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Novel Key Aroma Components of Galbanum Oil

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Galbanum oil is composed of monoterpenes in large amounts and pyrazines in small amounts. Although the monoterpenes are the main components of galbanum oil, they hardly contribute to the distinct galbanum aroma. The scanty amounts of pyrazines, in contrast, contribute significantly to the aroma. Considering the complexity and potency of the odor, the essential oil was assumed to contain so far not identified compounds with high odor contribution. By the gas chromatography−mass spectrometry−olfactometry (GC-MS-O) analysis of galbanum oil, fruity-green-balsamic notes were detected at two different retention times. The mass spectra (MS) of the newly discovered notes were elucidated by conducting multidimensional (MD) GC-MS-O. By analyzing the MS data, six chemical structures were proposed: (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one, (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one, and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one. The compounds were then synthesized in an attempt to match the MS, retention indices (RI), and odor qualities. The MD-GC-MS-O analyses of the candidate compounds led to the identification of the novel key aroma compounds (6*Z*,8*E*)-undeca-6,8,10-trien-3-one and (6*Z*,8*E*)-undeca-6,8,10-trien-4-one in galbanum oil.

KEYWORDS: Galbanum oil; novel aroma compounds; GC-MS-O; (6*Z*,8*E*)-undeca-6,8,10-trien-3-one; (6*Z*,8*E*)-undeca-6,8,10-trien-4-one

INTRODUCTION

Natural essential oils contain many complex unknown compounds that have hitherto been difficult to identify conclusively. With help from recent advances in analytical equipment and technologies, however, it is now possible to clarify many unknowns. Our laboratory has recently developed novel headspace techniques for analyses of volatiles (*1, 2*) and also clarified the potent odorants of celery (*3, 4*), roasted shrimp (*5*), and ambergris (*6*). In the present research we elucidated the aroma of galbanum oil obtained by steam distillation of the resin of *Ferula galbaniflua* Boissier et Buhse, a large umbellifer plant that grows wild mainly in Iran, Turkey, Afghanistan, and neighboring countries. The oil, a widely used ingredient in industry, has a powerful green odor with dry-woody, balsamic, and bark-like tonalities (*7, 8*). In perfumery, galbanum oil is used to confer green notes and augment fougére, chypre, and oriental notes. In flavoring, it contributes to the savory notes of curries and sauces.

Galbanum oil is composed of mainly hydrocarbon monoterpenes (*9*−*12*) such as β-pinene, α-pinene, and Δ^3-carene, but these components hardly contribute to the characteristic green notes. Instead, the tiny quantities of C11 hydrocarbons and methoxypyrazines present in the oil contribute most to the aroma (*13*−*16*). Further analytical investigations of galbanum oil have revealed the presence of novel thiol esters (*17, 18*), sesquiterpene alcohols (*19, 20*), and macrolides (*21*), but the complexity and potency of the green odor could not solely be explained with the so far identified compounds. Therefore, we assumed that there were clearly other hidden key compounds that contribute to the total aroma. In this study we used gas chromatography−mass spectrometry−olfactometry (GC-MS-O) to discover these components in a commercially available galbanum oil from Iran.

MATERIALS AND METHODS

Materials. Iranian galbanum oil prepared from galbanum (*F. galbaniflua* Boissier et Buhse) gum was purchased from Nihon SiberHegner (Tokyo, Japan). The oil was pale yellow.

Chemicals. The following compounds were purchased from the commercial sources: 2-isopropyl-3-methoxypyrazine, linalool, and guaiacol (Sigma-Aldrich Japan, Tokyo, Japan). (3*E*,5*Z*)-Undeca-1,3,5-triene (*22*) was synthesized as reported in the literature. (6*E*/*Z*,8*E*)-Undeca-6,8,10-trien-2-one (**1**) (6*E*:6*Z* = 47:53), (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**) (6*E*:6*Z* = 50:50), and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**) (6*E*:6*Z* = 46:54) were synthesized in our laboratory (**Figures 1** and **2**). All other reagents and solvents were of analytical grade.

Nuclear Magnetic Resonance (NMR) Spectra. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECX400 spectrometer at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard, δ 0.00 (coupling constants J in hertz). The geometric ratios of the synthesized compounds were determined by ^{1}H NMR.

Gas Chromatography−Mass Spectrometry (GC-MS). The GC-MS analyses were performed with an Agilent 6890 gas chromatograph (GC) combined with a 5973 mass selective detector and a flame ionization detector (FID; 250 °C) equipped with a TC-WAX capillary column (0.25 mm i.d. × 60 m; GL Sciences Co., Tokyo, Japan). The

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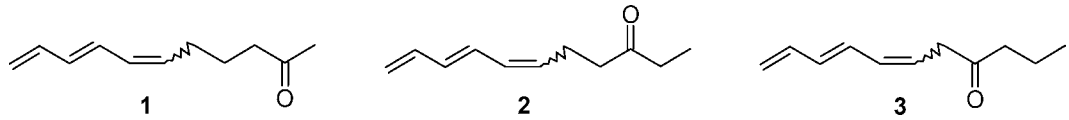

Figure 1. Chemical structures of candidate compounds for odor-active unknowns in galbanum oil: (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**) and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**) for unknown A, and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**) for unknown B.

