Screening of deodorizing active compounds from natural materials and deodorizing properties of cineole

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Plant extracts were screened to identify novel deodorizing natural products. Deodorizing activity was detected in an aqueous ethanol extract of cluster mallow leaves by measuring headspace gas by GC (deodorizing activity was defined as percent reduction in headspace odorant concentration following deodorant addition in vitro). The deodorant compound was purified using silica gel column chromatography, and the active principle was identified as 1,8-cineole by GC/MS analysis. 1,8-Cineole strongly deodorized (>90%) a relatively wide range of odorous gases, including 2-nonenal, skatole, dimethyl trisulfide, indole, isovaleric acid, and dimethyl disulfide. The compounds also moderately deodorized (>70%) allyl methyl sulfide, n-butyric acid, allyl mercaptan, and dimethyl sulfide. Organoleptic assessment conducted by sniffing headspace gas showed a reduction in odor score of 1.5 to 3. Correlative relationships were observed between 1,8-cineole’s deodorizing activity and odorant molecular weight and boiling point. Furthermore, odorants adsorbed onto 1,8-cineole desorbed with increasing temperature, suggesting a physical deodorizing mechanism of cineole. Cineole is known to mask or hide ambient odorants by overwhelming the malodor with pleasant odor. Our study suggests that in addition to odor-masking activity, 1,8-cineole exhibits another deodorizing mechanism in which the gaseous odorant concentration is reduced via adsorption involving physical interaction between 1,8-cineole and odorant molecules. 1,8-Cineole may thus serve as an effective agent for eliminating various unpleasant odors.

1. Introduction

In recent years, large-scale industries such as livestock agriculture, food processing, and wastewater treatment have expanded greatly. These industries often generate numerous types of unpleasant odors, sometimes resulting in complaints from nearby residents. Open-air incineration and restaurants (e.g., beef barbecue restaurants) become sources of odor-related complaints in some cases. In the course of daily life at home, we also often experience unpleasant odors. These odors can arise from a variety of sources, including pet waste, spoiled food (e.g., rotten onions/fish), and raw garbage. Unpleasant breath odor is also experienced at some time in our lives.

Odorous gases have a variety of chemical structures, and include aldehydes, esters, nitrogen-/sulfur-bearing compounds, and short-chain fatty acids. The number of odor compounds is estimated at over 400,0001. Odor control methods can be classified into 4 categories, depending on the deodorizing mechanism: (1) physical methods, such as the use of activated carbon or silica gel to absorb malodorous compounds; (2) biological methods, such as the use of sanitizers that inactivate malodor-producing bacteria; (3) chemical methods, which involve chemical inactivation of malodorous compounds; and (4) sensory methods, which involve masking unpleasant odors with fragrances.

Deodorant manufacturers have developed a variety of products employing these mechanisms. For example, green tea, whose primary components are polyphenols (catechins) such as (−)-epigallocatechin gallate, (−)-epigallocatechin, (−)-epicatechin gallate, and gallic acid, exhibits potent deodorizing activity2; thus, deodorant products containing green tea catechins are widely used. Kaki-tannin, the primary ingredient in astringent persimmon fruit, is also widely used in Japan and Southeast Asia for breath odor–neutralizing supplie-
ments, chewing gums, air fresheners, pet deodorants, deodorant lotions, etc.\textsuperscript{3} The deodorization mechanisms of polyphenolic compounds are reportedly chemical reactions including addition, degradation, and replacement\textsuperscript{4,5}. Several sulfur-containing gases arising from vegetables of the \textit{Allium} species can be reduced chemically or physicochemically by raw foods such as fruits, vegetables, and mushrooms\textsuperscript{6} (we will cover this point in more detail below). Among the odorous gases associated with breath odor, including garlic breath (i.e., an unpleasant odor released after garlic consumption), hydrogen sulfide (HS) and methyl mercaptan (MM) are almost totally deodorized by green tea \textit{in vitro}, and the levels of these odors are reduced significantly \textit{in vivo}\textsuperscript{2}, while allyl methyl sulfide (AMS) is poorly deodorized compared with HS and MM \textit{in vitro} and \textit{in vivo}\textsuperscript{3}. As such, compounds with potent deodorizing activity against AMS have attracted interest as screening targets for new odor-reducing agents.

In our screening programs to isolate active substances exhibiting deodorizing activity against AMS, we identified 1,8-cineole from cluster mallow leaves. Here, we focused upon 1,8-cineole and its isomer, 1,4-cineole, and investigated the deodorizing activity–related properties of these substances (\textit{Figure 1}).

\section{Materials and Methods}

\textbf{Chemicals.} 1,8-Cineole (hereafter 1,8-C; purity: 99.8\%), 1,4-cineole (hereafter 1,4-C; purity: >95\%, Sigma-Aldrich, St. Louis, MO, USA), silica gel (Wakosil C-300), MM, and dimethyl trisulfide (DMTS) were purchased from Wako Pure Chemical Industries (Tokyo, Japan). Finely ground leaves of cluster mallow (Chinese herbal preparation) were obtained from Kahya Co., Ltd. (Osaka, Japan). 2-Nonenal and AMS were obtained from Alfa Aesar (Ward Hill, MA, USA); skatole, allyl mercaptan (AM), and dimethyl sulfide (DMS) were obtained from Acros Organics (Pittsburgh, PA, USA); indole and butyric acid were obtained from Kishida Chemical Co. (Osaka, Japan); and dimethyl disulfide (DMDS), isovaleric acid, and diacetyl were obtained from Tokyo Chemical Industry (Tokyo, Japan).

