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Generation of Flavor-Active Compounds by Electrochemical Oxidation of (*R*)-Limonene

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Cite This: https://doi.org/10.1021/acs.jafc.2c01301

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ABSTRACT: Terpenes may be converted by electrochemical oxidation to various oxidized products with appealing aroma properties. In this study, (*R*)-limonene was anodically oxidized in the presence of ethanol, and the resulting mixture exhibited a pleasing fruity, herbal, citrus-like, and resinous odor. The aroma-active compounds were purified by means of preparative high-performance liquid chromatography, and their structures were elucidated by means of gas chromatography (GC)−mass spectrometry and nuclear magnetic resonance spectroscopy. In addition, the odor of the isolated compounds was determined by means of GC−olfactometry. Seventeen compounds were isolated, and for only four of them, analytical data had been reported previously in the literature. Furthermore, only for two of the compounds, an odor description had been available in the literature.

KEYWORDS: *aroma, terpenes, electrosynthesis, gas chromatography, structure elucidation*

■ INTRODUCTION

(*R*)-Limonene is the major constituent of orange oil, which can be obtained in huge amounts from the side streams of orange juice production by means of steam distillation or cold pressing.[1] The share of (*R*)-limonene in orange oil is up to 95%.[2] Besides the use of limonene as an important flavor and fragrance compound, it is also used as a platform chemical and extraction solvent.[3]

By natural oxidation reactions, further important aroma compounds may be generated from limonene, including carvone, limonene oxide, and menthol.[4,5] Other studies revealed that new flavor compounds may be generated by synthetic oxidation of terpenes.[6] Starting from, for example, linalool or citronellol, systematically oxidized derivatives thereof were produced, some of which exhibited highly interesting organoleptic properties. The odor impressions were sometimes fundamentally different from those of the original compounds.[7,8] Some of these compounds have not been described in the literature before.

Especially in view of the fact that (*R*)-limonene is obtained as a readily available starting material from a side stream of the food industry, it is alluring to generate new aroma substances from limonene. Therefore, in the current study, limonene was electrochemically oxidized in the presence of ethanol to create new aroma compounds with appealing olfactory impressions. Such an anodic oxidation of terpenes such as limonene is generally known.[9] Compared to other methods for the oxidation of terpenes, no environmentally harmful compounds, for example, aggressive chemicals or heavy metals or their respective salts, were used.[6,10−12] Therefore, the electrochemical oxidation of terpenes can be regarded as a sustainable alternative to generate valuable aroma compounds.

The aim of this study was to isolate and to structurally characterize the new aroma compounds prepared in a

sustainable way by means of electrochemical oxidation of terpenes. This method has an enormous potential to expand the spectrum of currently known and available aroma compounds.

■ MATERIALS AND METHODS

Chemicals. *tert*-Butyl methyl ether (99.9%) and (*R*)-carvone (99%) were purchased from Acros Organics (Geel, Belgium). Chloroform-*d* [99.8 atom % D, with 0.03 vol % tetramethylsilane (TMS), stabilized with Ag] was obtained from Carl Roth (Karlsruhe, Germany). Methylene chloride (99.9%) was purchased from Fisher Scientific (Darmstadt, Germany). *n*-Hexane (97%) was obtained from Honeywell (Darmstadt, Germany). Silica gel 60 was purchased from Macherey-Nagel (Düren, Germany). Propan-2-ol (99.8%) was obtained from VWR (Darmstadt, Germany). (*R*)-Limonene (97%, analytical standard), (*R*)-limonene (94%, for synthesis), geranyl acetate (98%), dihydrocarvone (98%; mixture of isomers), and thin-layer chromatography (TLC) silica gel 60G plates were purchased from Sigma-Aldrich (Taufkirchen, Germany). *p*-Cymene was obtained from TCI (Eschborn, Germany). Hydrogen (5.0) and helium (5.0) were obtained from Praxair (Düsseldorf, Germany) and nitrogen (5.0) from Air Liquide (Düsseldorf, Germany). Numbers in parentheses are minimum purities.

