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ARTICLE

Identification of Novel Aroma-Active Thiols in Pan-Roasted White Sesame Seeds

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Screening for aroma-active compounds in an aroma distillate obtained from freshly pan-roasted sesame seeds by aroma extract dilution analysis revealed 32 odorants in the FD factor range of 2−2048, 29 of which could be identified. The highest FD factors were found for the coffee-like smelling 2-furfurylthiol, the caramel-like smelling 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, the coffee-like smelling 2-thenylthiol (thiophen-2-yl-methylthiol), and the clove-like smelling 2-methoxy-4-vinylphenol. In addition, 9 odor-active thiols with sulfurous, meaty, and/or catty, black-currant-like odors were identified for the first time in roasted sesame seeds. Among them, 2-methyl-1-propene-1-thiol, (*Z*)-3-methyl-1-butene-1-thiol, (*E*)-3-methyl-1-butene-1-thiol, (*Z*)-2-methyl-1-butene-1-thiol, (*E*)-2-methyl-1-butene-1-thiol, and 4-mercapto-3-hexanone were previously unknown as food constituents. Their structures were confirmed by comparing their mass spectra and retention indices as well as their sensory properties with those of synthesized reference compounds. The relatively unstable 1-alkene-1-thiols represent a new class of food odorants and are suggested as the key contributors to the characteristic, but quickly vanishing, aroma of freshly ground roasted sesame seeds.

KEYWORDS: Roasted white sesame seeds; aroma extract dilution analysis; 2-methyl-1-propene-1-thiol; 2-methyl-1-butene-1-thiol; 3-methyl-1-butene-1-thiol; 4-mercapto-3-hexanone

INTRODUCTION

Sesame (*Sesamum indicum* L.) is an important oilseed crop of the tropics and subtropics. Its cultivation is believed to have begun in the African savannah ∼3000 B.C. During the period of the so-called four great civilizations (China, India, Mesopotamia, and Egypt), sesame was spread out all over the ancient world (*1*). Sesame seeds show high linoleic acid levels in combination with a high antioxidant capacity and, also, an advantageous amino acid balance.

Raw sesame seeds elicit only a weak odor, but the oil obtained by pressing is used as a valuable cooking oil, especially in the Asian cuisine. However, for other sesame products the seeds are roasted, resulting in a unique and highly attractive odor characterized by sulfurous, roasty, nutty, and meaty notes. In Europe and the United States the roasted seeds are a popular topping for bakery products, whereas in Asia the oil isolated from the roasted seeds is used as a seasoning in many dishes. In Japan, mainly ground roasted sesame seeds are consumed, and it is preferred to grind roasted sesame seeds in a small mortar just before consumption to ensure a fresh aroma.

The first attempts to clarify the compounds responsible for the aroma of roasted sesame seeds were performed in the 1960s (*2*−*4*), and these authors already assumed that sulfur-containing compounds may play an important role. Later, the identification of more than 300 volatile compounds was reported (*5*−*19*). However, the sensory contribution of the individual compounds identified to the overall aroma of roasted sesame was addressed in only a few studies (*12*−*17*). A systematic study on the key aroma compounds of roasted sesame seeds was performed by one of the authors of the present paper some years ago. Application of an aroma extract dilution analysis (AEDA) revealed 41 odor-active volatiles (*14*). Ten major aroma-active compounds were subsequently quantified by stable isotope dilution assays (*12*−*14*). According to their high odor activity values (OAV) calculated on the basis of concentrations and odor thresholds (*20*), 2-acetyl-1-pyrroline (popcorn-like), 2-furfurylthiol (coffee-like), 2-phenylethylthiol (rubbery), and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (caramel-like) were identified as key aroma compounds of roasted sesame seeds. However, in these studies the structures of eight compounds with sulfurous or catty aroma notes remained open. The aim of the present research was, therefore, to reinvestigate the aroma-active compounds present in roasted white sesame seeds with special emphasis on the identification of the presently unknown sulfurous and catty smelling odorants.

MATERIALS AND METHODS

Materials. White sesame seeds (Egypt) were purchased in a local supermarket in Garching, Germany. The seeds (250 g) were washed with tap water (500 mL), filtered with a strainer, and then roasted in a frying pan with continuous stirring for 15 min at 200 °C. After freezing with liquid nitrogen, the seeds were ground in a commercial blender.

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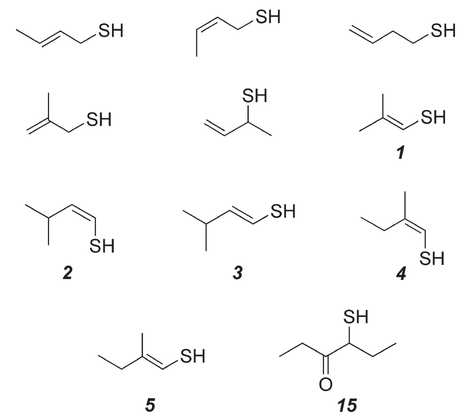


Figure 1. Structures of the 11 thiols prepared by synthesis. Only compounds also identified in sesame seeds are numbered. Numbers of synthesized reference compounds are italicized to differentiate them from the sesame odorants.

Reference Odorants. The following compounds were obtained from the commercial sources given in parentheses: 2-methyl-3-furanthiol, dimethyl disulfide, 2-ethyl-3,5(6)-dimethylpyrazine, and 2-thenylthiol (thiophen-2-yl-methylthiol) (Acros Organics, Geel, Belgium); 3-mercapto-2-pentanone and 2-methoxy-4-vinylphenol (Alfa Aesar, Karlsruhe, Germany); 2-phenylethylthiol (Aldrich, Milwaukee, WI); 4-hydroxy-3-methoxybenzaldehyde (vanillin) (Merck, Darmstadt, Germany); 3-methylthiopropanal (methional), 2-furfurylthiol, and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (Aldrich, Steinheim, Germany); 3-methyl-1*H*-indole (skatole) (Tokyo Chemical Industry Co., Tokyo, Japan). A reference standard from the product line of T. Hasegawa Co., Ltd., was used in the case of 1-octen-3-one. The following compounds were synthesized according to the literature cited: 2-mercapto-3-pentanone (*21*), 3-mercapto-3-methylbutyl formate (*22*), 2-methyl-3-thiophenethiol (*23*), 3-methyl-2-butene-1-thiol (*24*), 2-acetyl-1-pyrroline (*25*), and *trans*-4,5-epoxy-(*E*)-2-decenal (*26*).

Syntheses. General remark: The structures of all compounds newly synthesized are given in **Figure 1**. Only compounds that were also identified in roasted sesame seeds are numbered in bold, but italicized to differentiate them from the odorants having the same structure.