\textbf{Preparation of screening samples.} A variety of natural materials were purchased from local markets, including fruits (23 types), vegetables (18 types), seeds (12 types), teas/herbal plants (33 types), sea weeds (13 types), and mushrooms (10 types). The natural materials were initially lyophilized and processed by grinding using a mortar. Commercially dried and ground plant materials, such as a variety of teas/herbal plants, including leaves of cluster mallow, were also screened. A total of 109 samples were screened (\textit{Table 1}).

To prepare screening samples, natural material prepared as described above (10 g) was weighed in a conical flask, to which 100 mL of 50% aqueous ethanol was then added and stirred for 30 min at room temperature using a magnetic mixer. The sample was then centrifuged for 10 min (1500 g), and the supernatant was collected. The sample was re-extracted twice using the method described above. The ethanol was removed from the combined extract using a rotary evaporator. The final concentrated extract solutions were then lyophilized and powdered.

For gas chromatography (GC) analyses for screening, approximately 100 mg of the sample suspended in 1 mL of deionized water was placed in a separate 300-mL conical flask. A variety of phenolic compounds with deodorizing activity, such as catechins, have been isolated from plant extracts and identified to date. To minimize the possibility of isolating known phenolic compounds, we selected samples that gave negative results in a ferric chloride test (ferric chloride test: a few drops of 10\% ferric chloride solution are added to the test sample solution; the formation of bluish-black color indicates the presence of phenolic compounds). For specific analysis of the deodorizing activity against various odorous chemicals, cineole (a colorless liquid) was placed directly inside a 300-mL conical flask just below the neck using a micropipette (cineole volume: 110 µL, 220 µL, or 330 µL), and GC analyses were conducted.

\textit{GC and gas detector tube analyses.} Screening the natu-
reral materials for deodorizing activity was performed via GC. In each assay, the sample was placed in a 300-mL conical flask as described above, and then 10 µL of AMS (or other odorous chemical solution) was injected into the flask through the Parafilm® covering the flask mouth using a microsyringe and the same method described above for cineole. The mouth of the flask was sealed tightly with Parafilm® again (double sealed) immediately after addition of the odorous chemical solution. The flask was left to stand for 60 min at 25°C, and then 2 mL of the headspace gas was analyzed on a Shimadzu GC-2014AF GC apparatus. We assumed that the loss of odorous gases by permeation through the Parafilm and by adsorption onto the glass during 60 min of incubation at 25°C (deodorizing reaction completely or almost completely reached plateau values) was not significantly different between the sample flask and control flask. In the case of DMTS, the loss was 2.4% (average of three measurements). Details regarding GC conditions are shown in Table 2. The initial concentration of odorous chemical was 1 ppm in the gas phase, with the following exceptions: for skatole, indole, isovaleric acid, and diacetyl, the initial concentration was 10 ppm, because the GC peaks for these gases at a concentration of 1 ppm were too small under the GC conditions used to allow for quantification. We observed that the deodorizing activity of cineole was unaffected by the initial concentrations of odorous gases tested (Table 3).

Deodorizing activity, expressed as percent reduction in odorous gas concentration in the headspace, was calculated using the following formula: deodorizing activity (%) = (C – S)/C × 100, where C represents the peak area for the authentic chemical standard in the headspace gas of the reaction mixture without a test sample (control), and S represents the peak area for the headspace gas of the reaction mixture containing the test sample.

An AP-20 Kitagawa Gas Detector Tube System was used to detect acetic acid, trimethylamine (TMA), acetaldehyde, and ammonia. A tube connected to an aspirating pump was inserted through a slit in the Parafilm covering the sample flask made using a knife, and a 100-mL sample of the headspace gas was withdrawn and analyzed using the gas detector. The odorant concentration (ppm) was determined by direct reading from the scale on the tube. Deodorizing activity (%) was calculated using the formula described above for GC analyses. For gas detector analyses, the initial concentration of malodorous chemical was 10 ppm.

Solid-phase micro-extraction (SPME) and GC/MS conditions for determination of the active principle. A 2-mg sample was placed in a 2-mL screw-top vial. Collection of volatile compounds was accomplished using a 15-min adsorption period at 60°C, during which the sample was shaken. The SPME fiber introduced into the headspace of the sample vial was an 85-µm layer of Carboxen/PDMS Stable Flex (Sigma-Aldrich Co.). After SPME, the compounds were analyzed using GC/MS. GC/MS was performed using a Hewlett Packard HP5890 Series II gas chromatograph coupled to a Hewlett Packard HP5872 series mass spectrometer. A DB-WAX capillary column (60 m × 0.25 mm i.d.; film thickness: 0.25 µm) was used for separation. High-purity helium was used as the carrier gas at a flow rate of 1.2 mL/min. The column temperature was programmed to increase from 40°C (held for 4 min) to 200°C at 4°C/min. The injection and detection temperatures were 260 and 220°C, respectively. The ionization voltage was set at 70 eV. Chemical components were identified by comparing their mass spectra and retention times to those of commercially available library standards (NIST Chemistry WebBook).