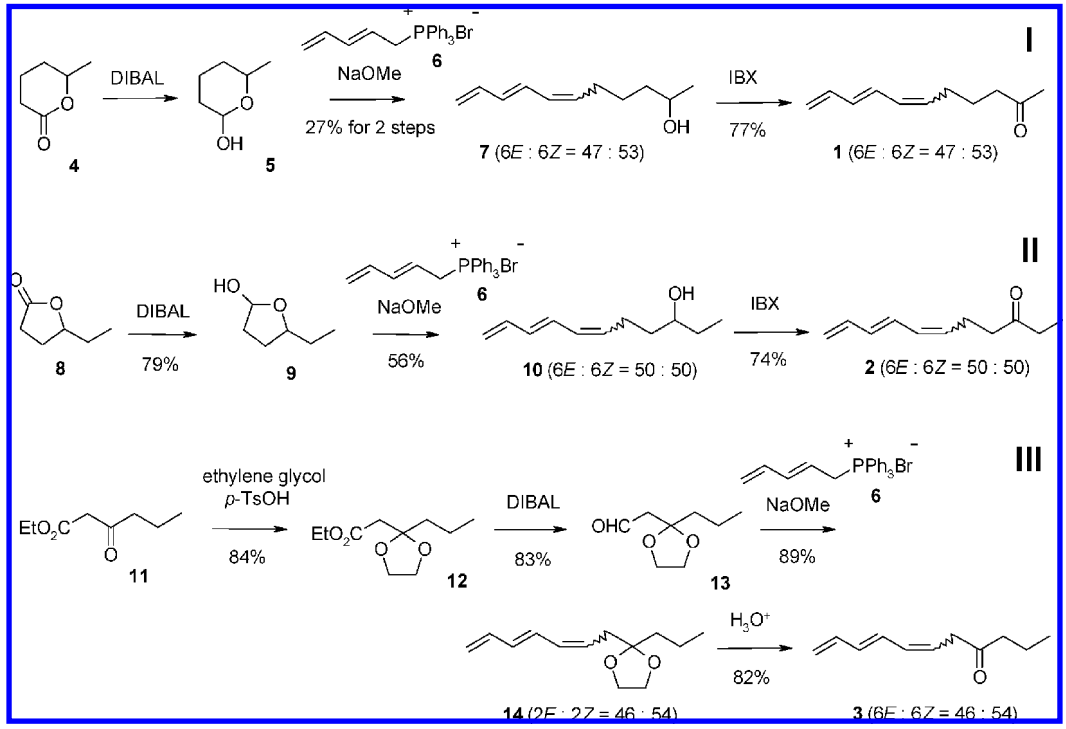

Figure 2. Syntheses of (**I**) (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**), (**II**) (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**), and (**III**) (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**).

effluent of the column at the end of the capillary was divided into two branches and routed by deactivated fused silica capillaries to the mass detector and FID, respectively. Each sample was injected in 1 μL volumes in a split mode (50:1) at a constant temperature of 250 °C. The oven temperature was kept at 40 °C for the initial 3 min and then increased to 230 °C at a rate of 3 °C/min, with a constant carrier helium gas flow of 1.8 mL/min. Mass spectra (MS) in the electron impact (EI) mode were recorded at 70 eV ionization energy. Linear retention indices (RI) of the compounds were calculated from the retention times of *n*-alkanes. The purity of the synthesized compounds was calculated by integration of the chromatogram obtained by the FID.

Infrared Absorption (IR) Spectra. IR spectra were recorded on a GC-IR, an Agilent 6890 GC connected to a Bio-Lad IRD II equipped with a TC-5 capillary column (0.32 mm i.d. × 60 m; GL Sciences Co.). The sample volume, split rate, injection temperature, oven temperature program, carrier gas, and flow rate were all the same as for GC-MS described above.

High-Resolution Mass Spectra (HRMS). The HRMS were recorded on a JEOL JMS-700.

Syntheses. *6-Methyltetrahydro-2H-pyran-2-ol (5) (23).* Under N_2 atmosphere, diisobutyl aluminum hydride (DIBAL, 0.98 M in *n*-hexane, 30 mL, 28.9 mmol) was added in drops to a solution of δ-hexalactone (**4**, 3.00 g, 26.3 mmol) in *n*-hexane (30 mL) and toluene (50 mL) at −65 °C for 20 min. After 20 min of stirring at −65 °C, the reaction mixture was poured into 5% aqueous oxalic acid and stirred at room temperature for 30 min. After the addition of NaCl and ethyl acetate, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated under high vacuum into a crude yellow oil of 6-methyltetrahydro-2*H*-pyran-2-ol (**5**, 3.54 g). This crude product was directly used in the next step.

(6E/Z,8E)-Undeca-6,8,10-trien-2-ol (7). Under N_2 atmosphere, the crude lactol **5** (3.54 g) and [(2*E*)-penta-2,4-dien-1-yl]triphenylphosphonium bromide (**6**, 10.8 g, 26.3 mmol) (*22*) were suspended in *N*,*N*-dimethylformamide (DMF, 20 mL), and then NaOMe (28% in MeOH, 5.57 g, 28.9 mmol) was added dropwise to the solution at 5 °C. After 2 h of stirring at 5 °C, the reaction mixture was warmed to room temperature, stirred overnight, poured into saturated aqueous NH_4Cl, and filtered. The organic layer of the filtrate was separated, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with water and brine, and dried over $MgSO_4$. After the addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT, 0.1 g), the organic solution was concentrated under high vacuum. The residue (9.18 g) was purified by silica gel (50 g) chromatography using *n*-hexane/ethyl acetate (60:1, v/v) and *n*-hexane/ethyl acetate (50:1, v/v) in sequence into a faintly yellowish oil of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-ol (**7**, 6*E*:6*Z* = 47:53, 1.19 g, yield = 27%, purity = 94%). The (6*Z*)-isomer **7a** and (6*E*)-isomer **7b** were determined by the coupling constants at δ 5.45 and 5.70, respectively. ^{1}H NMR (both isomers): δ 1.17, 1.18 (each d, J = 5.6, J = 5.6, total 3H); 1.31 (br s, 1H); 1.40−1.54 (m, 4H); 2.11, 2.21 (each q, J = 6.8, J = 7.2, total 2H); 3.78 (m, 1H); 5.02, 5.07 (each d, J = 10.0, J = 10.4, total 1H); 5.15, 5.20 (each d, J = 16.4, J = 16.8, total 1H); 5.45 (**7a**, dt, J = 7.6, 10.8, 0.53H); 5.70 (**7b**, dt, J = 7.2, 15.2, 0.47H); 5.99−6.50 (m, 4H). ^{13}C NMR (both isomers) δ 23.5, 25.4, 25.7, 27.7, 32.7, 38.7, 38.8, 67.9, 116.3, 117.0, 128.4, 128.6, 130.4, 131.1, 132.9, 133.1, 133.4, 135.4, 137.0, 137.1. MS-EI [(6*Z*)-isomer **7a**]: 166 (M^+, 5), 148 (2), 133 (4), 123 (14), 106 (29), 91 (100), 79 (61), 67 (22), 55 (11), 43 (30), 27 (8). MS-EI [(6*E*)-isomer **7b**]: 166 (M^+, 7), 148 (4), 133 (4), 123 (12), 106 (31), 91 (100), 79 (56), 67 (20), 55 (11), 43 (28), 27 (8). GC-IR [(6*Z*)-isomer **7a**, cm^{-1}]: 3658, 3094, 3019, 2937, 997. GC-IR [(6*E*)-isomer **7b**, cm^{-1}]: 3655, 3094, 3015, 2936, 998. HRMS (both isomers) (EI) calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1356.

