Alternatively, it might be generated during the cooking process from a precursor that is probably present in higher amount in the mature bell pepper compared to the green sample.

In conclusion, 2-heptanethiol was identified in red bell pepper extracts using combined analytical and synthetic approaches. Its sensory properties suggest that this new flavor compound plays a role in imparting the characteristic red bell pepper note in low concentrations. It may find applications in bell pepper or vegetable flavor compositions.

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NOTE ADDED AFTER ASAP

The original posting of December 3, 2003, contained an incorrect version of Figure 2. The correct version of this figure is included in the posting as of December 5, 2003.

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