Fractionation of cluster mallow leaf extract using silica gel column chromatography. The 50% aqueous ethanol extract of finely ground leaves of cluster mallow was re-extracted and fractionated as follows. Lyophilized and powdered extract (200 g), prepared as described above, was suspended in water (3.5 L), stirred for 30 min, and then divided into two portions by centrifugation: water soluble and insoluble. After the extraction procedure was repeated twice, 181.4 g of watersoluble material and 11.4 g of insoluble material were obtained. The water-insoluble material was soluble in CHCl₃ and exhibited relatively stronger deodorizing activity compared with the soluble material and a negative ferric chloride test result, which indicated the absence of phenolic compounds such as catechins in the insoluble portion. The silica gel column (silica gel: 170 mL) was prepared using a Komagome pipette with CHCl₃. The column was 20 cm in length, with a 4-cm internal diameter. The column was loaded with the CHCl₃-soluble extract material (8.9 g) and eluted with
| No. | English name     | Scientific name* | D.A.*  | No.          | English name          | Scientific name* | D.A.*  |
|-----|-----------------|------------------|--------|-------------|-----------------------|------------------|--------|
| 1   | Asparagus       | Asparagus        | 6.0    | 34          | Passion fruit         | Passiflora edulis| 19.0   |
| 2   | Bell pepper     | Capsicum annuum  | 0      | 35          | Peach                 | Amygdalus persica| 7.8    |
| 3   | Bitter melon    | Momordica charantia | 15.5  | 36          | Pineapple             | Ananas comosus   | 19.0   |
| 4   | Cabbage         | Brassica oleracea| 0      | 37          | Plum                  | Prunus           | 7.0    |
| 5   | Carrot          | Daucus carota    | 14.5   | 38          | Prune                 | Prunus domestica | 7.0    |
| 6   | Cauliflower     | Brassica oleracea| 28.5   | 39          | Raspberry             | Prunus           | 9.4    |
| 7   | Cucumber        | Cucumis sativus  | 0      | 40          | Watermelon            | Citrullus laurus | 0      |
| 8   | Crown daisy     | Arctium lapa     | 26.3   | 41          | Garden strawberry     | Fragaria         | 92.0   |
| 9   | Edible burdock  | Solanum melongena kouki | 52.2 | 42          | Almond                | Amygdalus dulcis | 13.0   |
| 10  | Eggplant        | Solanum lycopersicum | 0   | 43          | Common gardenia       | Gardenia jasminoides | 12.1 |
| 11  | Indian spinach  | Basella alba     | 0      | 44          | Common Hazelnut (Hazelnut) | Corylus avellana | 20.4   |
| 12  | Japanese radish | Raphanus sativus | 0      | 45          | Japanese Chestnut     | Castanea crenata | 7.8    |
| 13  | Kabocha squash  | Cucurbita maxima | 18.4   | 46          | Kabocha squash (seed) | Genus Cucurbita | 40.7   |
| 14  | Komatsuna       | Brassica rapa    | 15.8   | 47          | Macadamia nut         | Macadamia integrofolia | 11.4 |
| 15  | Okra            | Abelmoschus esculentus | 0   | 48          | Pecan                 | Carylla illiniosiens | 29.9 |
| 16  | Shallot         | Allium cepa      | 0      | 49          | Pine nut              | Genus Pinus      | 36.4   |
| 17  | Tomato          | Solanum lycopersicum | 0   | 50          | Pistachio             | Pistacia vera    | 21.6   |
| 18  | Zucchini        | Cucurbita pepo   | 0      | 51          | Pistachio (hull)      | Pistacia vera    | 25.7   |
| 19  | Apricot         | Prunus armeniaca | 5.2    | 52          | Sunflower             | Helianthus annuus | 17.3   |
| 20  | Apple           | Malus pumila     | 0      | 53          | Walnut                | Genus Juglandia | 22.2   |
| 21  | Banana          | Genus Musa       | 7.7    | 54          | Artab                | Coix lacryma-jobi | 12.6  |
| 22  | Blueberry       | Genus Vaccinium  | 11.1   | 55          | Bitter melon (fruit)  | Momordica charantia | 33.7 |
| 23  | Cherry          | Genus Prunus     | 6.3    | 56          | Cat’s Claw (root, bark) | Uncaria tomentosa | 0     |
| 24  | Dragon fruit    | Hyllocercus undatus | 10.3 | 57          | Cluster maize (leaf)  | Malva verticillata | 71.9   |
| 25  | Fig tree        | Ficus carica     | 6.5    | 58          | Dandelion (leaf)      | Taraxacum officinale | 39.3 |
| 26  | Grape (Delaware)| Genus Vitis      | 10.0   | 59          | Echinacea            | Echinacea purpurea | 13.9  |
| 27  | Grapefruit      | Citrus × paradisi| 11.9   | 60          | Field Horsetail (epigeal stem) | Equisetum arvense | 14.1   |
| 28  | Kiwifruit       | Actinidia delicosa| 0   | 61          | Fishwort (leaf)       | Houttuynia cordata | 46.8   |
| 29  | Lemon           | Citrus limon     | 5.0    | 62          | Gardenia             | Garcinia gummi-gutta | 18.6   |
| 30  | Lime            | Citrus aurantiifolia | 23.7  | 63          | Guava                | Psidium guajava  | 42.2   |
| 31  | Lychee          | Litchi chinensis | 6.7    | 64          | Gymnema              | Gymnema sylvestre | 35.5   |
| 32  | Nashi Pear      | Pyrus pyrifolia  | 9.6    | 65          | Hibiscus (flower)     | Hibiscus sabdariffa | 40     |
| 33  | Papaya          | Carica papaya    | 8.0    | 66          | Isodon Herb (Enmeisou) | Rhabdosia japonica | 57.3   |
| No. | Herbal Plants (continued)                                                                 | Genus/Species | Odor Activity |
|-----|------------------------------------------------------------------------------------------|----------------|---------------|
| 67  | Japanese Honeysuckle                                                                       | Lonicera japonica | 12.8          |
| 68  | Khat                                                                                     | Catha edulis    | 0             |
| 69  | Kothalhimbutu                                                                            | Salacia reticulata | 0             |
| 70  | Ku Ding tea (leaf)                                                                         | Ilex kudingcha  | 29.1          |
| 71  | Kumazasa (leaf)                                                                            | Sasa veitchii   | 12.6          |
| 72  | Loquat (leaf)                                                                              | Eriobotrya japonica | 14.6          |
| 73  | Lotus (flower)                                                                             | Nelumbo nucifera | 19.7          |
| 74  | Mate (leaf, twig)                                                                          | Ilex paraguariensis | 26.7          |
| 75  | Melilot (Sweet clover)                                                                     | Melilotus officinalis | 13.5          |
| 76  | Morning-glory                                                                             | Ipomoea nil     | 20.3          |
| 77  | Mulberry (leaf)                                                                            | Genus Morus     | 53.2          |
| 78  | Olive (leaf)                                                                               | Olea europaea   | 25.6          |
| 79  | Persimmon (leaf)                                                                           | Diospyros kaki  | 34            |
| 80  | Kothalhimbutu                                                                             | Salacia reticulata | 0             |
| 81  | Snow tea                                                                                 | Thamnomanes callianicae | 32          |
| 82  | Taheebo (inner bark)                                                                       | Tabebuia avellanedae | 10.7          |
| 83  | Green tea                                                                                | Camellia sinensis | 20.0          |
| 84  | Tencha                                                                                   | Rubus suavissimus | 61.7          |
| 85  | Tochu (leaf)                                                                              | Escaramia ulmoides | 32.7          |
| 86  | Rafuma (leaf)                                                                              | Apocynum venetum | 0             |