(6E/Z,8E)-Undeca-6,8,10-trien-2-one (1). 2-Iodoxybenzoic acid (IBX, 2.78 g, 9.94 mmol) (*24*, *25*) was added to dimethyl sulfoxide (DMSO, 20 mL) at room temperature and dissolved by continuous stirring. After the

addition of alcohol **7** (6*E*:6*Z* = 47:53, 1.18 g, 7.10 mmol) drop by drop at room temperature, the reaction mixture was stirred for 2 h at room temperature, poured into water, and filtered. The filtrate was extracted with ethyl acetate, and the ethyl acetate layer was washed with water and brine and dried over $MgSO_4$. After the addition of tocopherol (0.1 g), the ethyl acetate solution was concentrated under high vacuum. The residue (10.9 g) was purified by silica gel (50 g) chromatography using *n*-hexane/ethyl acetate (100:1, v/v) into a faintly yellowish oil of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**, 6*E*:6*Z* = 47:53, 894 mg, yield = 77%, purity = 94%). The (6*Z*)-isomer **1a** and (6*E*)-isomer **1b** were determined by the coupling constants at δ 5.40 and 5.64, respectively. ^{1}H NMR (both isomers): δ 1.66 (q, *J* = 7.6, 3H); 2.10 (s, 3H); 2.02, 2.19 (each dt, *J* = 7.2, 9.2, *J* = 7.2, 7.6, total 2H); 2.40, 2.42 (each t, *J* = 7.2, *J* = 7.6, total 2H); 5.03, 5.07 (each d, *J* = 10.0, *J* = 10.0, total 1H); 5.16, 5.20 (each d, *J* = 16.0, *J* = 16.0, total 1H); 5.40 (**1a**, dt, *J* = 7.6, 10.4, 0.53H); 5.64 (**1b**, dt, *J* = 6.8, 15.2, 0.47H); 6.00−6.46 (m, 4H). ^{13}C NMR (both isomers): δ 23.1, 23.4, 27.0, 30.0, 32.0, 42.7, 42.8, 116.6, 117.2, 128.2, 129.3, 130.9, 131.5, 131.9, 133.2, 133.4, 134.5, 136.98, 137.03, 208.8. MS-EI [(6*Z*)-isomer **1a**]: 164 (M^+, 15), 106 (71), 91 (100), 78 (50), 65 (10), 43 (37), 27 (5). MS-EI [(6*E*)-isomer **1b**]: 164 (M^+, 16), 106 (69), 91 (100), 78 (50), 65 (9), 43 (36), 27 (4). GC-IR [(6*Z*)-isomer **1a**, cm^{-1}]: 3093, 3019, 2947, 1731, 1361, 998. GC-IR [(6*E*)-isomer **1b**, cm^{-1}]: 3094, 3015, 2943, 1731, 1361, 998. HRMS (both isomers) (EI) calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1201.

*5-Ethyltetrahydrofuran-2-ol (**9**) (26).* Under N_2 atmosphere, DIBAL (1.02 M in *n*-hexane, 500 mL, 510 mmol) was added in drops to a solution of γ-hexalactone (**8**, 53.0 g, 464 mmol) in *n*-hexane (100 mL) and toluene (50 mL) at −15 °C for 1.5 h. After 1 h of stirring at −15 °C, the reaction mixture was poured into 5% aqueous oxalic acid and stirred at room temperature for 30 min. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated under high vacuum. The residue (72.0 g) was distilled (bp 57−59 °C/0.60 kPa) into a colorless oil of 5-ethyltetrahydrofuran-2-ol (**9**, 42.4 g, yield = 79%, purity = 95%).

*(6E/Z,8E)-Undeca-6,8,10-trien-3-ol (**10**).* Under N_2 atmosphere, the lactol **9** (17.0 g, 147 mmol) and [(2*E*)-penta-2,4-dien-1-yl]triphenylphosphonium bromide (**6**, 66.0 g, 162 mmol) were suspended in DMF (85 mL). After the dropwise addition of NaOMe (28% in MeOH, 28.3 g, 147 mmol) at 5 °C and 2 h of stirring at 5 °C, the reaction mixture was poured into saturated aqueous NH_4Cl and filtered. The organic layer of the filtrate was separated and the aqueous layer was extracted with *n*-hexane. The organic layers were combined, washed with water and brine, and dried over $MgSO_4$. After the addition of tocopherol (0.6 g), the organic solution was concentrated under high vacuum. The residue (33.7 g) was distilled (bp 96−97 °C/0.20 kPa) into a colorless oil of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-ol (**10**, 6*E*:6*Z* = 50:50, 9.29 g, yield = 56%, purity = 94%). The (6*Z*)-isomer **10a** and (6*E*)-isomer **10b** were determined by the coupling constants at δ 5.47 and 5.72, respectively. ^{1}H NMR (both isomers): δ 0.92 (t, *J* = 7.2, 3H); 1.40−1.57 (m, 4H); 2.02−2.32 (m, 2H); 3.57 (br q, *J* = 3.6, 1H); 5.03, 5.07 (each d, *J* = 10.0, *J* = 10.4, total 1H); 5.15, 5.20 (each d, *J* = 16.4, *J* = 16.8, total 1H); 5.47 (**10a**, dt, *J* = 7.6, 10.8, 0.5H); 5.72 (**10b**, dt, *J* = 6.8, 15.6, 0.5H); 5.99−6.54 (m, 4H). ^{13}C NMR (both isomers): δ 9.86, 9.88, 24.2, 29.1, 30.2, 30.3, 36.3, 36.6 72.7, 116.5, 117.1, 128.3, 128.8, 130.5, 131.3, 132.6, 133.2, 133.3, 135.2, 137.0, 137.1. MS-EI [(6*Z*)-isomer **10a**]: 166 (M^+, 10), 119 (23), 105 (51), 91 (100), 79 (64), 67 (20), 57 (25), 41 (36), 31 (13). MS-EI [(6*E*)-isomer **10b**]: 166 (M^+, 13), 119 (23), 105 (51), 91 (100), 79 (59), 67 (17), 57 (21), 41 (34), 31 (12). GC-IR [(6*Z*)-isomer **10a**, cm^{-1}]: 3653, 3094, 3020, 2970, 2937, 997. GC-IR [(6*E*)-isomer **10b**, cm^{-1}]: 3655, 3094, 3015, 2972, 2937, 998. HRMS (both isomers) (EI) calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1344.