(E)-2-Butene-1-thiol and (Z)-2-Butene-1-thiol (***Figure 1***). A mixture of (*E*)- and (*Z*)-2-buten-1-ol (96:4, 21.5 g, 300 mmol) was dropwise added to a solution of thiourea (29.5 g, 390 mmol) in hydrochloric acid (6 mol/L, 65 mL) kept at room temperature during 15 min. After further stirring for 4 h at 45 °C, sodium hydroxide (10% in water, 158 g) was added. The reaction mixture was heated to 100 °C, and the crude product was distilled off together with the water. The organic layer was separated, dried over anhydrous Na_2SO_4, and distilled under atmospheric pressure (bp, 101 °C) to yield an oil consisting of (*E*)- and (*Z*)-2-butene-1-thiol (5.1 g; yield = 19%). The (*E*)/(*Z*) ratio was determined by GC to be 93:7.

MS-EI (*E*), *m*/*z* (%) 88 (M^+, 91), 73 (10), 55 (100), 54 (43), 53 (24), 47 (11), 45 (21), 39 (31), 29 (24).

MS-EI (*Z*), *m*/*z* (%) 88 (M^+, 89), 73 (10), 55 (100), 54 (58), 53 (25), 47 (11), 45 (21), 39 (36), 29 (25).

3-Butene-1-thiol (***Figure 1***). Thiourea (6.8 g, 88.9 mmol) and 4-bromo-1-butene (10.0 g, 74.1 mmol) were dissolved in ethanol (95%, 50 mL) under an atmosphere of nitrogen. After stirring for 8 h at 80 °C, the reaction mixture was cooled to room temperature, and sodium hydroxide (50% in water, 12 g) was added. After a further 8 h of stirring at 80 °C, the reaction mixture was cooled to 0 °C, acidified to pH ~3 with citric acid (27% in water, 35.5 g), and extracted with *n*-pentane. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed under atmospheric pressure. The crude product was then distilled under atmospheric pressure (bp, ~70−80 °C) to yield 3-butene-1-thiol (560 mg; yield = 9%).

^1H NMR, δ 1.43 (t, J = 7.6 Hz, 1H), 2.38 (dt, J = 7.2, 7.2 Hz, 2H), 2.59 (dt, J = 7.2, 7.6 Hz, 2H), 5.07−5.13 (m, 2H), 5.77 (ddt, J = 7.2, 10.0, 17.2 Hz, 1H).

^{13}C NMR, δ 23.9, 37.9, 116.8, 136.0.

MS-EI, *m*/*z* (%) 88 (M^+, 65), 60 (39), 59 (10), 55 (26), 54 (38), 53 (15), 47 (100), 46 (28), 45 (26), 41 (16), 39 (42).

2-Methyl-2-propene-1-thiol (***Figure 1***). The compound was prepared from 3-chloro-2-methyl-1-propene following the method described above for 3-butene-1-thiol (yield = 12%).

^1H NMR, δ 1.47 (t, J = 8.0 Hz, 1H), 1.85 (s, 3H), 3.14 (d, J = 8.0 Hz, 2H), 4.78 (s, 1H), 4.91 (s, 1H).

^{13}C NMR, δ 20.6, 31.8, 112.1, 144.5.

MS-EI, *m*/*z* (%) 88 (M^+, 98), 73 (18), 60 (15), 59 (11), 55 (100), 54 (46), 53 (34), 51 (10), 50 (10), 47 (20), 45 (31), 41 (13), 39 (66), 29 (22).

3-Butene-2-thiol (***Figure 1***). The target compound was synthesized in a two-step procedure as follows:

(*a*) *3-Buten-2-yl Methyl Dithiocarbonate*. NaH (60%, 48.5 g, 1.21 mol, washed with *n*-hexane prior to use) was suspended in a solution of *N*,*N*-dimethyl-4-aminopyridine (DMAP, 1.22 g, 10 mmol) in tetrahydrofuran (THF, 500 mL). Then, 2-buten-1-ol (30.0 g, 416 mmol) in THF (1 L) was slowly added, and after for 1.5 h of stirring at room temperature, CS_2 (158 g, 2.08 mol) was added to the reaction mixture within 45 min. After further stirring for 30 min at room temperature, methyl iodide (285 g, 2.01 mol) was slowly added within 1 h. The mixture was stirred overnight, and then acetic acid (131 g, 2.18 mol) followed by water (1 L) was added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were successively washed with water and brine, then dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield a colored oil (105.8 g). The crude product was purified by distillation (bp, 69−77 °C/0.8 kPa), yielding 3-buten-2-yl methyl dithiocarbonate (65.2 g; yield = 97%; purity = 79%) as an oil.

MS-EI, *m*/*z* (%) 102 (31), 87 (5), 75 (10), 55 (100), 54 (19), 53 (12), 47 (10), 45 (15), 39 (11), 29 (11).

(*b*) *The synthesis of 3-butene-2-thiol* was finished following a procedure as given by Taguchi et al. (*27*). A mixture of 3-buten-2-yl methyl dithiocarbonate (20.0 g, 123 mmol), 2-aminoethanol (7.5 g, 123 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 0.1 g) was heated to 80 °C with continuous stirring. After a few minutes, the reaction mixture was distilled under atmospheric pressure (bp, ~25−47 °C) to yield a colorless oil (2.0 g). The crude product obtained was further purified by distillation under atmospheric pressure (bp, ~79−80 °C) to yield 3-butene-2-thiol (400 mg; yield = 4%; purity = 89%).

^1H NMR, δ 1.41 (d, J = 7.2 Hz, 3H), 1.66 (d, J = 5.6 Hz, 1H), 3.59 (ddq, J = 5.6, 7.2, 7.2 Hz, 1H), 4.93 (d, J = 10.0 Hz, 1H), 5.09 (d, J = 17.2 Hz, 1H), 5.90 (ddd, J = 7.2, 10.0, 17.2 Hz, 1H).

^{13}C NMR, δ 24.0, 37.4, 112.6, 142.9.

MS-EI, *m*/*z* (%) 88 (M^+, 50), 73 (10), 59 (17), 55 (100), 54 (26), 53 (22), 51 (10), 45 (20), 39 (29), 29 (19).

4-Mercapto-3-hexanone (***15***). The target compound was synthesized in a three-step procedure starting from 4-hydroxy-3-hexanone (**Figure 2**).

(*a*) *4-(Methanesulfonyloxy)-3-hexanone*. 4-Hydroxy-3-hexanone (5.0 g, 43.0 mmol) and triethylamine (13.0 g, 129.0 mmol) were dissolved in diethyl ether (43 mL), and methanesulfonyl chloride (5.9 g, 51.6 mmol) in diethyl ether (10 mL) was added to the solution at 0 °C. After 5.5 h of stirring, water was added, and the organic layer was separated and successively washed with citric acid (10% in water), brine, an aqueous sodium bicarbonate solution (10%), and again with brine and was finally dried over anhydrous $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure to yield crude 4-(methanesulfonyloxy)-3-hexanone (7.3 g), which was directly used in the next step.

MS-EI, *m*/*z* (%) 137 (7), 136 (6), 79 (13), 69 (3), 59 (11), 58 (4), 57 (100), 55 (4), 41 (7), 29 (18).