Samples. Samples were prepared by BASF SE by electrochemical oxidation of (*R*)-limonene. Therefore, (*R*)-limonene (5%) and methyl-tri-*n*-butylammonium methylsulfate (12%) were dissolved in ethanol (83%). The solution was electrolyzed at 25 °C in a capillary gap cell. This lab cell resembles in principal BASF's capillary gap cell employed at the production scale.[12] It contains a stack of bipolar

A

Table 1. Overview over the Solvent Composition for the Isolation of the Respective Compounds by Means of Preparative HPLC and Their Odor Properties as Determined by GC−FID−O Analysis

isolate no.	preseparated fraction	eluents used for prep. HPLC (*n*-hexane = A, methylene chloride = B, *tert*-butyl methyl ether = C)	odor impression
1a	3	solvents: A + B; 0 min 100% A, 15 min 97% A, 30 min 90% A, 50 min 70% A, 60 min 50% A	herbal, parsley root-like
1b	3	solvents: A + B; 0 min 95% A, 20 min 95% A	herbal, parsley root-like
2a	4	solvents: A + C; 0 min 100% A, 30 min 98.75% A, 40 min 87.5% A, 50 min 75% A, 60 min 75% A	herbal, fresh, green, dill
2b	4	solvents: A + B; 0 min 100% A, 45 min 65% A, 55 min 40% A, 60 min 0% A	herbal, spicy, earthy, juniper
3a	6	see **2b**	sweetish, fruity, anise, licorice
3b	6	solvents: A + B; 0 min 100% A, 20 min 97% A, 30 min 94% A, 40 min 90% A, 50 min 75% A, 55 min 50% A, 60 min 25% A	spicy, anise, cinnamon, clove
4a	6	solvents: A + B; 0 min 100% A, 20 min 96% A, 30 min 92% A, 50 min 75% A, 60 min 60% A, 65 min 45% A, 70 min 25% A, 75 min 0% A	herbal, green, floral, parsley root-like
4b	5/6	solvents: A + B; 0 min 100% A, 20 min 95% A, 30 min 90% A, 45 min 75% A, 55 min 50% A, 60 min 25% A	herbal, parsley root-like
5	5	solvents: A + B; 0 min 100% A, 48 min 0% A, 52 min 0% A	fruity, sweetish, green, coriander
6	5	see **2b**	herbal, earthy, parsley root-like
7	6	see **4a**	minerally, woody, earthy, spicy
8a	6	see **2a**	fresh, minty, herbal, minerally, caraway
8b	6	solvents: A + B + C; 0 min 99% A 0% B, 60 min 50% A 50% B	fresh, minty, herbal, minerally
9a	5	solvents: A + B + C; 0 min 100% A, 60 min 2% A 96% B	herbal, dill-like, earthy
9b	6	solvents: A + B; 0 min 90% A, 20 min 80% A, 40 min 55% A, 55 min 20% A, 60 min 0% A, 75 min 0% A	fresh, menthol like, floral, citrus-like
10a	6	see **9a**	minty, tart, floral, fruity, fresh, citrus-like
10b	6	see **9a**	minty, tart, resinous-like, green, spicy
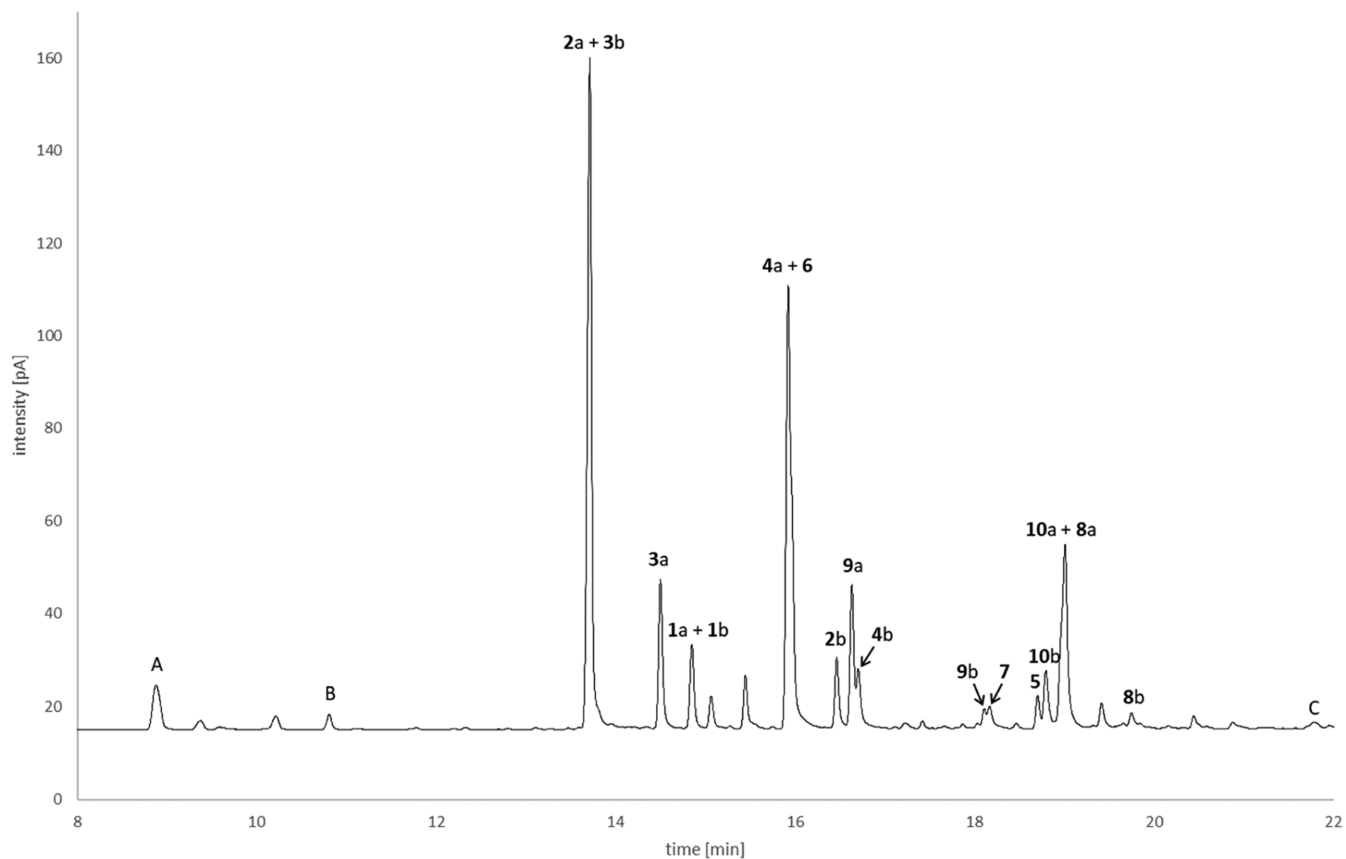
Figure 1. Representative GC−FID chromatogram of the diluted original sample (A: limonene; B: *p*-cymene; C: carvone) determined on an Agilent HP-INNOWAX column.