*(6E/Z,8E)-Undeca-6,8,10-trien-3-one (**2**).* IBX (36.8 g, 131 mmol) was added to DMSO (170 mL) at room temperature and dissolved by continuous stirring. After the dropwise addition of alcohol **10** (6*E*:6*Z* = 50:50, 15.6 g, 93.8 mmol) to the solution at 15 °C, the reaction mixture was stirred for 3 h at room temperature, poured into water, and filtered. The filtrate was extracted with ethyl acetate, and the ethyl acetate layer was washed with water and brine and dried over $MgSO_4$. After the addition of tocopherol (0.3 g), the ethyl acetate solution was concentrated under high vacuum. The residue (20.1 g) was distilled (bp 88−90 °C/0.30 kPa) into a colorless oil of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**, 6*E*:6*Z* = 50:50, 11.4 g, yield = 74%, purity = 96%). The (6*Z*)-isomer **2a** and (6*E*)-isomer **2b** were determined by the coupling constants at δ 5.40 and 5.68, respectively. ^{1}H NMR (both isomers): δ 1.04 (t, *J* = 7.3, 3H); 2.41 (q, *J* = 7.3, 2H); 2.34−2.51 (m, 4H); 5.04, 5.08 (dd, d, *J* = 1.4, 9.6, *J* = 10.1, total 1H); 5.16, 5.20 (each d, *J* = 16.9, *J* = 17.0, total 1H); 5.40 (**2a**, dt, *J* = 6.8, 11.0, 0.5H); 5.68 (**2b**, dt, *J* = 7.3, 14.6, 0.5H); 5.98−6.52 (m, 4H). ^{13}C NMR (both isomers): δ 7.8, 22.3, 27.0, 36.0, 41.7, 42.0, 116.7, 117.4, 128.1, 129.2, 130.9, 131.0, 131.7, 133.0, 133.6, 133.7, 137.0, 137.1, 210.6, 210.7. MS-EI [(6*Z*)-isomer **2a**]: 164 (M^+, 27), 135 (3), 117 (8), 107 (15), 91 (53), 77 (33), 65 (11), 57 (100), 41 (13), 29 (22). MS-EI [(6*E*)-isomer **2b**]: 164 (M^+, 29), 135 (3), 117 (8), 107 (15), 91 (52), 77 (32), 65 (10), 57 (100), 41 (13), 29 (22). GC-IR [(6*Z*)-isomer **2a**, cm^{-1}]: 3095, 3021, 2982, 1728, 998. GC-IR [(6*E*)-isomer **2b**, cm^{-1}]: 3095, 3015, 2984, 1729, 998. HRMS (both isomers) (EI), calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1190.

*Ethyl (2-propyl-1,3-dioxolane-2-yl)acetate (**12**) (27).* A solution of ethyl 3-oxohexanoate (**11**, 13.8 g, 87.2 mmol), ethylene glycol (9.8 g, 158 mmol), *p*-TsOH·H_2O (0.2 g) and cyclohexane (50 mL) was refluxed for 4 h using a Dean−Stark apparatus. The reaction mixture was cooled to room temperature and poured into saturated aqeuous $NaHCO_3$. The organic layer was separated, washed with water and brine, dried over $MgSO_4$, and concentrated under high vacuum. The residue (18.1 g) was distilled (bp 74−79 °C/0.40 kPa) into a colorless oil of ethyl (2-propyl-1,3-dioxolane-2-yl)acetate (**12**, 14.9 g, yield = 84%, purity = 99%).

*(2-Propyl-1,3-dioxolane-2-yl)acetaldehyde (**13**) (27, 28).* Under N_2 atmosphere, DIBAL (0.99 M in toluene, 102 mL, 101 mmol) was added in drops to a solution of the acetate **12** (20.5 g, 101 mmol) and toluene (100 mL) at −63 °C for 1.5 h. After 1 h of stirring at −15 °C, the reaction mixture was poured into 5% aqueous oxalic acid and stirred at room temperature for 30 min. After the addition of NaCl and ethyl acetate, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated under high vacuum. The residue (23.2 g) was distilled (bp 58−62 °C/0.30 kPa) into a colorless oil of (2-propyl-1,3-dioxolane-2-yl)acetaldehyde (**13**, 13.4 g, yield = 83%, purity = 91%).

*2-[(2E/Z,4E)-Hepta-2,4,6-trien-1-yl]-2-propyl-1,3-dioxolane (**14**).* Under N_2 atmosphere, the aldehyde **13** (13.8 g, 87.2 mmol) and [(2*E*)-penta-2,4-dien-1-yl]triphenylphosphonium bromide (**6**, 39.3 g, 96.0 mmol) were suspended in DMF (70 mL). After the dropwise addition of NaOMe (28% in MeOH, 17.7 g, 91.6 mmol) to the solution at 5 °C and stirring for 2 h at 5 °C, the reaction mixture was poured into saturated aqueous NH_4Cl (200 mL) and *n*-hexane (200 mL) and filtered. The *n*-hexane layer of the filtrate was separated, and the aqueous layer was extracted with *n*-hexane. The *n*-hexane layers were combined, washed with water and brine, and dried over $MgSO_4$. After the addition of tocopherol (0.2 g), the organic solution was concentrated under high vacuum. The residue (18.7 g) was purified by silica gel (100 g) chromatography using *n*-hexane/ethyl acetate (100:1, v/v) and *n*-hexane/ethyl acetate (80:1, v/v) in sequence into a faintly yellowish oil of 2-[(2*E*/*Z*,4*E*)-hepta-2,4,6-trien-1-yl]-2-propyl-1,3-dioxolane (**14**, 2*E*:2*Z* = 46:54, 16.1 g, yield = 89%, purity = 96%). The (2*Z*)-isomer **14a** and (2*E*)-isomer **14b** were determined by the coupling constants at δ 5.50 and 5.69, respectively. ^{1}H NMR (both isomers): δ 0.89 (t, *J* = 7.6, 3H); 1.34−1.41 (m, 2H); 1.56−1.62 (m, 2H); 2.39, 2.50 (d, dd, *J* = 7.6, *J* = 1.2, 7.6, total 2H); 3.92−3.95 (m, 4H); 5.04, 5.08 (dd, d, *J* = 1.2, 9.6, *J* = 10.0, total 1H); 5.17, 5.21 (each d, *J* = 14.4, *J* = 15.2, total 1H); 5.50 (**14a**, dt, *J* = 7.6, 10.4, 0.54H); 5.69 (**14b**, dt, *J* = 7.2, 15.2, 0.46H); 6.09−6.49 (m, 4H). ^{13}C NMR (both isomers): δ 14.3, 16.78, 16.83, 36.0, 39.7, 39.8, 41.0, 65.06, 65.09, 111.2, 111.4, 116.7, 117.3, 127.0, 128.4, 128.5, 128.6, 129.7, 130.7, 131.8, 133.2, 133.6, 133.77, 133.81, 137.0, 137.1. MS-EI [(2*Z*)-isomer **14a**]: 208 (M^+, 1), 165 (7), 115 (100), 91 (8), 77 (8), 71 (20), 43 (22). MS-EI [(2*E*)-isomer **14b**]: 208 (M^+, 1), 165 (10), 115 (100), 91 (8), 77 (8), 71 (20), 43 (22). GC-IR [(2*Z*)-isomer **14a**, cm^{-1}]: 3093, 3029, 2966, 1071. GC-IR [(2*E*)-isomer **14b**, cm^{-1}]: 3094, 3014, 2965, 1074. HRMS (both isomers) (EI) calcd for $C_{13}H_{20}O_2$: 208.1463. Found: 208.1457.