| No. | Marine Algae                                                                            | Genus/Species   | Odor Activity |
|-----|-----------------------------------------------------------------------------------------|----------------|---------------|
| 87  | Wakame                                                                                  | Undaria pinnatifida | 29.2          |
| 88  | Kombu                                                                                   | Saccharina japonica | 62            |
| 89  | Arame                                                                                   | Eisenia bicyclis | 56.3          |
| 90  | Hijiki (stalk)                                                                            | Sargassum fusiforme | 15.5          |
| 91  | Hijiki (bud)                                                                              | Sargassum fusiforme | 16.6          |
| 92  | Mozuku                                                                                    | Nemacystus decipiens | 97            |
| 93  | Tosakanori                                                                               | Meristotheca paupulosa | 11.8          |
| 94  | Tsunomata                                                                                | Chondrus ocellatus | 38.0          |
| 95  | Akamoku                                                                                  | Sargassum horneri | 12.5          |
| 96  | Kuhiretsuta                                                                              | Caulerpa lentillifera | 86           |
| 97  | Matsumo                                                                                  | Analips japonicus | 86            |
| 98  | Funori                                                                                   | Genus Gloiopeltis | 73            |
| 99  | Tengusa (agar)                                                                            | Gelidium elegans | 10.3          |
| 100 | Shiitake mushroom                                                                         | Lentinula edodes | 11.8          |
| 101 | Enokitake                                                                                | Flammulina velutipes | 0            |
| 102 | King trumpet mushroom                                                                     | Pleurotus eryngii | 0             |
| 103 | Butterscotch mushroom                                                                     | Pholiota microspora | 17.7          |
| 104 | Golden oyster mushroom                                                                   | Pleurotus cornucopia | 52.5          |
| 105 | White mushroom                                                                           | Agaricus bisporus | 11.8          |
| 106 | Buna shimeji                                                                             | Hypsizigus marmoreus | 10.9        |
| 107 | Maitake                                                                                  | Grifola frondosa | 0             |
| 108 | Jew’s Ear Fungus                                                                         | Auricularia auricula-judae | 66          |
| 109 | Snow fungus                                                                              | Tremella fusiformis | 61            |

a) Genus and species or genus alone are cited from Wikipedia.
b) D.A.: deodorizing activity
CHCl₃. The fraction volume was 200 mL, and a total of 20 fractions were collected. For analysis of the deodorizing activity of each fraction, 100 µL of chloroform eluate from each fraction was added to a 300-mL conical flask, and the chloroform was evaporated to dryness by incubation at room temperature.

**Desorption analyses.** Desorption experiments were conducted using a Shimadzu headspace sampler HS-20 and GCMS-TQ8040 system. A total of 50 mg of 1,8-C and 100 ppm of odorous gas, including 2-nonenal, DMDS, isovaleric acid, n-Butyric acid, 2-Nonenal, Indole, Skatole, DMDS, and Indole, was placed directly inside a 20-mL HS vial and incubated at 37℃ for 1 h. Under these conditions, 99.5–99.7% of each odorous gas was adsorbed to 1,8-C. The HS-20 vial containing 1,8-C with adsorbed odorous gas was left to stand for 60 min at 50, 75, 100, or 150℃, and then the desorbed gas was measured.

**Organoleptic measurement (OM).** OMs were performed as follows. A 300-mL conical flask containing 50 mg of cineole was incubated with a variety of odorous gases at 25℃ for 60 min. To prepare odorous gas solutions, 1:10 or 1:2 dilutions of original odorous solutions were prepared to give a range of concentrations appropriate for organoleptic measurements with a 3–4 malodor intensity level. The volume of odorous gas solution injected into the 300-mL flask was 2–10 µL. The judges sniffed the odorant-containing air inside the odor flask directly after giving oral consent to participate in the study, which was conducted with reference to the “Olfactory Measurement Method Safety Management Manual,” published by the Ministry of the Environment, Government of Japan.

### Table 2  Gas chromatography conditions.

| Malodorous gas | Column  | Detector | Temperature (℃) | Carrier gas flow rate a |
|---------------|---------|----------|------------------|-------------------------|
| DMDS, DMTS   | Unisole F-200 30/60 | FPD | 120 | 80 | 20 |
| MM, AMS, AMS | Unisole F-200 30/60 | FPD | 120 | 50 | 20 |
| Isovaleric acid n-Butyric acid 2-Nonenal | Unisole F-200 30/60 | FPD | 200 | 120 | 50 |
| Indole, Skatole | OV-17 60/80 | FID | 200 | 120 | 50 |
| Diacetyl | Sunpak-A 50/80 | FID | 230 | 180 | 50 |

Notes: a Nitrogen, mL/min; b Detector temperature, 200℃.