electrodes (147 cm² area per electrode). For this stack, Sigrafine MKUS (SGL Carbon, Wiesbaden) graphite electrodes were each covered on one side with a steel foil (25 μm) and then assembled with 1.5 mm spacers forming a stack with nine gaps. It was operated in the bipolar mode, resulting in a graphite anode and steel cathode at each gap. The cell was embedded in a circuit, and the electrolysis was conducted in a batch mode cycling the electrolyte. 3 F was applied at a constant current density of 17 mA/cm².[13]

Preseparation of the Sample. Various solvent combinations were tested by means of TLC for the separation of the substances. Combinations of *n*-hexane and methylene chloride with a polar stationary phase were found to be suitable for an efficient separation of the substances. Subsequently, the aroma compounds were preseparated by means of column chromatography on silica gel 60 as a stationary phase. The mobile phase was composed of *n*-hexane (A) and methylene chloride (B) in different ratios (100% A; 80% A + 20% B; 60% A + 40% B; 40% A + 60% B; 20% A + 80% B; 100% B). Six fractions of approximately 100 mL each, respectively, and 200 mL for the last fraction were collected, and the solvent was removed under a stream of nitrogen.

Preparative High-Performance Liquid Chromatography. The six fractions were further subjected to preparative high-performance liquid chromatography (HPLC) according to a previously developed protocol.[14] Therefore, the samples were dissolved in the respective starting eluent (Table 1). The preparative HPLC system used was a Young Lin Instrument (Anyang-si, South Korea) YL9110S with a quaternary pump (flow: 15 mL/min) equipped with a polar column (guard column: Macherey-Nagel, Nucleodur 100−5, 10 × 16 mm; preparative column: Macherey-Nagel, Nucleodur 100−5, 250 × 21 mm) coupled with a YL9120S UV/Vis detector (wavelengths: 210 and 235 nm) and an Advantec (Dublin, CA) CHF 112SC fraction collector. 7.5 mL was collected per fraction.