*(6E/Z,8E)-Undeca-6,8,10-trien-4-one (**3**).* A solution of the triene **14** (2*E*:2*Z* = 46:54, 2.94 g, 14.1 mmol) in diethyl ether (30 mL) was added drop by drop to a mixture of 35% aqueous perchloric acid (40 mL) and

Table 1. Characteristic Odor Volatiles in Galbanum Oil

odorant[a]	odor quality[b]	RI on TC-WAX	identification mode[c]
(3*E*,5*Z*)-undeca-1,3,5-triene	fruity, pineapple-like	1403	MS, RI, GC-O
2-isopropyl-3-methoxypyrazine	earthy	1446	MS, RI, GC-O
linalool	fruity, floral	1550	MS, RI, GC-O
guaiacol	medicinal	1863	MS, RI, GC-O
unknown	fruity, green, balsamic	1899	GC-O

[a] The odorant was identified by matching the mass spectrum, retention index, and odor quality with the reference odorant. [b] Odor quality perceived at the sniffing port. [c] MS, reference mass spectrum; RI, reference retention index; GC-O, gas chromatography coupled with olfactometry.

Table 2. RI on TC-WAX and TC-1 of Unknowns and (6*E*/*Z*,8*E*)-Undeca-6,8,10-trienones

no.	compound	RI on TC-WAX	RI on TC-1
	unknown A	1899	1316
	unknown B	1899	1328
1a	(6*Z*,8*E*)-undeca-6,8,10-trien-2-one	1913	1320
1b	(6*E*,8*E*)-undeca-6,8,10-trien-2-one	1947	1338
2a	(6*Z*,8*E*)-undeca-6,8,10-trien-3-one	1899	1328
2b	(6*E*,8*E*)-undeca-6,8,10-trien-3-one	1924	1339
3a	(6*Z*,8*E*)-undeca-6,8,10-trien-4-one	1899	1316
3b	(6*E*,8*E*)-undeca-6,8,10-trien-4-one	1899	1328

diethyl ether (10 mL) at 5 °C for 10 min. After 20 min of stirring at 5 °C, the reaction mixture was neutralized by saturated aqueous $NaHCO_3$. The diethyl ether layer was separated, and the aqueous layer was extracted with diethyl ether. The diethyl ether layers were combined, washed with water and brine, and dried over $MgSO_4$. After the addition of tocopherol (0.1 g), the diethyl ether solution was concentrated under high vacuum. The residue (2.61 g) was purified by silica gel (15 g) chromatography using *n*-hexane/ethyl acetate (80:1, v/v) into a yellow oil of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**, 6*E*:6*Z* = 46:54, 1.90 g, yield = 82%, purity = 95%). The (6*Z*)-isomer **3a** and (6*E*)-isomer **3b** were determined by the coupling constants at δ 5.62 and 5.78, respectively.^{1}H NMR (both isomers): δ 0.89, 0.90 (each t, J = 7.2, J = 7.2, total 3H); 1.55−1.64 (m, 2H); 2.40, 2.42 (each t, J = 6.8, J = 7.6, total 2H); 3.18 (d, J = 7.2, 1H); 3.29 (d, J = 7.2, 1H); 5.07, 5.12 (each d, J = 10.0, J = 10.4, total 1H); 5.20, 5.24 (each d, J = 18.0, J = 18.4, total 1H); 5.62 (**3a**, dt, J = 7.6, 10.8, 0.54H); 5.78 (**3b**, dt, J = 7.2, 15.2, 0.46H); 6.08−6.43 (m, 4H). ^{13}C NMR (both isomers): δ 13.7, 17.1, 17.2, 42.1, 44.3, 46.8, 117.4, 118.2, 123.3, 126.2, 127.5, 131.2, 132.5, 132.8, 133.7, 134.8, 136.8, 208.1, 208.6. MS-EI [(6*Z*)-isomer **3a**]: 164 (M^+, 18), 91 (25), 77 (25), 71 (98), 43 (100), 41 (21). MS-EI [(6*E*)-isomer **3b**]: 164 (M^+, 20), 91 (25), 77 (26), 71 (97), 43 (100), 41 (21). GC-IR [(6*Z*)-isomer **3a**, cm^{-1}]: 3096, 3031, 2969, 1728, 998. GC-IR [(6*E*)-isomer **3b**, cm^{-1}]: 3095, 3015, 2969, 1727, 1000. HRMS (both isomers) (EI) calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1197.

GC-MS-O. The GC-MS-O analyses were performed with an Agilent 6890 GC combined with a 5973 mass selective detector and a sniffing port equipped with a TC-WAX capillary column (0.25 mm i.d. × 60 m; GL Sciences Co.). The effluent of the column at the end of the capillary was divided into two branches and routed by deactivated fused silica capillaries to the mass detector and sniffing port, respectively. The sample volume, split rate, injection temperature, oven temperature program, carrier gas, flow rate, and ionization mode were all the same as for GC-MS described above.

Concentration of the Key Aroma. *Distillation.* Commercial galbanum oil (950 g) was stirred in a round flask connected to a high-vacuum pump. The temperature was then increased to 121 °C at 0.05 kPa to yield six fractions, fraction i-1 (266.2 g; ∼39 °C), fraction i-2 (335.7 g; ∼40 °C), fraction i-3 (172.0 g; ∼66 °C), fraction i-4 (43.8 g; ∼84 °C), fraction i-5 (52.3 g; ∼104 °C), and fraction i-6 (50.9 g; ∼121 °C), and residue (22.6 g). Each of the fractions was subjected to GC-MS-O directly, and a 103.2 g sample of distillate was collected from the fractions i-5 and i-6, both of which were confirmed to have the target odor of fruity-green-balsamic notes.