(*b*) *4-Acetylthio-3-hexanone*. Potassium thioacetate (9.1 g, 80.0 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF, 100 mL), and 4-(methanesulfonyloxy)-3-hexanone (14.0 g, 80.0 mmol) in DMF (140 mL) was added to the solution at 20−30 °C within 1 h. After stirring for 3 h at 35 °C, the reaction mixture was extracted with diethyl ether. The organic layer was washed with an aqueous sodium bicarbonate solution (10%) and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to obtain 4-acetylthio-3-hexanone, which was purified by distillation (bp, ~55−58 °C/0.4 kPa) to yield 4-acetylthio-3-hexanone (10.0 g; yield = 80%; purity > 99%).

MS-EI, *m*/*z* (%) 174 (M^+, 5), 132 (16), 131 (24), 117 (20), 99 (5), 75 (25), 74 (5), 58 (5), 57 (100), 55 (7), 45 (6), 43 (94), 41 (12), 39 (6), 29 (18).

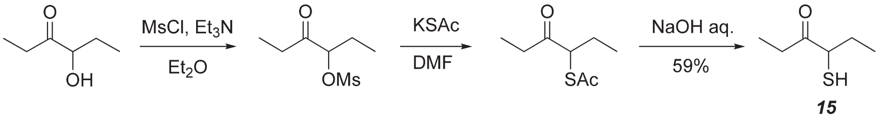


Figure 2. Synthetic approach used in the preparation of 4-mercapto-3-hexanone (***15***).

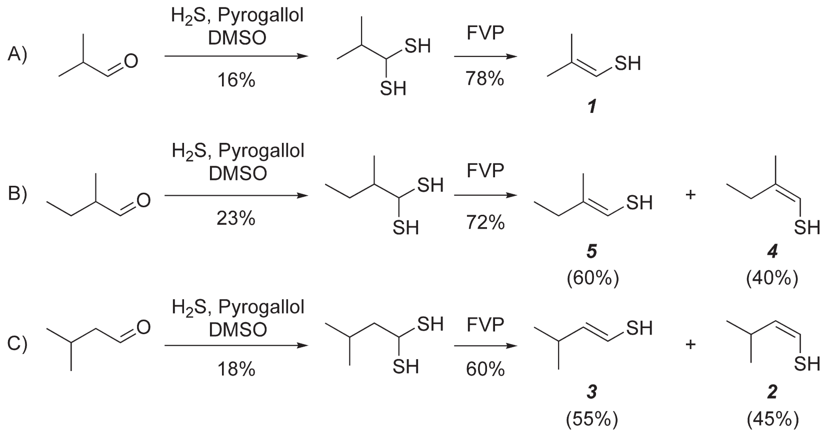


Figure 3. Synthetic approach used in the preparation of (**A**) 2-methyl-1-propene-1-thiol (***1***), (**B**) (*E*)-2-methyl-1-butene-1-thiol (***5***) and (*Z*)-2-methyl-1-butene-1-thiol (***4***), and (**C**) (*E*)-3-methyl-1-butene-1-thiol (***3***) and (*Z*)-3-methyl-1-butene-1-thiol (***2***).

(*c*) *To obtain the thiol,* an aqueous solution of NaOH (5%, 140.0 g, 175.0 mmol) was added to a solution of 4-acetylthio-3-hexanone (8.7 g, 50.0 mmol) in diethyl ether (62.0 g) at ~0−10 °C within 30 min. After stirring for 2 h, the reaction mixture was separated, and the aqueous layer was acidified to pH 4.0 with citric acid (10% in water) and extracted with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue (9.0 g) was distilled (bp, ~45−46 °C/0.8 kPa) to yield the target compound (3.9 g; yield = 59%; purity > 99%).

^{1}H NMR, δ 0.98 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H), 1.70 (ddq, J = 7.2 Hz, 7.2, 14.4, 1H), 1.71 (d, J = 10.4 Hz, 1H), 1.95 (ddq, J = 7.2, 7.2, 14.4 Hz, 1H), 2.53 (dq, J = 7.2, 17.2 Hz, 1H), 2.74 (dq, J = 7.2, 17.2 Hz, 1H), 3.24 (ddd, J = 7.2, 7.2, 10.4 Hz, 1H).

^{13}C NMR, δ 8.2, 11.9, 27.7, 33.3, 48.6, 208.8.

MS-EI, *m*/*z* (%) 132 (M$^+$, 20), 130 (5), 75 (45), 74 (32), 73 (12), 57 (100), 55 (7), 47 (17), 41 (33), 39 (11), 29 (26).

2-Methyl-1-propene-1-thiol (***1***; ***Figure 1***). The target compound was prepared in a two-step synthesis starting from methylpropanal (**Figure 3A**).

(*a*) *2-Methylpropane-1,1-dithiol.* Pyrogallol (0.5 g, 4 mmol) and dimethyl sulfoxide (DMSO, 400 g) were added to 2-methylpropanal (132.3 g, 1835 mmol) at room temperature, and the mixture was slowly cooled to 10 °C. H_2S (102.1 g, 2996 mmol) was passed through the solution for 2 h while the temperature was maintained below 20 °C. Then, the reaction mixture was poured into ice water (600 g) and extracted with diethyl ether. The combined organic phases were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue (77.8 g) was subjected to vacuum distillation, and the distillate was washed with aqueous sodium bicarbonate (10%), dried over anhydrous $MgSO_4$, and filtered to yield a pale yellowish oil of 2-methylpropane-1,1-dithiol (36.7 g; yield = 16%; purity = 97%).

^{1}H NMR, δ 1.03 (d, J = 6.8 Hz, 6H), 2.01 (double septuplet, J = 4.4, 6.8 Hz, 1H), 2.20 (d, J = 6.8 Hz, 2H), 4.08 (dt, J = 4.4, 6.8 Hz, 1H).

^{13}C NMR, δ 18.8, 37.2, 45.7.

MS-EI, *m*/*z* (%) 122 (M$^+$, 25), 89 (69), 88 (40), 79 (28), 73 (17), 59 (15), 55 (100), 47 (16), 45 (41), 41 (17), 39 (23).

(*b*) *To obtain* ***1****,* 2-methylpropane-1,1-dithiol (1.1 g, 9.0 mmol) was subjected to flash vacuum pyrolysis (FVP, 380 °C/0.4 kPa) (*28*, *29*) over 20 min, and a yellowish oil of 2-methyl-1-propene-1-thiol (0.6 g; yield = 78%; purity = 86%) was collected.

^{1}H NMR, δ 1.73 (s, 3H), 1.77 (s, 3H), 2.52 (d, J = 6.8 Hz, 1H), 5.69 (d, J = 6.8 Hz, 1H).

^{13}C NMR, δ 18.8, 25.3, 107.3, 135.8.

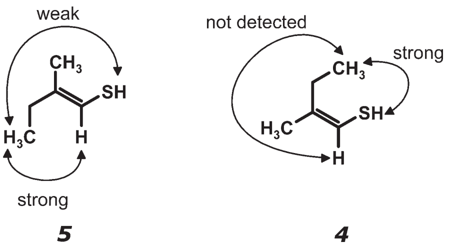


Figure 4. NOE observed for synthesized (*E*)-2-methyl-1-butene-1-thiol (***5***) and (*Z*)-2-methyl-1-butene-1-thiol (***4***).