Purity Check by Means of Gas Chromatography. Every fraction obtained from preparative HPLC was analyzed by means of gas chromatography (GC) coupled with a flame ionization detector (FID). The gas chromatographic system was an Agilent (Waldbronn, Germany) 7890A gas chromatograph equipped with an Agilent HP-INNOWAX column [30 m × 0.32 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 20 °C/min to 240 °C (7 min); carrier gas: hydrogen, 2.0 mL/min, constant], a split/splitless inlet (250 °C; injection volume 1 μL; split ratio 1:20 or 1:50), and a FID (250 °C; hydrogen, 40 mL/min; air, 400 mL/min; nitrogen, 30 mL/min).

Description of Odor Impressions. In order to avoid a falsification of the odor impressions of the purified isolates due to possible traces of impurities, the odor impressions of the isolated compounds were determined by means of GC−FID−olfactometry (GC−FID−O). The gas chromatographic system used was an Agilent 7890A gas chromatograph equipped with an Agilent HP-INNOWAX column [30 m × 0.32 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 5 °C/min to 240 °C (7 min); carrier gas: hydrogen, 2.2 mL/min, constant] and a split/splitless inlet (250 °C; injection volume 1 μL; split ratio 1:10 or splitless; splitless time: 1 min). After the column, the carrier gas was split 1:1 by a GERSTEL μFlowManager Splitter to a FID (250 °C; hydrogen, 40 mL/min; air, 400 mL/min; nitrogen, 30 mL/min) and a GERSTEL ODP3 olfactory detection port (transfer line, 250 °C; mixing chamber, 150 °C; make up gas nitrogen). A section of the chromatogram of the sample is shown in Figure 1; the odor impressions are presented in Table 1.

Structure Elucidation of the Isolated Compounds. Pure compounds obtained from preparative HPLC were analyzed by means of GC−mass spectrometry (MS) on two columns of different polarities. The first gas chromatographic system used was an Agilent 7890A gas chromatograph equipped with an Agilent VF-WAXms column [30 m × 0.25 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 5 °C/min to 240 °C (7 min); carrier gas: helium, 1.2 mL/min, constant] and a split/splitless inlet (250 °C; injection volume 1 μL; split ratio 1:20 or 1:50) coupled to an Agilent 5975C quadrupole mass spectrometer (ionization energy: 70 eV; ion source: 230 °C; quadrupole: 150 °C; *m/z* 33−300). The retention indices were calculated by linear interpolation from the retention times of *n*-alkanes (C$_7$−C$_{30}$).[15] The second gas chromatographic system used for the determination of retention indices on a nonpolar column was an Agilent 7890B gas chromatograph equipped with an AgilentDB-5ms column [30 m × 0.25 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 5 °C/min to 300 °C (7 min);

carrier gas: helium, 1.2 mL/min, constant] and a split/splitless inlet (250 °C; split ratio 1:50 or 1:100) coupled to an Agilent 5977B quadrupole mass spectrometer (ionization energy, 70 eV; ion source, 230 °C; quadrupole, 150 °C; *m/z* 33−300).

Nuclear Magnetic Resonance Analyses of the Isolated Compounds. All isolated compounds were analyzed by means of nuclear magnetic resonance (NMR) spectroscopy. Therefore, the solvent of pure fractions was removed under a nitrogen stream, and the resulting residue was dissolved in CDCl$_3$. NMR spectra were recorded using a Bruker (Rheinstetten, Germany) Avance II 400 MHz [working at 400.130 MHz (^{1}H) and 100.613 MHz (^{13}C)] spectrometer equipped with a 5 mm inverse detection *z*-gradient BBI probe, a Bruker Avance III HD 400 MHz [working at 400.250 MHz (^{1}H) and 100.643 MHz (^{13}C)] spectrometer equipped with a 5 mm *z*-gradient PA TBO probe, or a Bruker Avance III HD 600 MHz [working at 600.050 MHz (^{1}H) and 150.883 MHz (^{13}C)] spectrometer equipped with a 5 mm *z*-gradient BBO probe at room temperature unless otherwise stated. The ^{1}H chemical shifts (δ) are reported in parts per million (ppm) relative to the TMS signal (CDCl$_3$: δ = 7.26 ppm relative to TMS δ = 0 ppm) and the ^{13}C chemical shifts corresponding to the deuterated solvent (CDCl$_3$: δ = 77.0 ppm). Coupling constants (J) are reported in hertz (Hz). ^{13}C NMR experiments (^{13}C{^{1}H} and DEPT) were proton-decoupled.