### Table 3  Deodorizing activity (%) of 1,8-cineole against different initial concentrations of malodorous gases.

| Initial concentration (ppm) | 1  | 10 | 50 | 100 |
|-----------------------------|----|----|----|-----|
| DMDS                        | 91±0.5 | 96±0.4 | n.d. | 95±0.7 |
| Isovaleric acid             | n.d. | 91±1.9 | 82±1.2 | 86±2.6 |
| Indole                      | n.d. | 91±0.7 | 89±2.1 | 94±1.3 |
| Skatole                     | n.d. | 85±2.2 | 94±0.5 | 94±3.1 |
| DMDS                        | n.d. | 91±1.9 | 81±1.2 | 86±2.6 |

Notes: Concentration of 1,8-cineole, 100 mg/300-mL flask; n.d., not determined.

3. Results and Discussion

**Identification of the active principle in cluster mallow extract.** In this study, we conducted a screening of extracts of a variety of natural materials in an attempt to identify new deodorizing compounds, using an
AMS-targeted GC-based approach. Table 1 summarizes the results of our screening of 109 natural material-derived extracts. Among the samples screened, there was a relatively high rate of detection in the tea/herbal plant category and seed category, and cluster mallow leaves exhibited the highest deodorizing activity. The second highest activity against AMS was detected in a Tencha extract, for which deodorizing activity has not been reported to date; thus, a detailed study will be reported elsewhere), the compound is an interesting candidate odor-reducing agent. However, as pheophorbide-a is reportedly toxic to rats, we did not investigate this compound further.

The chemical constituents of fraction 17 (80 mg) were analyzed by GC/MS, which revealed that 80 components were present (data not shown). Six major components identified by GC/MS analysis included 1,8-C, 2-nonenal, acetic acid, 2-ethyl-1-hexanol, hexanoic acid, and 2-amino-4-methoxyphenol, each of which individually constituted greater than 2% of the total GC peak area and together constituted 30.8% of the total peak area. These compounds were chosen for further analysis. Of the 6 selected compounds, 2-nonenal and acetic acid are typical malodors experienced in daily life. On the other hand, 2-ethyl-1-hexanol, hexanoic acid, and 2-amino-4-methoxyphenol, while less common, are also strongly pungent compounds, in which we are not interested. Furthermore, these 3 compounds exhibited weak deodorizing activities of 18.3%, 0.7%, and 7.7%, respectively, for 300 mg/300-mL flask. The last compound, 1,8-C, exhibited potent deodorizing activity against AMS, which was our screening target (88% for

### Table 4  Deodorizing activity, initial concentration, molecular weight, boiling point, solubility, and generation source of odorous gases.

| Malodorous gas | Deodorizing activity (%) | Initial conc. (ppm) | MW | Boiling point (°C) | Solubility in water | Generation source (example) |
|----------------|--------------------------|---------------------|----|-------------------|---------------------|-----------------------------|
| 2-Nonenal      | 95.6 ± 0.6               | 1                   | 140.22 | 88-90             | −d                  | Body (over middle aged)     |
| Skatole        | 92.7 ± 1.7               | 10                  | 131.17 | 265               | −d                  | feces                       |
| DMTS           | 97.3 ± 0.5               | 1                   | 126.27 | 170               | ±′                  | cancer wound                |
| Indole         | 94.3 ± 0.5               | 10                  | 117.15 | 253               | ±′                  | feces                       |
| Isovaleric acid| 97.0 ± 1.0               | 10                  | 102.13 | 176               | ±′                  | sole of foot                |
| DMS            | 94.6 ± 0.4               | 1                   | 94.19  | 110               | ±′                  | garlic breath               |
| AMS            | 88.0 ± 0.4               | 1                   | 88.17  | 92                | ±′                  | garlic breath               |
| n-Butyric acid | 74.5 ± 7.6               | 1                   | 88.11  | 163               | ±′                  | sole of foot                |
| Diacetyl       | 40.8 ± 0.2               | 10                  | 86.09  | 88                | +↑                  | axillae, foot, head         |
| AM             | 72.4 ± 5.4               | 1                   | 74.14  | 67-68             | −d                  | garlic breath               |
| DMS            | 76.8 ± 0.7               | 1                   | 62.13  | 37.3              | ±′                  | rotten meat                 |
| MM             | 69.1 ± 0.7               | 1                   | 48.11  | 595               | ±′                  | garlic breath               |
| Acetic acid    | 17.0a                    | 10                  | 60.05  | 110               | ++‡                 | kitchen garbage             |
| TMA            | 0b                       | 10                  | 59.11  | 29                | ++‡                 | rotten fish                 |
| Acetaldehyde   | 0b                       | 10                  | 44.05  | 29                | ++‡                 | cigarette smoke             |
| Ammonia        | 0b                       | 10                  | 17.03  | −33.3             | ++‡                 | livestock waste             |

Notes: °Concentration of cineole, 300 mg/300-mL flask; † Molecular weight (g/mol); ‡ Deodorizing activity was measured using a gas detector tube system; § Insoluble; † Slightly soluble; ‡ Soluble; † Very soluble; § Values are expressed as the mean of two independent assays.
300 mg of 1,8-C/300-mL flask (Table 4, Table 5). Thus, we concluded that 1,8-C was the deodorizing active principle in fraction 17.

1,8-C, also known as eucalyptol, is a liquid terpene present in many plants, particularly Eucalyptus species, and was not included among our 109 screening materials. 1,8-C exhibits a camphor-like odor and is known for its ability to mask offensive odors by its fragrant aroma. We report here for the first time that 1,8-C deodorizes offensive malodors not only by masking them but also by reducing the concentration of odorous gases (Japan Patent 6342382). We will discuss the physical mechanism of deodorization in more detail later. Among essential oil components, 1,8-C is generally more useful, as it is easily extractable on a commercial scale. 1,4-C, which is also used as a flavoring and fragrance compound, is found in red wines and plant essential oils. We examined the deodorizing activity of both terpenes using commercially available authentic reagents.