MS-EI, *m*/*z* (%) 88 (M$^+$, 78), 69 (5), 60 (15), 59 (20), 55 (100), 53 (37), 45 (54), 39 (45), 29 (17).

(*Z*)*-2-Methyl-1-butene-1-thiol and* (*E*)*-2-Methyl-1-butene-1-thiol* (***4*** *and* ***5****;* ***Figure 1***). The target compounds were synthesized starting from 2-methylbutanal as reported above for compound ***1*** following the reaction scheme detailed in **Figure 3B**.

(*a*) *2-Methylbutane-1,1-dithiol.* 2-Methylbutanal was treated with H_2S using the method described above for the synthesis of ***1*** (yield = 24%; purity = 97%).

^{1}H NMR, δ 0.92 (t, J = 7.2 Hz, 3H), 1.04 (d, J = 6.4 Hz, 3H), 1.32 (ddq, J = 7.2, 7.2, 15.2 Hz, 1H), 1.51−1.61 (m, 1H), 1.71−1.80 (m, 1H), 2.14 (d, J = 6.4 Hz, 1H), 2.29 (d, J = 6.4 Hz, 1H), 4.23 (ddd, J = 3.6, 6.4, 6.4 Hz, 1H).

^{13}C NMR, δ 11.6, 14.8, 26.7, 43.7, 44.2.

MS-EI, *m*/*z* (%) 136 (M$^+$, 22), 103 (81), 102 (70), 87 (33), 79 (30), 69 (100), 61 (46), 53 (23), 47 (23), 45(53), 41 (81), 39 (27).

(*b*) *The target compounds* ***4*** *and* ***5*** were prepared by FVP of 2-methylbutane-1,1-dithiol using the parameters described above for the synthesis of ***1*** (yield = 72%; purity = 92%). The (*E*)/(*Z*) ratio was determined by GC to be 60:40. The correct assignment of the GC peaks was achieved by NOESY-NMR of the mixture (**Figure 4**).

^{1}H NMR (***5***), δ 1.00 (t, J = 7.6 Hz, 3H), 1.72 (s, 3H), 2.07 (q, J = 7.6 Hz, 2H), 2.54 (d, J = 7.2 Hz, 1H), 5.71 (d, J = 7.2 Hz, 1H).

^{1}H NMR (***4***), δ 1.00 (t, J = 7.6 Hz, 3H), 1.75 (s, 3H), 2.16 (q, J = 7.6 Hz, 2H), 2.51 (d, J = 7.2 Hz, 1H), 5.67 (d, J = 7.2 Hz, 1H).

^{13}C NMR (***5***), δ 12.4, 22.4, 32.1, 106.4, 140.6.

^{13}C NMR (***4***), δ 11.4, 17.0, 25.8, 106.6, 141.1.

MS-EI (***5***), *m*/*z* (%) 102 (M$^+$, 100), 85 (12), 73 (22), 69 (77), 59 (29), 53 (63), 47 (26), 45 (67), 41 (100).

MS-EI (*4*), *m*/*z* (%) 102 (M^+, 63), 85 (17), 73 (22), 68 (61), 59 (15), 53 (33), 47 (13), 45 (37), 41 (100).

(*Z*)-*3-Methyl-1-butene-1-thiol and* (*E*)-*3-Methyl-1-butene-1-thiol* (*2 and 3*; ***Figure 1***). The target compounds were synthesized by a two-step synthesis as outlined in **Figure 3C**.

(*a*) *3-Methylbutane-1,1-dithiol*. The target compound was prepared by treatment of 3-methylbutanal with H_2S as described above for compound *1* (yield = 18%; purity = 98%).

^{1}H NMR, δ 0.92 (d, J = 6.4 Hz, 6H), 1.74 (dd, J = 7.2, 7.2 Hz, 2H), 1.79−1.93 (m, 1H), 2.36 (d, J = 6.4 Hz, 2H), 4.11 (tt, J = 6.4, 7.2 Hz, 1H).

^{13}C NMR, δ 21.9, 26.7, 37.2, 52.6.

MS-EI, *m*/*z* (%) 136 (M^+, 21), 103 (65), 102 (58), 87 (40), 69 (100), 61 (42), 60 (36), 59 (27), 45(40), 43 (46), 41 (62), 39 (22).

(*b*) *The 1-butene-1-thiol isomers* were prepared by FVP of 3-methylbutane-1,1-dithiol (yield = 60%; purity = 96%). The (*E*)/(*Z*) ratio was determined by GC to be 55:45. The correct assignment of the GC peaks was achieved by ^{1}H NMR of the mixture using the coupling constants of the neighboring olefinic protons at a chemical shift of δ 5.74 and 5.48, respectively.

^{1}H NMR (*3*), δ 0.98 (d, J = 6.8 Hz, 6H, $(CH_3)_2$), 2.61 (double septuplet, J = 6.8, 9.2 Hz, 1H, $CH(Me)_2$), 2.62 (d, J = 9.2 Hz, 1H, SH), 5.48 (dd, J = 9.2, 9.2 Hz, 1H, *i*-Pr—CH=R), 5.87 (dd, J = 9.2 Hz, 1H, R=CH—SH).

^{1}H NMR (*2*), δ 0.97 (d, J = 6.4 Hz, 6H, $(CH_3)_2$), 2.30 (double septuplet, J = 6.4, 6.4 Hz, 1H, $CH(Me)_2$), 2.68 (d, J = 6.4 Hz, 1H, SH), 5.74 (dd, J = 6.4, 15.2 Hz, 1H, *i*-Pr—CH=R), 5.76 (dd, J = 6.4, 15.2 Hz, 1H, R=CH—SH).

^{13}C NMR (*3*), δ 22.1, 31.9, 111.0, 141.4.

^{13}C NMR (*2*), δ 22.0, 27.8, 112.0, 138.5.

MS-EI (*3*), *m*/*z* (%) 102 (M^+, 76), 87 (83), 85 (24), 69 (100), 59 (30), 53 (65), 47 (22), 45 (67), 41 (79), 39 (33).

MS-EI (*2*), *m*/*z* (%) 102 (M^+, 81), 87 (90), 85 (24), 69 (100), 59 (32), 53 (64), 47 (24), 45 (69), 41 (80), 39 (31).

Isolation of the Volatiles. Roasted, ground white sesame seeds (2.5 g) were extracted with dichloromethane (50 mL) at room temperature for 1 h. After filtration, the residue was twice extracted for 30 min with dichloromethane (total volume = 100 mL). The organic phases were combined, and the volatiles were isolated by solvent assisted flavor evaporation (SAFE) (*30*). The SAFE distillate was concentrated to 200 μL at 45 °C using a Vigreux column (60 cm × 1 cm).