The complete ^{1}H and ^{13}C NMR assignments for the isolated compounds were achieved using a combination of 1D (^{1}H NMR, ^{13}C NMR, DEPT135) and 2D [^{1}H,^{1}H correlation spectroscopy (COSY), heteronuclear single-quantum correlation, heteronuclear multiple-bond correlation, and nuclear Overhauser effect spectroscopy] experiments using standard Bruker pulse programs. The data were collected and processed by TOPSPIN software (Bruker).

Semiquantitation of the Identified Components in the Original Samples. The amount of the isolated compounds in the original samples was determined semiquantitatively by means of GC−FID using geranyl acetate as an internal standard. Therefore, 84.7 mg of the sample and 11.1 mg of geranyl acetate were diluted to 20 mL with *n*-hexane. 1 μL thereof was analyzed by means of GC−FID. The gas chromatographic system was an Agilent 7890A gas chromatograph equipped with an Agilent HP-INNOWAX column [30 m × 0.32 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 3 °C/min to 240 °C (7 min); carrier gas: hydrogen, 2.0 mL/min, constant], an Agilent DB-5 column [30 m × 0.32 mm, 0.25 μm film thickness; temperature program: 40 °C (3 min), 3 °C/min to 300 °C (7 min); carrier gas: hydrogen, 2.0 mL/min, constant], a split/splitless inlet (250 °C; different split ratios between 1:10 and 1:500), and a FID (250 °C; hydrogen, 40 mL/min; air, 400 mL/min; nitrogen, 30 mL/min). For the semiquantitative calculation, the response factor of the internal standard was assumed to be 1 (Table 2).

Statistics. The GC−O experiments were performed in triplicate by four trained panelists. The panelists, three men and one woman, were between 23 and 30 years old. A compound was considered to be odor active if at least three of the four panelists could perceive and describe the substance. The semiquantitative experiments were run in duplicate.

■ RESULTS AND DISCUSSION

The sample was prepared as described above. The resulting material was colored amber-like and exhibited a fruity, herbal, citrus, and resinous odor. From this sample, 17 compounds were isolated by means of preparative HPLC (Figure 2). Their structures were elucidated by means of NMR and GC−MS. Additionally, limonene, *p*-cymene, and carvone were identified by means of GC−MS by comparing their retention indices and mass spectra with those of commercially available standards on two columns of different polarities (Table 2). Thus, in total, 20 different compounds were identified in the oxidized (*R*)-limonene sample.

Compound Identification by GC−MS and NMR Spectroscopy. *NMR and GC−MS Data of Compound 1a.*

Table 2. Determined Retention Indices of the Isolated and Identified Compounds on Two Columns of Different Polarities Compared with Those of Commercially Available Standards (n.a.: Not Available) and Their Determined Approximate Amounts in the Sample

compound/ isolate no.	retention index$_{sample}$		retention index$_{standard}$		approx. amount [mg/kg]
	VF-WAXms	DB-5	VF-WAXms	DB-5	
1a	1431	1226	n.a.	n.a.	69
1b	1431	1228	n.a.	n.a.	71
2a	1384	1192	n.a.	n.a.	1005
2b	1498	1241	n.a.	n.a.	122
3a	1418	1207	n.a.	n.a.	266
3b	1386	1188	n.a.	n.a.	337
4a	1477	1232	n.a.	n.a.	272
4b	1509	1259	n.a.	n.a.	86
5	1591	1313	n.a.	n.a.	123
6	1475	1234	n.a.	n.a.	782
7	1565	1373	n.a.	n.a.	41
8a	1617	1197	1612	1197	401
8b	1637	1204	1629	1203	11
9a	1501	1351	n.a.	n.a.	251
9b	1563	1369	n.a.	n.a.	31
10a	1611	1191	n.a.	n.a.	71
10b	1600	1186	n.a.	n.a.	9
limonene	1187	1029	1179	1028	136
p-cymene	1259	1026	1254	1023	8
carvone	1714	1243	1708	1243	5