Silica Gel Chromatography. The distillate (103.2 g) was pipetted into the top of a glass column filled with silica gel slurry (2 kg) in *n*-hexane. Chromatography was performed using *n*-hexane, followed by *n*-hexane/ethyl acetate (100:1, v/v), *n*-hexane/ethyl acetate (50:1, v/v), *n*-hexane/ethyl acetate (20:1, v/v), and *n*-hexane/ethyl acetate (10:1, v/v) to yield 13 fractions (fractions ii-1−13), each of which was freed of the solvent under high vacuum and subjected to GC-MS-O. A 28.7 g sample of concentrated effluent was collected from the fractions ii-11 and ii-12, both of which were confirmed to have the target odor. This concentrated effluent (28.7 g) obtained from the chromatography was pipetted into the top of a glass column filled with silica gel slurry (1.2 kg) in *n*-hexane. A second chromatography was performed using *n*-hexane/ethyl acetate (30:1, v/v) to yield 15 fractions (fractions iii-1−15), each of which was freed of the solvent under high vacuum and subjected to GC-MS-O. A 1.36 g sample of concentrated effluent was collected from fractions iii-8−10, all of which were confirmed to have the target odor. Next, this concentrated effluent (1.36 g) obtained from the second chromatography was pipetted into the top of a glass column filled with silica gel slurry (50 g) in toluene. A third chromatography was performed using toluene/diethyl ether (40:1, v/v) to yield 13 fractions (fractions iv-1−13), each of which was freed of the solvent under high vacuum and subjected to GC-MS-O. We finally obtained three fractions, fraction iv-4 (37 mg), fraction iv-5 (96 mg), and fraction iv-6 (527 mg), all of which were confirmed to have the target odor.

Multidimensional Gas Chromatography−Mass Spectrometry−Olfactometry (MD-GC-MS-O). The MD-GC-MS-O analyses were performed with an Agilent 6890 GC combined with an FID (250 °C), connected to an Agilent 6890 GC combined with a 5973 mass selective detector and a sniffing port equipped with a Gerstel multicolumn switching system. The effluent of the first column (TC-WAX capillary column; 0.25 mm i.d. × 60 m; GL Sciences Co.) at the end of the capillary was divided into two branches and routed by deactivated fused silica capillaries to the FID and to the column switching device, where the compounds eluted from the first column could be eliminated or transferred directly into the second column (TC-1 capillary column; 0.25 mm i.d. × 60 m; GL Sciences Co.). The effluent of the second column at the end of the capillary was divided into two branches and routed by deactivated fused silica capillaries to the mass detector and sniffing port, respectively. The fraction iv-4 sample obtained by the third silica gel chromatography of galbanum oil was injected in 1 μL volumes in a splitless mode. The injection temperature, oven temperature program, carrier gas, and flow rate were all the same as for GC-MS described above. At 36.9 min, the effluent was transferred to a cold trap at −50 °C under liquid nitrogen. After 0.4 min, the effluent was eliminated again, whereupon the trapped material was heated to 250 °C and then directed to the second column. The oven temperature of the second GC was kept at 40 °C for the initial 3 min and then increased to 300 °C at a rate of 3 °C/min. The carrier gas, flow rate, and ionization mode were the same as for GC-MS described above. The fraction iv-5 and iv-6 samples were also analyzed under the same conditions as described above.

RESULTS AND DISCUSSION

Identification of Characteristic Odor Compounds. To identify the odor-active compounds, we analyzed the oil by GC-MS-O (*29*) and detected characteristic odors at five different retention times. We were able to identify four odor-active compounds of five characteristic odors by matching them with the MS, RIs, and odor qualities, as follows: (3*E*,5*Z*)-undeca-1,3,5-triene (*15*) for the fruity and pineapple-like odor; 2-isopropyl-3-methoxypyrazine (*13*) for the earthy odor; linalool (*11*) for the fruity and floral odor; and guaiacol for the medicinal odor (**Table 1**). For the fruity, green, and balsamic odor (RI = 1899), however, a low content of the odor-active compound and overlapping in the chromatogram with other compounds thwarted our attempt to obtain the MS. Therefore, we attempted to obtain the MS by concentrating the compound using a combined method of distillation and repeated silica gel chromatography.

Concentration of the Key Aroma. After thorough studies, we realized that we needed to concentrate about 1 kg of the

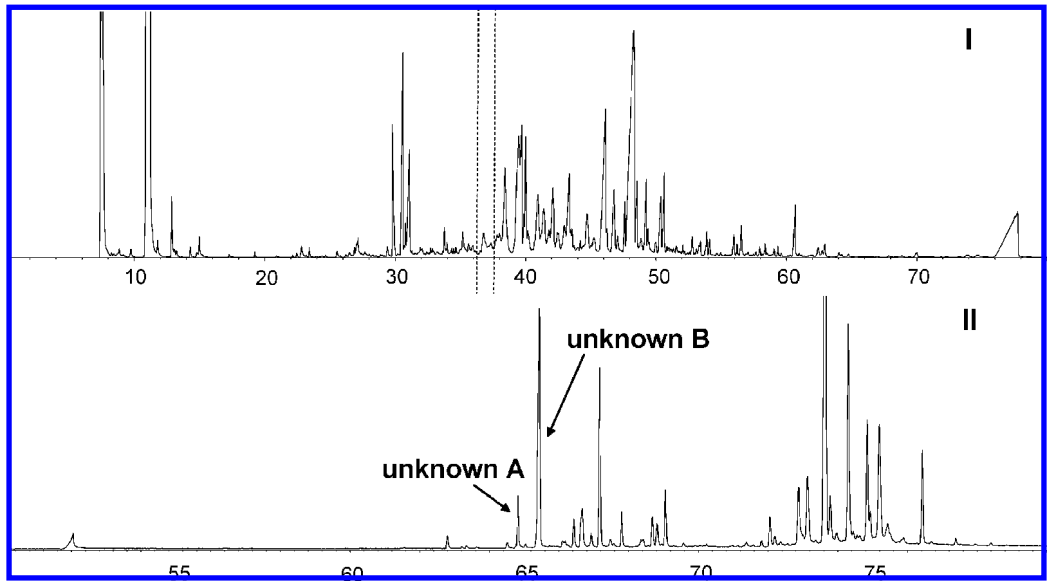

Figure 3. MD-GC-MS-O analysis of fraction iv-4 obtained from the third silica gel chromatography of galbanum oil; (**I**) gas chromatogram on the first GC equipped TC-WAX, the section (36.9−37.3 min) of which was selectively injected to the second GC; (**II**) total ion chromatogram on the second GC equipped TC-1.