Gas Chromatography−Olfactometry (GC-O). GC-O was performed using a Trace GC (Thermo Scientific, Dreieich, Germany) and the following fused silica capillary columns: DB-5, DB-1701, and DB-FFAP (all 30 m × 0.32 mm, 0.25 μm film thickness) (J&W Scientific, Waldbronn, Germany). Samples (0.5 μL) were applied by cold-on-column injection at an oven temperature of 40 °C. Helium at a flow rate of 2.5 mL/min was used as the carrier gas. After 2 min, the temperature was raised at a rate of 6 °C/min to 250 °C (DB-5) or 240 °C (DB-1701) or 230 °C (DB-FFAP), respectively. The column effluent was split 1:1 by volume at the end of the capillary column using a glass splitter and two deactivated fused silica capillaries (50 cm × 0.20 mm). The first was connected to a flame ionization detector (FID) and the second to a heated (250 °C) sniffing port. Linear retention indices (RI) were calculated from the retention times of *n*-alkanes.

Aroma Extract Dilution Analysis (AEDA). The SAFE distillate (200 μL) was stepwise diluted with dichloromethane to prepare dilutions of 1:2, 1:4, 1:8, 1:16, ..., etc. of the original extract. GC-O of the diluted extracts was performed on capillary DB-5, and dilution was continued until no odor was detected during the whole run. Each single odorant was, thus, assigned a flavor dilution factor (FD factor) representing the highest dilution in which the odorant was detected at the sniffing port.

Fractionation of Volatiles by Column Chromatography. For the identification experiments, roasted white sesame seeds (2.5 kg) were extracted with dichloromethane (2.5 L) at room temperature for 1 h. After filtration, the residue was further extracted for 30 min with two more portions of dichloromethane (1.25 L). The combined extracts were concentrated to 2 L, and the volatiles were isolated by SAFE distillation. The distillate was concentrated to 2 mL and applied onto a water-cooled glass column (39 cm × 2.5 cm i.d.) filled with a slurry of purified silica gel (75 g, 7% water) in *n*-pentane (*26*). Elution was performed using four *n*-pentane/diethyl ether mixtures of increasing polarity (100:0, 90:10, 70:30, 50:50, v/v, 450 mL each; fractions A−D). The eluate was collected in four equal portions (fractions A−D), and each fraction was concentrated to 200 μL.

For selective enrichment of thiols, fractions A and B were concentrated to 5 mL and thiols were isolated by affinity chromatography on mercurated agarose gel (*31*).

Gas Chromatography−Mass Spectrometry (GC-MS). For compound identification, mass spectra were generated using a sector field mass spectrometer type MAT 95 S (Finnigan, Bremen, Germany) in the electron impact mode (EI mode) at 70 eV using the columns and the temperature programs detailed above.

When coeluting compounds did not allow unequivocal mass spectra of the target compounds to be obtained, a two-dimensional heart-cut technique using a GC-O/GC-O/MS system was used. This system consisted of a GC Mega 2 (Fisons Instruments, Egelsbach, Germany) equipped with an FFAP column and a GC 5160 (Carlo Erba, Hofheim, Germany) equipped with a DB-5 column (both columns 30 m × 0.32 mm, 0.25 μm film thickness) (J&W Scientific, Waldbronn, Germany). The first GC housed a moving column stream switching system (MCSS) leading the effluent of the first column either to an FID and a sniffing port or via a deactivated fused silica transfer line to the column in the second oven. The end of the second column was simultaneously connected to an ion trap ITD 800 (Finnigan, Bremen, Germany) and a second sniffing port via a Y-shaped glass splitter. To obtain a mass spectrum of an unknown odorant, at its elution time from the first column, which was determined by GC-O in a preliminary run, the MCSS was switched to the transfer line. While collecting the effluent of the first column, a trap section of the transfer line was held at −80 °C. After the collection was stopped, the trap was heated to 250 °C to flush the target compound onto the second column. Elution of the target compound from the second column was monitored at the second sniffing port, and its mass spectrum was simultaneously recorded.

Mass spectra of the synthesized reference odorants and the intermediates were obtained using an Agilent 6890 gas chromatograph connected to a 5973 mass selective detector equipped with a TC-1 capillary column (60 m × 0.25 mm, 0.25 μm film thickness) (GL Sciences Co., Tokyo, Japan). Samples were applied in the split mode (1:50) at 250 °C, and helium at a flow rate of 1.8 mL/min served as the carrier gas. The initial oven temperature was 40 °C. It was held for 2 min, and then the temperature was raised at 3 °C/min to a final temperature of 280 °C. Mass spectra were generated in the EI mode at 70 eV.

Nuclear Magnetic Resonance (NMR) Spectra. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ by means of a JEOL JNM-LA400 spectrometer (JEOL Ltd., Tokyo, Japan) at 400 or 100 MHz, respectively. Chemical shift was recorded in parts per million (ppm) using tetramethylsilane as the internal standard (δ = 0.00 ppm). Coupling constants J are denoted in hertz.

RESULTS AND DISCUSSION

Characterization of Aroma-Active Compounds in Roasted Sesame Seeds. Application of the AEDA on a distillate eliciting the typical aroma of roasted sesame seed, when checked on a strip of filter paper, revealed 32 odor-active compounds in the FD factor range of 2−2048. On the basis of our previous study (*14*), the structures of 16 odorants could readily be assigned and confirmed by means of reference compounds (**Table 1**). In agreement with the earlier results (*14*), 2-furfurylthiol (**10**, coffee-like) and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**21**; caramel-like) showed the highest FD factors, followed by 2-thenylthiol (**24**; thiophen-2-yl-methylthiol; coffee-like) and 2-methoxy-4-vinylphenol (**29**; clove-like). With somewhat lower odor activities, dimethyl trisulfide (**13**), 2-ethyl-3,5-dimethylpyrazine (**23**), and *trans*-4,5-epoxy-(*E*)-2-decenal (**30**) were identified. However, the structures of 14 odorants could not be assigned on the basis of previous data, although 8 of them (**1**, **5−7**, **9**, **15**, **19**, **20**) had already been detected as odor-active compounds in roasted sesame before (*14*), but remained unidentified. Due to their meaty, catty, and/or black-currant-like odors, it can, however, be assumed that these odorants might play a crucial role in the characteristic sulfurous

Table 1. Odor-Active Compounds (FD ≥ 2) in the Aroma Distillate Obtained from Roasted White Sesame Seeds