^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.75 (1H, m, H−C9), 4.73 (1H, m, H−C9), 4.44 (1H, d, J = 3 Hz, H−C2), 3.69 (2H, m, H−C11), 2.82 (1H, m, H−C3), 2.24 (1H, m, H−C6), 1.86 (1H, m, H−C5), 1.76 (1H, m, H−C4), 1.72 (3H, brs, H−C10), 1.36 (1H, m, H−C4), 1.28 (3H, t, J = 7 Hz, H−C12), 1.26 (1H, m, H−C5), 1.07 (3H, d, J = 7 Hz, H−C7).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 158.7 (s (C−q), C1), 150.2 (s (C−q), C8), 109.8 (t (=CH$_2$), C9), 97.0 (d (= CH), C2), 61.8 (t (−O−CH$_2$), C11), 42.6 (d (CH), C3), 32.4 (d (CH), C6), 30.2 (t (CH$_2$), C5), 26.3 (t (CH$_2$), C4), 20.7 (q (CH$_3$), C10), 18.8 (q (CH$_3$), C7), 14.7 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) m/z (%): 180 (100) [M$^{•+}$], 165 (99), 43 (68), 137 (63), 109 (61), 95 (60), 81 (56), 123 (50), 41 (38), 67 (37).

NMR and GC−MS Data of Compound 1b. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.76 (1H, m, H−C9), 4.74 (1H, m, H−C9), 4.42 (1H, d, J = 3 Hz, H−C2), 3.70 (2H, m, H−C11), 2.83 (1H, m, H−C3), 2.21 (1H, sext, J = 6 Hz, H−C6), 1.73 (1H, m, H−C5), 1.72 (3H, brs, H−C10), 1.61 (1H, m, H−C4), 1.49 (1H, m, H−C5), 1.47 (1H, m, H−C4), 1.28 (3H, t, J = 7 Hz, H−C12), 1.09 (3H, d, J = 7 Hz, H−C7).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 159.1 (s (C−q), C1), 150.3 (s (C−q), C8), 109.8 (t (=CH$_2$), C9), 96.9 (d (= CH), C2), 61.7 (t (−O−CH$_2$), C11), 42.9 (d (CH), C3), 31.8 (d (CH), C6), 29.2 (t (CH$_2$), C5), 24.6 (t (CH$_2$), C4), 20.4 (q (CH$_3$), C10), 19.1 (q (CH$_3$), C7), 14.7 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) m/z (%): 180 (100) [M$^{•+}$], 165 (99), 43 (68), 109 (64), 137 (63), 95 (62), 81 (57), 123 (51), 41 (38), 67 (38).

NMR and GC−MS Data of Compound 2a. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 4.86 (1H, m, H−C7), 4.81 (1H, m, H−C7), 4.70 (2H, m, H−C9), 3.87 (1H, t, J = 3 Hz, H−C2), 3.43

(1H, dq, J = 10/7 Hz, H−C11), 3.29 (1H, dq, J = 10/7 Hz, H−C11), 2.53 (1H, tt, J = 12/3 Hz, H−C4), 2.33 (1H, tdt, J = 13/5/2 Hz, H−C6), 2.18 (1H, m, H−C6), 2.06 (1H, m, H−C3), 1.87 (1H, m, H−C5), 1.73 (3H, brs, H−C10), 1.48 (1H, ddd, J = 13/11/3 Hz, H−C3), 1.27 (1H, m, H−C5), 1.20 (3H, t, J = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 149.8 (s (C−q), C8), 148.0 (s (C−q), C1), 110.6 (t (=CH$_2$), C7), 108.6 (t (= CH$_2$), C9), 79.0 (d (−O−CH), C2), 62.6 (t (−O−CH$_2$), C11), 38.6 (d (CH), C4), 38.2 (t (CH$_2$), C3), 32.9 (t (CH$_2$), C5), 30.4 (t (CH$_2$), C6), 21.0 (q (CH$_3$), C10), 15.4 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) m/z (%): 134 (100), 119 (68), 91 (59), 93 (44), 137 (37), 41 (32), 83 (32), 79 (30), 67 (27), 92 (26), 180 (1) [M$^{•+}$].