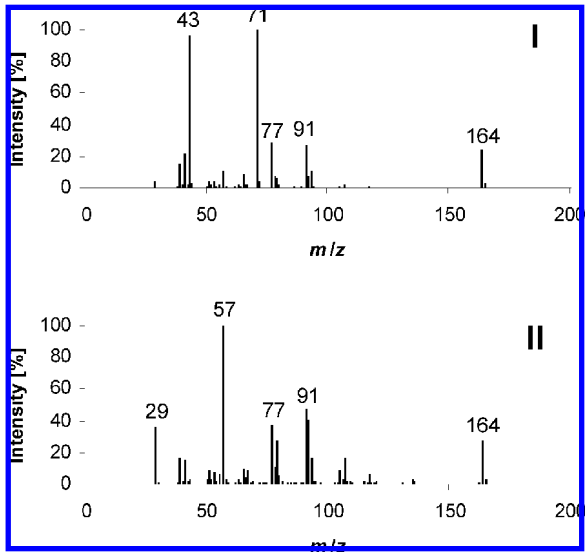

Figure 4. Mass spectra (MS-EI) of (**I**) unknown A and (**II**) unknown B.

oil. We also found that the target compound was fairly low in both volatility and polarity. As the first step to concentrate the key aroma, the monoterpenes (including β-pinene, which is the most major component of galbanum oil) and low-boiling-temperature compounds were removed from 950 g of commercial oil by distillation. Next, 103.2 g of distillate was obtained by collecting the fractions (fractions i-5 and i-6) in which we detected the target odor. As the second step, the sesquiterpenes and nonpolar compounds were removed from the distillate by silica gel chromatography eluted by gradient combination of *n*-hexane and ethyl acetate. Next, 28.7 g of concentrated effluent was obtained by collecting the fractions (fractions ii-11 and ii-12) in which we detected the target odor by GC-MS-O. As the third step, oxygenated sesquiterpenes were removed by silica gel chromatography of fixed elution of *n*-hexane and ethyl acetate, whereupon 1.36 g of concentrated effluent was obtained by collecting the fractions (fractions iii-8, iii-9, and iii-10) in which we detected the target odor by GC-MS-O. It was difficult, however, to obtain the MS by MD-GC-MS analyses of the concentrated samples. After further studies, we found that we could concentrate the compound by changing the elution solvents to a combination of toluene and diethyl ether. We finally obtained three fractions (fractions iv-4, iv-5, and iv-6) in which we detected the target odor by GC-MS-O and analyzed them by MD-GC-MS-O.

Detection of the Mass Spectrum of the Key Aroma. On MD-GC-MS-O of fraction iv-4 obtained from the third silica gel chromatography, the section (36.9−37.3 min) of the chromatogram that was obtained via the first GC equipped polar column (TC-WAX) as containing the compound with the target odor was selectively injected to the second GC equipped nonpolar column (TC-1) and analyzed by GC-MS-O. Although we had presumed that the aroma would originate from only one compound, we were surprised to detect the target fruity-green-balsamic odor at two different retention times (RI = 1316 and 1328) (**Table 2**; **Figure 3**). We thus obtained the pure MS of two compounds (hereinafter referred to as "unknown A" and "unknown B"), both of which were found to be novel in subsequent steps (**Figure 4**). Moreover, the MD-GC-MS-O analysis of fraction iv-5 also detected unknowns A and B, whereas that of fraction iv-6 detected only unknown B. To identify both unknown compounds we needed to assume their chemical structures by analyzing their MS data.

Assumption of the Structures of the Key Aroma. Two features of unknowns A and B suggested that the compounds were structural isomers: first, their similar fruity-green-balsamic odor; and second, the correspondence of a part of their MS data, namely, the molecular weight of 164 (**Figure 4**). The fragment ion at *m*/*z* 43 of unknown A was characteristic of an acetyl group, whereas the fragment ion at *m*/*z* 57 of unknown B was characteristic of a propionyl group. These data suggested that an oxygen atom was present in their molecules. The molecular weight of the unknowns (164) minus that of an oxygen atom (16) plus that of two hydrogen atoms (2) is 150, exactly the same molecular weight of (3*E*,5*Z*)-undeca-1,3,5-triene, one of the characteristic odor components of galbanum oil (**Table 1**). Moreover, the fragment ions at *m*/*z* 77 and 91 of the unknowns, respectively, were similar to those of (3*E*,5*E*/*Z*)-undeca-1,3,5-triene. Thus, we assumed that the chemical structures of the unknowns were oxygenated isomers of (3*E*,5*E*/*Z*)-undeca-1,3,5-