			RI on			
no.	odorant[a]	odor quality[b]	DB-5	FFAP	fraction[c]	FD factor
1	2-methyl-1-propene-1-thiol	sulfurous, meaty	718	1013	A	4
2	(*Z*)-3-methyl-1-butene-1-thiol	sulfurous, meaty	770	nd[d]	A	4
3	(*E*)-3-methyl-1-butene-1-thiol	sulfurous, meaty	788	nd[d]	A	16
4	(*Z*)-2-methyl-1-butene-1-thiol	sulfurous, meaty	807	1098	A	4
5	(*E*)-2-methyl-1-butene-1-thiol	sulfurous, meaty	818	1105	A	64
6	2-methyl-3-furanthiol	meaty	865	1300	A	256
7	3-mercapto-2-pentanone	catty, black-currant-like	895	1344	B	4
8	3-(methylthio)propanal (methional)	potato-like	902	1452	C	32
9	2-mercapto-3-pentanone	catty, black-currant-like	905	1361	B	2
10	2-furfurylthiol	coffee-like	911	1426	B	2048
11	2-acetyl-1-pyrroline	nutty	924	1326	B	16
12	4-methyl-3-thiazoline[e]	earthy, burnt	932	1422	D	128
13	dimethyl trisulfide	sulfurous, onion-like	967	1370	A	256
14	1-octen-3-one	mushroom-like	978	1295	B	128
15	4-mercapto-3-hexanone	catty, black-currant-like	987	1405	B	4
16	unknown	roasty	996	nd	C	16
17	2-acetylthiazole[e]	popcorn-like	1019	1611	C	16
18	unknown	roasty	1032	nd	C	}256
19	3-mercapto-3-methylbutyl formate	sulfurous, catty	1032	1517	B	
20	2-methyl-3-thiophenethiol	meaty, sulfurous	1054	1556	A	64
21	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	caramel-like	1059	2029	D	1024
22	2-ethyl-3,6-dimethylpyrazine	earthy, potato-like	1079	1449	D	64
23	2-ethyl-3,5-dimethylpyrazine	earthy, potato-like	1086	1449	D	256
24	2-thenylthiol	coffee-like	1088	1676	B	512
25	unknown	roasty	1126	nd	B	128
26	2-phenylethylthiol	rubber-like	1177	1611	B	64
27	2-pentylpyridine[e]	fatty	1198	1507	B	32
28	(*E*,*Z*)-2,4-decadienal[f]	fatty	1296	1763	B	128
29	2-methoxy-4-vinylphenol	clove-like	1315	2193	C	512
30	*trans*-4,5-epoxy-(*E*)-2-decenal	metallic	1383	1997	C	256
31	3-methyl-1*H*-indole (skatole)	fecal	1391	2497	D	64
32	4-hydroxy-3-methoxybenzaldehyde (vanillin)	vanilla-like	1404	2569	D	128

[a] The odorant was identified by comparing it with the reference compound on the basis of the following criteria: retention indices on the stationary phases detailed in the table, odor quality perceived at the sniffing port, and mass spectrum obtained by MS-EI. [b] Odor quality perceived at the sniffing port. [c] Silica gel fractions (*n*-pentane/diethyl ether, v/v): A, 100:0; B, 90:10; C, 70:30; D, 50:50. [d] Due to bad chromatographic behavior a retention index on FFAP could not be determined. Identification was based on the remaining criteria given in footnote *a*. nd, not determined. [e] Tentative identification based on published data (*14*). [f] No unequivocal mass spectrum was obtained. Identification was based on the remaining criteria given in footnote *a*.

aroma of roasted sesame seeds, in particular in the freshly ground state.

Identification of New Aroma Compounds. GC-MS analysis of the SAFE distillate did not allow mass spectra of several unknown odorants to be obtained due to coeluting substances. Therefore, fractionation of the distillate was done to avoid coelutions and to obtain unequivocal mass spectra of the target compounds.

First, column chromatography on silica gel using *n*-pentane/diethyl ether mixtures of different polarities was performed. The eluate was separated into four fractions, and in all fractions the odorants were located by GC-O (**Table 1**).

Identification of Odorants 7 and 9. Compounds **7** and **9**, both showing catty, black-currant-like odors at the low FD factors of 4 and 2, respectively, could be detected in fraction B (**Table 1**). Enrichment from a total of 2.5 kg of sesame seeds succeeded in obtaining a mass spectrum, and finally, by means of the respective reference odorants, these compounds could be identified as 3-mercapto-2-pentanone (**7**) and 2-mercapto-3-pentanone (**9**). The latter was recently also reported by Takeda and co-workers (*19*) as a volatile constituent of ground roasted sesame seeds.

Identification of Odorants 6, 19, and 20. The meat-like smelling compound **6**, showing the highest FD factor among the previously unknown odorants, and, also, compound **20** were enriched in fraction A. Because the odor qualities suggested that these compounds were also thiols, selective enrichment of thiols by affinity chromatography on mercurated agarose gel was applied to fraction A. A further increase in sensitivity was achieved by using a GC-O/GC-O/MS system with a heart-cut interface to monitor their mass spectra. Using this approach allowed the identification of **6** as 2-methyl-3-furanthiol and that of **20** as the corresponding 2-methyl-3-thiophenethiol (**Table 1**).

Compound **19** was found to coelute with a roasty smelling odorant (**18**), but could be separated from **18** in fraction B (**Table 1**). Finally, a mass spectrum was obtained, and the structure of **19** could be assigned as 3-mercapto-3-methylbutyl formate.

Identification of Odorant 1. Using the GC-O/GC-O/MS system, a mass spectrum of odorant **1** was obtained by isolating all thiols from fraction A using the mercurated agarose gel (**Figure 5A**). However, no reference spectrum could be found in the literature. The mass spectrum suggested a formula weight of 88 and the additional fragment *m*/*z* 90, amounting to 4.3% of the intensity of *m*/*z* 88, proposed the presence of one sulfur atom in the molecule. In addition, the fragment ion *m*/*z* 55 indicated the cleavage of an SH group ($M^+ - 33$) and, also, the presence of a butenyl moiety. Thus, the structure of odorant **1** was proposed to be a butenethiol.

To check this assumption, five possible butenethiol isomers were synthesized, namely (*E*)- and (*Z*)-2-butene-1-thiol, 3-butene-1-thiol, 3-butene-2-thiol, and 2-methyl-2-propene-1-thiol (**Figure 1**). First, their retention indices and odor qualities were compared to those of **1**. Due to their clearly different retention indices as