NMR and GC−MS Data of Compound 2b. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 4.95 (1H, q, J = 2 Hz, H−C7), 4.76 (1H, q, J = 2 Hz, H−C7), 4.70 (2H, m, H−C9), 3.68 (1H, m, H−C2), 3.60 (2H, m, H−C11), 2.42 (1H, ddd, J = 13/4/3 Hz, H−C6), 2.17 (1H, m, H−C4), 2.15 (1H, m, H−C3), 2.02 (1H, m, H−C6), 1.79 (1H, m, H−C5), 1.71 (3H, brs, H−C10), 1.27 (1H, m, H−C3), 1.24 (1H, m, H−C12), 1.23 (3H, t, J = 7 Hz, H−C5).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 148.9 (s (C−q), C8), 148.8 (s (C−q), C1), 109.1 (t (=CH$_2$), C9), 104.5 (t (= CH$_2$), C7), 79.6 (d (−O−CH), C2), 65.0 (t (−O−CH$_2$), C11), 44.4 (d (CH), C4), 39.7 (t (CH$_2$), C3), 34.1 (t (CH$_2$), C6), 33.1 (t (CH$_2$), C5), 20.6 (q (CH$_3$), C10), 15.6 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) m/z (%): 137 (100), 93 (98), 91 (91), 119 (90), 83 (76), 79 (75), 134 (73), 41 (71), 67 (67), 55 (65), 180 (11) [M$^{•+}$].

NMR and GC−MS Data of Compound 3a. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.66 (1H, m, H−C1), 5.65 (1H, m, H−C2), 4.76 (1H, m, H−C9), 4.70 (1H, m, H−C9), 3.43 (2H, qq, J = 9/7 Hz, H−C11), 2.75 (1H, m, H−C6), 1.90 (1H, m, H−C5), 1.86 (1H, m, H−C4), 1.72 (3H, brs, H−C10), 1.62 (1H, m, H−C4), 1.51 (1H, m, H−C5), 1.26 (3H, s, H−C7), 1.17 (3H, t, J = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 148.1 (s (C−q), C8), 133.4 (d (=CH), C2), 132.0 (d (=CH), C1), 110.5 (t (= CH$_2$), C9), 73.4 (s (−O−C), C3), 57.2 (t (−O−CH$_2$), C11), 43.1 (d (CH), C6), 32.2 (t (CH$_2$), C4), 26.6 (q (CH$_3$), C7), 25.9 (t (CH$_2$), C5), 20.9 (q (CH$_3$), C10), 16.4 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) m/z (%): 165 (100), 137 (60), 134 (60), 93 (52), 43 (51), 91 (47), 109 (47), 107 (46), 79 (38), 77 (33), 180 (1) [M$^{•+}$].