**Deodorizing activity of cineole against various malodorous gases in vitro.** We investigated the deodorizing effect of cineole on a variety of odorous gases, such as those associated with garlic breath, animal waste, cigarette smoke, and rotten meat (Table 4). The deodorizing activity of 1,4-C and 1,8-C was tested against a total of 12 odorous gases using GC.

The review by Iwasaki indicated that the human olfactory sense is generally capable of clearly discriminating differences in odor intensity when there is a 10-fold difference between two odor concentrations and can recognize as little as a 3-fold difference in odor concentration. As such, it is preferable for newly developed deodorant products to exhibit deodorizing activity of approximately 90% against odorous gases. We determined the concentration of cineole necessary to capture >80% of AMS in a 300-mL flask. We also investigated the dose dependence of cineole on deodorizing activity at three doses, 100, 200, and 300 mg/300-mL flask.

In our assay system, 1,8-C exhibited strong deodorizing activity (94–97% for 300 mg of 1,8-C/300-mL flask) against 2-nonenal, skatole, DMTS, indole, isovaleric acid, and DMDS and moderate deodorizing activity (69–88%) against AMS, n-butyric acid, AM, DMS, and MM. In contrast, 1,8-C exhibited only weak deodorizing activity against diacetyl (Fig. 2A, Table 4).

Compared with 1,8-C, 1,4-C exhibited slightly weaker deodorizing activity, especially against MM and DMS (Fig. 2B). It is possible that differences in hydrophobicity (water solubility: 1,8-C, 0.022 g/L and 1,4-C, 0.058 g/L) and boiling point (1,8-C, 176.5°C; 1,4-C, 173.5°C) between 1,8-C and 1,4-C could be responsible for the difference in deodorizing activity. However, whether such moderate differences in physicochemical properties could produce the observed differences in deodorizing activity is unclear. We will discuss the influence of boiling point on deodorizing activity later. Both 1,4- and 1,8-C exhibited dose-dependent deodorizing activity against the odorous gases examined.

The deodorizing activity of 1,8-C against 2-nonenal was investigated in more detail. The activity decreased markedly at a concentration of <50 mg/300-mL flask. The relationship between deodorizing activity and 1,8-C concentration was sigmoidal rather than linear (data not shown).

Table 3 shows that 1,8-C exerts a constant deodorizing effect against a variety of gases over a wide range.

### Table 5 Six major compounds identified by SPME/GC/MS analysis of fraction 17.

| Identified compound                   | Retention time (min) | GC peak area (%) |
|--------------------------------------|----------------------|-----------------|
| 1,8-Cineole                          | 19.0                 | 13.2            |
| 2-Nonenal                            | 24.8                 | 6.6             |
| Acetic acid                          | 26.2                 | 3.8             |
| 2-Ethyl-1-hexanol                    | 27.5                 | 2.7             |
| Hexanoic acid                        | 36.7                 | 2.3             |
| 2-Amino-4-methoxyphenol              | 46.9                 | 2.2             |
| **Total peak area**                  |                      | **30.8**        |

Note: The SPME contaminant, hexamethyl cyclotrisiloxane (6.4%; deodorizing activity: zero) was observed.
of concentrations, from 1 to 100 ppm. This means that deodorant products containing 1,8-C could be used to treat ambient malodors exhibiting a wide odor intensity range.

**Organoleptic assessment of cineole on various odorous gases.** The changes in mean organoleptic scores for the head space of flasks containing 1,8-C incubated with various odorous gases at 25°C for 1 h are shown in Table 6. The organoleptic score was determined by two trained judges who had a national deodorization navigator license. The judges rated the characteristic odor (e.g., greasy or grassy smell for 2-nonenal) of each odorous gas with a score of 0 to 5, where 0 represented the absence of odor, 1 barely noticeable odor, 2 slight malodor, 3 moderate malodor, 4 strong malodor, and 5 severe malodor. The mean odor score was used as the representative score. 1,8-C reduced the organoleptic scores of 2-nonenal, skatole, DMTS, AMS, n-butyric acid, isovaleric acid, and DMDS by more than 2 units.

Greenman et al. investigated the relationship between organoleptic score and the concentrations of pure odorous gases likely responsible for human oral malodor. Various concentrations of odorous gases that are constituents of oral malodor were subjectively scored by trained odor judges based on intensity level as 0 (below threshold) to 5 (extremely strong). The authors showed that the organoleptic score was proportional to the log concentration of pure odorous gas. Furthermore, they calculated values indicating the level of increase in gas concentration required to increase the organoleptic score by 1 unit. These values were a 10-fold increase for n-butyric acid and DMDS (in this case, reduction to one-tenth is equivalent to a deodorizing activity of 90%), 42-fold increase for isovaleric acid (deodorizing activity: 97%), 8-fold increase for skatole (deodorizing activity: 87%), and 7.2-fold increase for MM (deodorizing activity: 86%). These data show that deodorizing activities stronger than approximately 90% produce more than a 1-unit reduction in organoleptic score.

A comparison of the organoleptic score data shown in Table 6 with data from Greenman et al. revealed that the reductions in organoleptic scores in this study...
were more than 1 unit greater than those reported by Greenman et al. The effect of odor-masking fragrances reportedly involves different mechanisms. Osada et al. reported that citrus odorants such as citronellal can mask the odor of DMDS via a mechanism other than overwhelming the malodor\(^1\). This suggests that in addition to reducing the odorous gas concentration, a masking activity of 1,8-C contributes in part to its deodorizing effect.