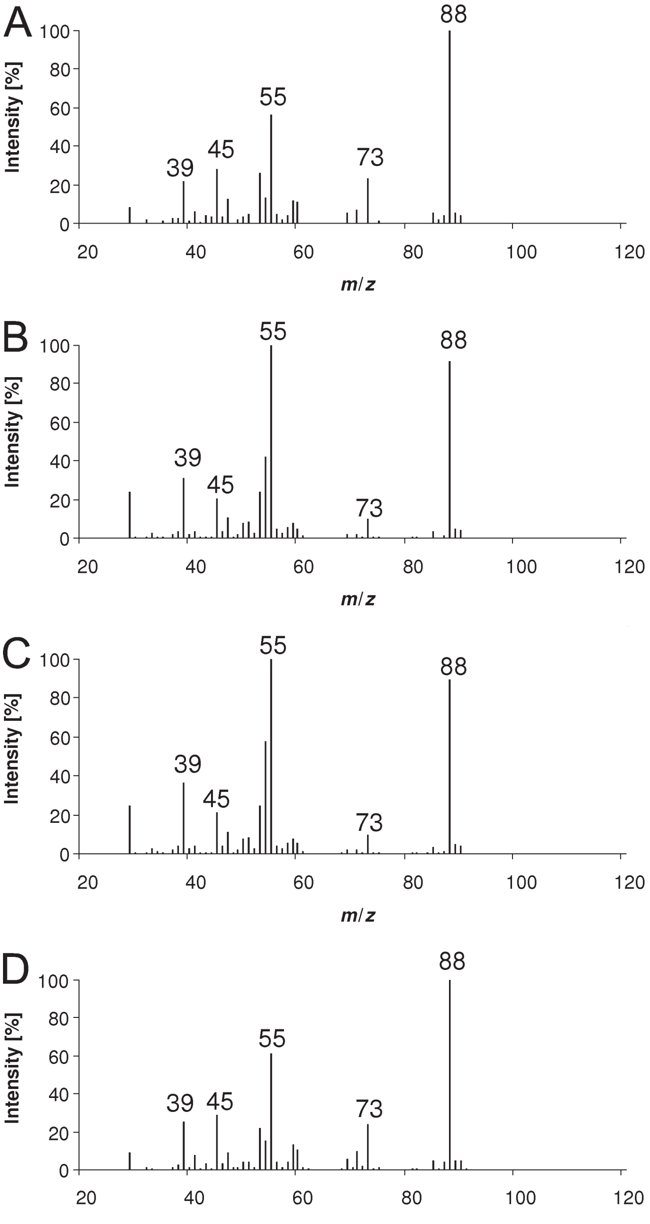


Figure 5. Mass spectra (MS-EI) of odorant **1** (**A**), (*E*)-2-butene-1-thiol (**B**), (*Z*)-2-butene-1-thiol (**C**), and 2-methyl-1-propene-1-thiol (**D**; ***1***).

compared to **1** (DB-5, 718; FFAP, 1013), 3-butene-1-thiol, 3-butene-2-thiol, and 2-methyl-2-propene-1-thiol could be excluded (**Table 2**).

On the other hand, (*E*)- and (*Z*)-2-butene-1-thiol showed similar retention indices, but differed somehow in the mass spectrometric fragmentation patterns (**Figure 5B**,**C**) as well as in their odor qualities (**Table 2**).

At this point it was considered that the thiol group in **1** might be directly bound to the double bond. Because the fragment ion *m*/*z* 73 ($M^+ - 15$), indicating the cleavage of a methyl group (**Figure 5A**), was more abundant in the mass spectrum of **1** than in the mass spectra of the 2-butene-1-thiols (**Figure 5B**,**C**), a branched carbon skeleton was assumed. Consequently, the structure of **1** was proposed to be 2-methyl-1-propene-1-thiol (***1***; **Figure 1**).

Approaches to synthesize 2-methyl-1-propene-1-thiol have already been reported (*32−34*), but these were far from practical. Thus, a new synthetic route leading from the corresponding aldehydes to 1-alkene-1-thiols via the alkane-1,1-dithiols was developed (**Figure 3A**). First, 2-methylpropanal was converted to 2-methylpropane-1,1-dithiol by treatment with H_2S, which was then submitted to flash vacuum pyrolysis (FVP) to induce H_2S elimination leading to the target compound 2-methyl-1-propene-1-thiol (***1***).

Table 2. Odor Qualities and Retention Indices of the Synthesized Thiols

no.	compound	odor quality[a]	RI[b] on DB-5	RI[b] on FFAP
	3-butene-2-thiol	sulfurous	677	<900
	2-methyl-2-propene-1-thiol	sulfurous	689	996
	3-butene-1-thiol	rotten	700	980
	(*E*)-2-butene-1-thiol	sulfurous	717	1006
1	2-methyl-1-propene-1-thiol	sulfurous, meaty	718	1013
	(*Z*)-2-butene-1-thiol	sulfurous	721	1014
2	(*Z*)-3-methyl-1-butene-1-thiol	sulfurous, meaty	770	nd
3	(*E*)-3-methyl-1-butene-1-thiol	sulfurous, meaty	788	nd
4	(*Z*)-2-methyl-1-butene-1-thiol	sulfurous, meaty	807	1098
5	(*E*)-2-methyl-1-butene-1-thiol	sulfurous, meaty	818	1105
15	4-mercapto-3-hexanone	catty, black-currant-like	987	1405

[a] Odor quality perceived at the sniffing port. [b] RI, retention index correlated to a homologous series of *n*-alkanes.

The analytical data of ***1***, such as retention indices (**Table 2**), the mass spectrum (**Figure 5D**), and the odor quality, were identical with those of **1**, and thus, this compound was identified as 2-methyl-1-propene-1-thiol (**Table 1**).

Identification of Odorants 2−5. Odorant **5** (**Table 1**) was first suggested to be 3-methyl-2-butene-1-thiol, because its retention indices (DB-5, 818; DB-FFAP, 1105) were very similar to those of the reference compound (DB-5, 820; DB-FFAP, 1101). In addition, both exhibited a sulfurous, meaty odor quality. However, GC-O/GC-O/MS analysis yielded a mass spectrum (**Figure 6A**) which differed in the intensities from that of 3-methyl-2-butene-1-thiol (**Figure 6B**). Furthermore, the mass spectra of odorants **2**, **3**, and **4**, obtained by GC-O/GC-O/MS analysis of the thiol isolate of fraction A, exhibited similar fragmentation patterns and, also, the same molecular ion (*m*/*z* 102; data not shown), indicating that all four compounds might be isomers of a similar structure.

A comparison of the mass spectrum of **5** (**Figure 6A**) to that of 2-methyl-1-propene-1-thiol (**1**; **Figure 5D**) showed similar cleavage patterns, but indicated a skeleton consisting of five instead of four carbon atoms. Thus, odorant **5** was proposed to be either (*E*)-2-methyl-1-butene-1-thiol or (*Z*)-2-methyl-1-butene-1-thiol or (*E*)-3-methyl-1-butene-1-thiol or (*Z*)-3-methyl-1-butene-1-thiol, respectively, because all fragments in **5** were shifted by 14 mass units as compared to ***1***.

To corroborate this assumption, first (*E*)-2-methyl-1-butene-1-thiol (***5***) and (*Z*)-2-methyl-1-butene-1-thiol (***4***) were synthesized following the synthetic approach used for 2-methyl-1-propene-1-thiol, but using 2-methylbutanal instead as the starting material (**Figure 3B**). Because the aldehydes were converted via the dithiols into 2-methyl-1-butene-1-thiol, the compound was obtained as mixture of (*E*)- and (*Z*)-isomers. The two GC peaks obtained in the synthesis of 2-methyl-1-butene-1-thiol were assigned the correct stereochemistry according to data obtained by NOESY-NMR (**Figure 4**).

Comparison of the retention indices, the mass spectra, and the olfactory properties of synthesized (*E*)-2-methyl-1-butene-1-thiol (***5***; **Figure 1**) and (*Z*)-2-methyl-1-butene-1-thiol (***4***) identified **4** as (*Z*)-2-methyl-1-butene-1-thiol and **5** as (*E*)-2-methyl-1-butene-1-thiol.