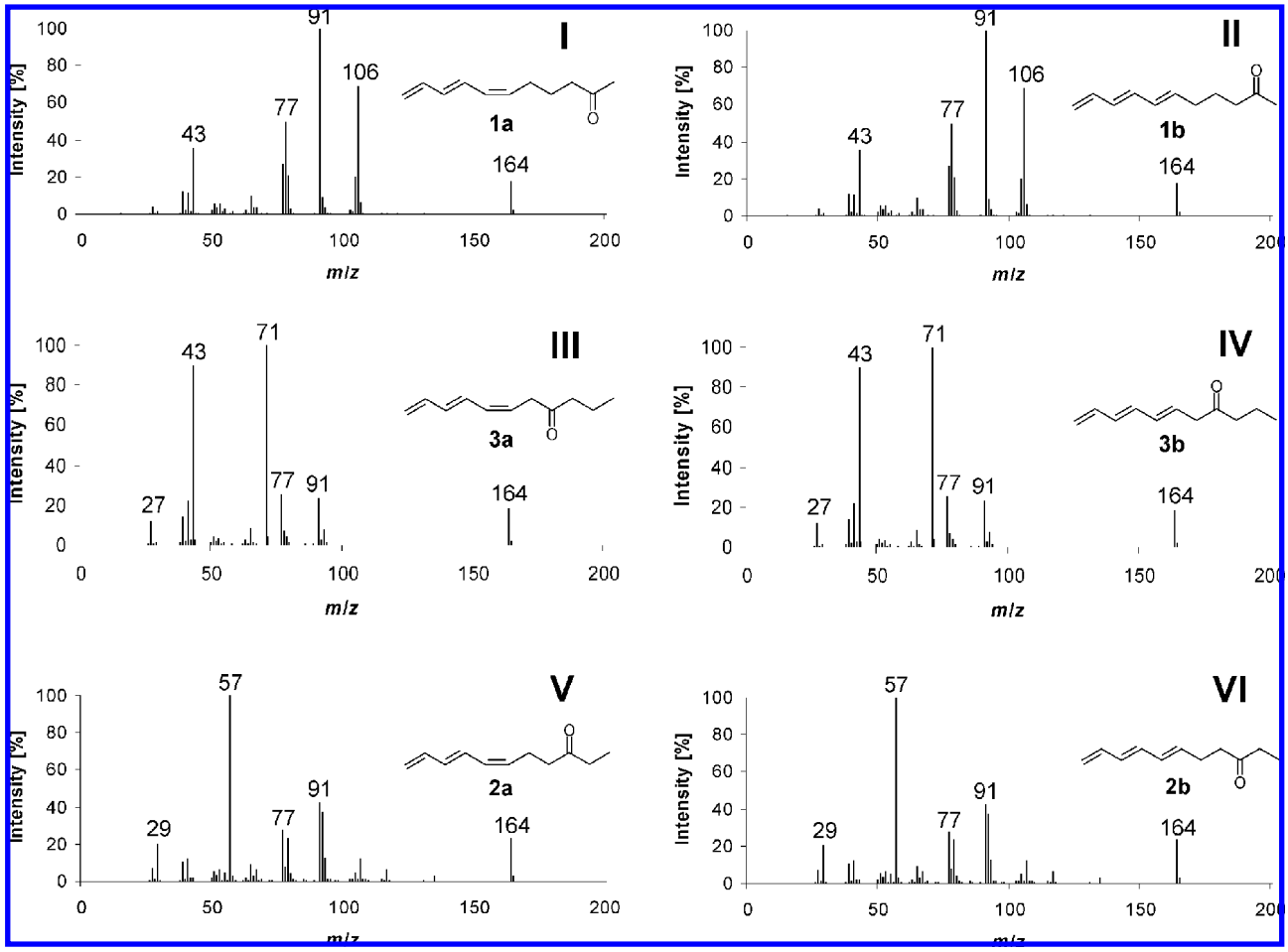

Figure 5. Mass spectra (MS-EI) of (**I**) (6*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1a**), (**II**) (6*E*,8*E*)-undeca-6,8,10-trien-2-one (**1b**), (**III**) (6*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3a**), (**IV**) (6*E*,8*E*)-undeca-6,8,10-trien-4-one (**3b**), (**V**) (6*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2a**), and (**VI**) (6*E*,8*E*)-undeca-6,8,10-trien-3-one (**2b**).

triene, namely, (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**) for unknown A and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**) for unknown B (**Figure 1**).

Identification of the Target Compounds. *Unknown A.* First, we synthesized (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**) for unknown A (**Figure 2**). δ-Hexalactone (**4**) was reduced to the lactol **5,** which was then combined with the phosphonium salt **6** prepared from (2*E*)-1-bromopenta-2,4-diene by a Wittig reaction to produce a mixture (6*E*:6*Z* = 47:53) of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-ol (**7**). Then (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**) (6*E*:6*Z* = 47:53) was synthesized by oxidizing the alcohol **7**. Although the odor of the ketone **1** was similar to that of unknown A, the MS and RI of the ketone **1** did not match those of unknown A (**Table 2**; **Figure 5**). Again, we analyzed the MS data in detail and found that the ion at *m*/*z* 71 of unknown A was characteristic of a butyroyl group. Thus, the chemical structure of unknown A was determined to be (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**) (**Figure 1**). Next we synthesized the compound for confirmation by matching.

The same strategy was selected for the synthesis of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**), using ethyl 3-oxohexanoate (**11**) as a starting material (**Figure 2**). The carbonyl group of the ketoester **11** was protected by ethylene glycol, and the ester moiety was reduced to an aldehyde moiety. Then the aldehyde **13** was combined with the same phosphonium salt **6** above by a Wittig reaction to produce a mixture (2*E*:2*Z* = 46:54) of the triene **14**. The (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**) (6*E*:6*Z* = 46:54) was then synthesized after deprotection of the acetal moiety. For confirmation, the ketone **3** was analyzed according to the same method used to analyze unknown A in galbanum oil. Finally, we identified one of the two unknowns as (6*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3a**), a novel compound in galbanum oil, by matching the MS, RI, and odor quality (**Table 2**; **Figure 5**). Although the MS data of the (6*Z*) and (6*E*)-isomers were almost the same, differences in their RIs allowed us to identify unknown A as the (6*Z*)-isomer **3a**. We also confirmed the existence of (6*E*,8*E*)-undeca-6,8,10-trien-4-one (**3b**) in galbanum oil by matching the MS and RI, although the odor of the (6*E*)-isomer **3b** noted at the sniffing port was weaker than that of the (6*Z*)-isomer **3a**. This odor intensity phenomenon was similar to the relationships between the (5*Z*) and (5*E*)-isomers of (3*E*,5*E*/*Z*)-undeca-1,3,5-triene (*30*), the (5*Z*) and (5*E*)-isomers of (3*E*,5*E*/*Z*,8*Z*)-undeca-1,3,5,8-tetraene (*31*), and the (5*Z*) and (5*E*)-isomers of (3*E*,5*E*/*Z*,9*Z*)-undeca-1,3,5,9-tetraene (*32*).

Unknown B. The synthesis of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**) was achieved according to the same scheme used for the synthesis of (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-2-one (**1**), with the exception of the starting material of γ-hexalactone (**8**) (**Figure 2**). The candidate compound, (6*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2a**), was also identified as a novel compound in galbanum oil by matching the MS, RI, and odor quality (**Table 2**; **Figure 5**). Again, we confirmed the existence of (6*E*,8*E*)-undeca-6,8,10-trien-3-one (**2b**) in galbanum oil by matching the MS and RI, although the odor character of the (6*E*)-isomer **2b** was weaker than that of the (6*Z*)-isomer **2a**.

In conclusion, we identified (6*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2a**) and (6*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3a**) as novel key aroma components responsible for the fruity-green-balsamic notes in galbanum oil by matching them with the authentic samples synthesized in our laboratory. We point out that the compounds (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-3-one (**2**) and (6*E*/*Z*,8*E*)-undeca-6,8,10-trien-4-one (**3**) were identified for the first time solely in galbanum oil and not in other natural products.

ABBREVIATIONS USED

BHT, 2,6-di-*tert*-butyl-4-methylphenol; DIBAL, diisobutyl aluminum hydride; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; EI, electron impact; FID, flame ionization detector; GC, gas chromatograph; GC-MS, gas chromatography−mass spectrometry; GC-MS-O, gas chromatography−mass spectrometry−olfactometry; HRMS, high-resolution mass spectrum; IBX, 2-iodoxybenzoic acid; IR, infrared absorption; MD-GC-MS-O, multidimensional gas chromatography−mass spectrometry−olfactometry; MS, mass spectrum; NMR, nuclear magnetic resonance; RI, retention index.

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