Fungating wounds sometimes occur in patients with advanced cancer. One of the physical symptoms of a fungating wound is malodor caused by bacteria. The primary odorant emanating from fungating wounds of advanced cancer patients was recently identified as DMTS\(^1\).

A popular conception holds that middle-aged persons have a particularly unpleasant odor known as “aging odor”, which is described as an unpleasant greasy or grassy odor emitted from some individuals 40 years of age or older\(^1\). As is the case of aging odor, microorganisms residing on the skin play an important role in the formation of human body odors, including foot odor. Short-chain fatty acids such as isovaleric acid and butyric acid are believed to be the major contributors to foot odor\(^1\). The potent deodorizing activity of 1,8-C against DMTS, 2-nonenal, and isovaleric acid suggests that it could be used in products designed to eliminate or reduce these microorganism-associated body malodors.

Possible mechanism of the deodorizing activity of cineole. The general structures of the malodorous compounds deodorized by 1,8-C are quite different. For example, DMTS, DMDS, AMS, AM, DMS, and MM are sulfur-containing compounds, whereas 2-nonenal is an unsaturated aldehyde, isovaleric acid and n-butyric acid are fatty acids, and skatole and indole are aromatic heterocyclic compounds. However, like cineole, which is a cyclic ether and monoterpenoid, all of these compounds are hydrophobic. As shown in Table 4, 2-nonenal, skatole, and AM are insoluble in water, whereas DMTS, DMDS, AMS, DMS, MM, indole, isovaleric acid, and n-butyric acid are slightly soluble in water (solubility: 0.19–6 g/100 mL), and diacetyl is water soluble (solubility: 20 g/100 mL).

Negishi et al. proposed a possible mechanism for the deodorizing effects of foods, including lipids, against diallyl disulfide and diallyl sulfide\(^1\). The mechanism involves affinity-based physical and chemical interactions between these sulfur-containing compounds and specific food ingredients, each of which has hydrophobic properties.

In another study screening for deodorant compounds, we identified two hydrophobic compounds from plants. One was a high-molecular-weight, nonpolar lipid triolein (MW: 885.4 g/mol), and the other was a low-molecular-weight oleic acid (MW: 282.5 g/mol), both of which exhibited potent deodorizing activity against hydrophobic odorous gases (data not shown). This suggests that both high- and low-molecular-weight hydrophobic compounds exhibit deodorizing activity against hydrophobic gases. Taking the above into account, this suggests that 1,8-C, a low-molecular-

\begin{center}
\begin{table}
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\caption{Changes in organoleptic measurement (OM) score.\(^a\)}
\begin{tabular}{llllll}
\hline
Odorous gas & Without incubation\(^b\) & With incubation\(^c\) & Reduction of OM score & Deodorizing activity (%)\(^d\) & Deodorizing activity (%)\(^e\) \\
\hline
2-Nonenal & 3 & 0 & 3 & 96 & –

Skatole & 3.5 & 0.5 & 3 & 93 & 87

DMTS & 3 & 0 & 3 & 97 & –

AMS & 3 & 1.5 & 1.5 & 88 & –

n-Butyric acid & 3 & 1 & 2 & 75 & 90

Isovaleric acid & 3 & 1 & 2 & 97 & 97

Dimethyl disulfide & 3 & 0 & 3 & 95 & 90

\hline
\end{tabular}
\end{table}
\end{center}

Notes: a Scores are expressed as the mean of two independent assays conducted by two trained judges.

b Odorant was incubated at 25°C for 60 min without 1,8-C.

c Odorant was incubated at 25°C for 60 min with 1,8-C.

d Excerpted from Table 4.

e Deodorizing activity required to decrease OM score by 1 unit. Adapted from Greenman et al. data (reference 15).
weight compound (MW: 154.3 g/mol), interacts with hydrophobic odor molecules to draw them together, forming hydrophobic aggregates and thus reducing the intensity of the odor released.

In order to test this hypothesis further, the deodorizing activity of 1,8-C against hydrophilic odorants such as acetic acid, acetaldehyde, TMA, and ammonia was examined. As these odorous compounds could not be easily quantified by GC in the present study, we used a gas detector tube system. We found that 1,8-C exhibited no or weak deodorizing activity against hydrophilic odorants, including acetic acid, acetaldehyde, TMA, and ammonia (solubility: 144 g/100 mL to infinite, deodorizing activity: 0 to 17% at 300 mg/300-mL flask. Table 4). From this observation, it is clear that 1,8-C does not physically interact with hydrophilic odorants. This observation supports the hypothesis that the deodorizing mechanism of cineole involves hydrophobic interactions between the cineole and odorant molecules.

As shown in Table 4, the solubility of diacetyl in water is much higher than that of the slightly soluble compounds but much lower than that of the highly soluble compounds. It is interesting to note that diacetyl exhibited much less potent deodorizing activity than the other insoluble or slightly soluble compounds.
The relatively poorer deodorizing activity of diacetyl may thus be due to its intermediate hydrophobicity.

It is well known that adsorption of a water insoluble adsorbate to an adsorbent such as activated carbon occurs primarily via hydrophobic interactions, which are based on van der Waals forces between the adsorbate and adsorbent. Adsorption via van der Waals forces is reportedly affected by molecular properties such as hydrophobicity as well as a variety of other factors, including molecular weight and boiling point. In general, the greater the molecular weight, the stronger the van der Waals forces between the adsorbate and adsorbent, and consequently, the greater the extent of adsorption, which will, in turn, produce a stronger deodorizing effect.