The mass spectra of compounds **2** and **3** were quite identical and also showed similarities to compounds **4** and **5** (data not shown). It was, thus, suggested that these odorants might be (*Z*)- and (*E*)-3-methyl-1-butene-1-thiol. Following the approach shown in **Figure 3C**, both compounds were synthesized starting from 3-methylbutanal. The two peaks obtained during synthesis

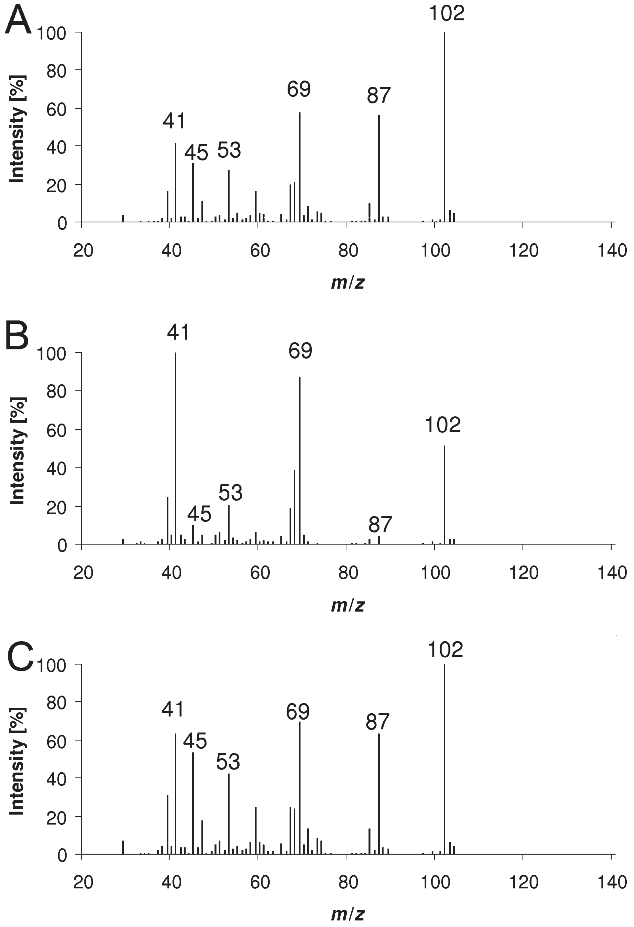


Figure 6. Mass spectra (MS-EI) of odorant **5** (**A**), 3-methyl-2-butene-1-thiol (**B**), and (*E*)-2-methyl-1-butene-1-thiol (**C**; *5*).

were assigned the correct stereochemistry according to the (*E*)/(*Z*) ratio, which was determined by ^{1}H NMR on the basis of the different coupling constants of the protons at the double bond. By comparing the mass spectra, the retention indices, and the odor properties (**Table 2**) of synthesized (*Z*)-3-methyl-1-butene-1-thiol (*2*; **Figure 1**) and (*E*)-3-methyl-1-butene-1-thiol (*3*; **Figure 1**), **2** was identified as (*Z*)-3-methyl-1-butene-1-thiol and **3** as the corresponding (*E*)-isomer.

Identification of Odorant 15. GC-O/GC-O/MS analysis of the thiol isolate of fraction B yielded a mass spectrum for the catty, black-currant-like smelling odorant **15** (**Figure 7**). The identical odor quality suggested that **15** might be a homologue of 3-mercapto-2-pentanone or 2-mercapto-3-pentanone, respectively. Because the retention indices and the molecular mass of 132 pointed to a C-6 compound and the fragment *m/z* 57 suggested a propionyl moiety in the molecule, the structure was proposed to be 4-mercapto-3-hexanone.

To check this assumption, 4-mercapto-3-hexanone was synthesized following a three-step synthesis (*15*, **Figure 2**). Because the reference compound exhibited the same odor quality as odorant **15** and yielded the same mass spectrum as well as the same retention indices, **15** was finally identified as 4-mercapto-3-hexanone.

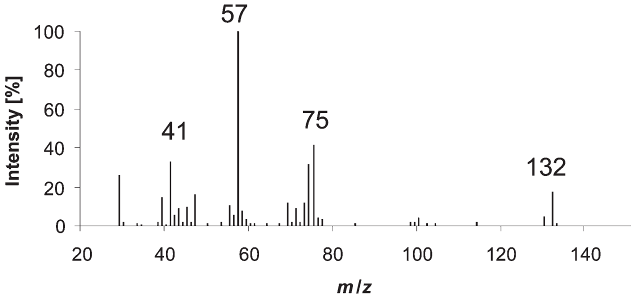
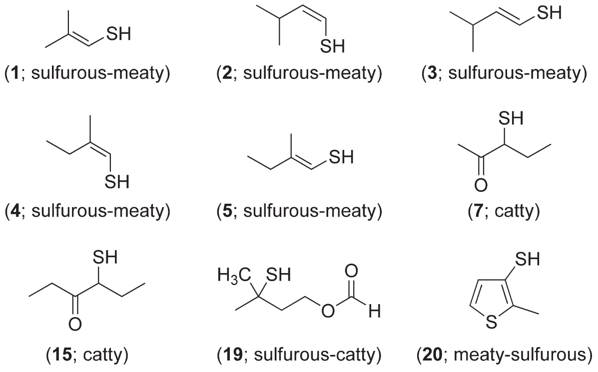


Figure 7. Mass spectrum (MS-EI) of odorant **15** (4-mercapto-3-hexanone).



(**1**; sulfurous-meaty) (**2**; sulfurous-meaty) (**3**; sulfurous-meaty)
(**4**; sulfurous-meaty) (**5**; sulfurous-meaty) (**7**; catty)
(**15**; catty) (**19**; sulfurous-catty) (**20**; meaty-sulfurous)

Figure 8. Chemical structures of the compounds identified for the first time in roasted sesame or in foods (**1**−**5**, **15**), respectively.

In summary, nine odor-active thiols with sulfury, meaty, and/or catty, black-currant-like odor qualities, so far unknown in roasted sesame seeds, were identified in this study (**Figure 8**). Among them, to the best of our knowledge, 2-methyl-1-propene-1-thiol (**1**), (*Z*)-3-methyl-1-butene-1-thiol (**2**), (*E*)-3-methyl-1-butene-1-thiol (**3**), (*Z*)-2-methyl-1-butene-1-thiol (**4**), (*E*)-2-methyl-1-butene-1-thiol (**5**), and 4-mercapto-3-hexanone (**15**) were identified for the first time in a food product. In particular, the 1-alkene-1-thiols might play an important role in the characteristic and intense aroma of freshly ground sesame. Their instability and their high volatility might explain the fact that the aroma of roasted sesame quickly loses its freshness after grinding (*35*) and may also account for their relatively low FD factors found in AEDA. To unequivocally evaluate the aroma impact of these novel odorants, their quantitation by stable isotope dilution assay, followed by calculation of odor activity values (OAV: ratio of concentration to odor threshold), is underway.

ABBREVIATIONS USED

AEDA, aroma extract dilution analysis; BHT, 2,6-di-*tert*-butyl-4-methylphenol; DMAP, *N*,*N*-dimethyl-4-aminopyridine; FD factor, flavor dilution factor; FID, flame ionization detector; FVP, flash vacuum pyrolysis; GC-O, gas chromatography−olfactometry; MCSS, moving column stream switching system; NOESY, nuclear Overhauser effect correlated spectroscopy; OAV, odor activity value; RI, retention index; SAFE, solvent assisted flavor evaporation; SIDA, stable isotope dilution assay.

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