We found a correlation between the deodorizing activity of 1,8-C and the molecular weight of the odorous gases tested. 1,8-C tended to deodorize high-molecular-weight (>90 g/mol) odorous gases more effectively than low-molecular-weight (<90 g/mol) gases. The coefficient of determination (R²) between the deodorizing activity of 1,8-C against the odorous gases shown in Table 4 and their molecular weight was high, at 0.6198. When considering only hydrophobic gases, the coefficient of determination was very high, at 0.7027 (Fig. 3). These correlation data suggest that the deodorizing mechanism of cineole is, at least in part, due to adsorption involving van der Waals forces.

It is also known that van der Waals forces are affected by the boiling point of adsorbates. The higher the boiling point, the stronger the van der Waals forces. We found a correlation between the deodorizing activity of 1,8-C and the molecular weight of the odorous gases tested.
activity of 1,8-C and the boiling point of the odorous gases tested (Fig. 4), although there were several exceptions, including 2-nonenal. The coefficient of determination ($R^2$) between the deodorizing activity of 1,8-C against the odorous gases and boiling points of the gases was 0.3286, indicating a moderate correlation.

The van der Waals forces between 1,8-C and 2-nonenal may be governed by the combined effects of their molecular properties. The number of carbons on hydrophobic molecules is important because the greater the number of carbons, the stronger the hydrophobic interaction. Linear carbon chain molecules can produce stronger hydrophobic interactions than branched molecules, because carbon branches produce steric hindrance. The fact that 2-nonenal has a long thin structure may explain its stronger deodorizing activity, although the boiling point of 2-nonenal is not higher than that of the other high-molecular-weight gases tested (Table 4).

As van der Waals forces are relatively weak, physical adsorption is a readily reversible phenomenon. Because of their hydrophobicity, by raising the temperature, adsorbed hydrophobic gas molecules would be desorbed from 1,8-C, similar to the case of thermal desorption of an adsorbate from activated carbon surfaces. In view of the temperature dependence of adsorbate desorption, a desorption experiment was conducted at 50, 75, 100, and 150°C at a constant 1,8-C dose of 50mg/35-mL vial. The effect of temperature on the desorption of gases (including DMTS, 2-nonenal, isovaleric acid, and skatole) from 1,8-C is shown in Figure 5. The desorption of gases from 1,8-C was proportional to the incubation temperature. DMTS and 2-nonenal reached 53.3 ppm and 38.6 ppm at 150°C, respectively, suggesting that the adsorption process involves a physical mechanism associated with van der Waals forces. The desorbed concentrations of isovaleric acid and skatole (21.8 ppm and 4.1 ppm, respectively) were lower than those of 2-nonenal and DMTS.

Deodorization of isovaleric acid and skatole could involve additional mechanisms. In addition to van der Waals forces, hydrogen bonding is another type of force in physical adsorption. Isovaleric acid and skatole could form hydrogen bonds with the oxygen atom in 1,8-C (Fig. 6). From the above, the lower level of thermal desorption could be due to the formation of hydrogen bonds between those gases and 1,8-C. Additional investigations, such as adsorption isotherm measurements, may be necessary to clarify the adsorption mechanism of 1,8-C in more detail.

Concluding remarks

The aim of this work was to discover novel natural products exhibiting deodorizing activity from natural material extracts. The screening target was AMS, which is a major component of garlic breath, and 1,8-C was identified from cluster mallow leaves as active against AMS. 1,8-C exhibited potent deodorizing activity against not only AMS but also other odorous gases that are components of diet- and disease-associated malodors, such as foot odor, aging-associated odor, and malodors emitted from fungating cancer wounds and feces. Our data indicate that 1,8-C could be a particularly useful odor-reducing agent. The possible deodorizing mechanism of cineole is suggested to involve van der Waals forces, and to a lesser extent, hydrogen bonding.

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Our interest in the topic of hydrophobic interactions between cineole and odorous molecules was inspired and complemented by communications with Zenzaburo Tozuka (Osaka University).

Key words: cineole, malodor, deodorizing activity, hydrophobic interaction

Abbreviations: GC, gas chromatography; MS, mass spectrometry; DMTS, dimethyl trisulfide; DMDS, dimethyl disulfide; AMS, allyl methyl sulfide; DMS, dimethyl sulfide; AM, allyl mercaptan; MM, methyl mercaptan; TMA, trimethylamine, SPME, solid-phase micro-extraction.

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天然物からの消臭活性物質の探索とシネオールの消臭作用の特性

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要旨：天然物由来の新しい消臭物質の発見を目的として、活性の測定にガスクロマトグラフィー（GC）を用いて、植物抽出物からのスクリーニングを試みた。その結果、フユオイの50%エタノール水による抽出物に消臭活性を検出した。活性の本体をシリカゲルクロマトグラフィーにより精製し、1,8-シネオールと同定した。1,8-シネオールは、比較的広い範囲の悪臭ガス（2-ノネナール、スクトール、インドール、ジメチルトリスルフィド、ジメチルジスルフィド、イソプロピ酸）に対して、消臭率90%以上の強い活性を示した。また、アリルメチルスルフィド、アリルメチルカプロン、ジメチルスルフィドに対し70%以上の消臭率を示した。なお、消臭活性の強さを表す消臭率は、消臭物質を含むin vitroの測定系に悪臭ガスを添加して反応させ、その際に消失したガス量の原ガス量に対する割合（％）である。官能試験（6段階評価）では、1,8-シネオールは臭気強度を1.5~3段階低減させた。1,8-シネオールには、芳香によって臭気強度を低下させるマスキング効果が知られている。一方、1,8-シネオールは消臭活性の強さと分子量、または消臭活性と沸点との間に相関関係が認められた。また1,8-シネオールに一旦吸着された悪臭ガスは高温で物理的に脱着した。これらの知見から、1,8-シネオールはマスキング以外に、悪臭ガスを吸着することにより、その濃度を低下させる物理的機序の存在が推定された。

キーワード：シネオール、悪臭、消臭活性、疎水性相互作用

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