NMR and GC−MS Data of Compound 3b. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.69 (1H, m, H−C1), 5.69 (1H, m, H−C2), 4.79 (1H, m, H−C9), 4.75 (1H, m, H−C9), 3.43 (2H, qd, J = 7/2 Hz, H−C11), 2.65 (1H, m, H−C6), 1.94 (1H, m, H−C4), 1.74 (3H, m, H−C10), 1.71 (2H, m, H−C5), 1.40 (1H, m, H−C4), 1.24 (3H, s, H−C7), 1.15 (3H, t, J = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 148.1 (s (C−q), C8), 133.0 (d (=CH), C2), 132.6 (d (=CH), C1), 110.8 (t (= CH$_2$), C9), 71.9 (s (−O−C), C3), 57.4 (t (−O−CH$_2$), C11), 43.1 (d (CH), C6), 32.6 (t (CH$_2$), C4), 26.6 (q (CH$_3$), C7), 24.6 (t (CH$_2$), C5), 21.0 (q (CH$_3$), C10), 16.4 (q (CH$_3$), C12).
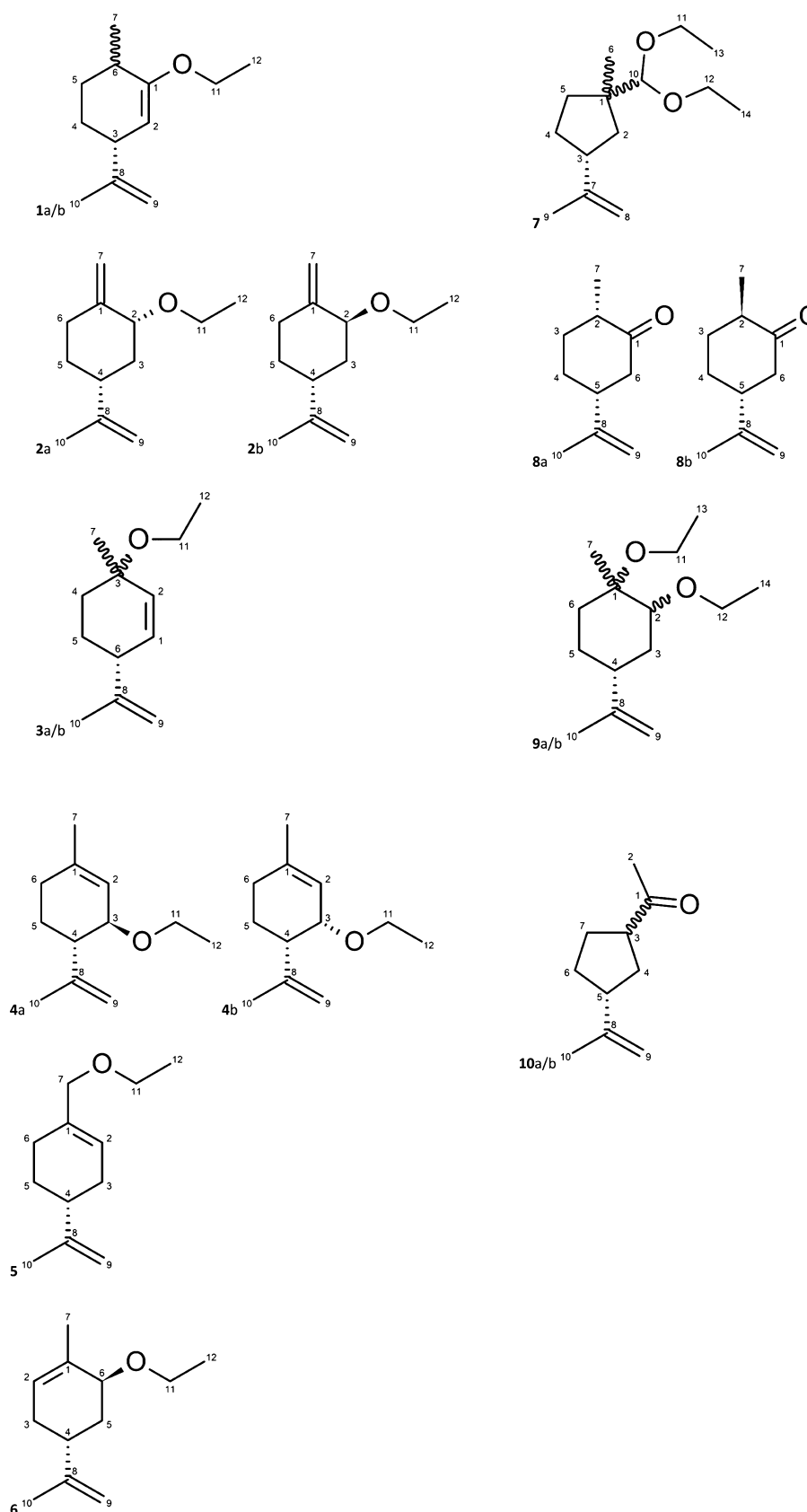
Figure 2. Structures of the isolated compounds {**1**a/b, 1-ethoxy-6-methyl-(*R*)-3-(prop-1-en-2-yl)cyclohex-1-ene; **2**a/b, 2-ethoxy-1-methylidene-(*R*)-4-(prop-1-en-2-yl)cyclohexane; **3**a/b, 3-ethoxy-3-methyl-6-(prop-1-en-2-yl)cyclohex-1-ene; **4**a/b, 3-ethoxy-1-methyl-(*R*)-4-(prop-1-en-2-yl)cyclohex-1-ene; **5**, 1-(ethoxymethyl)-(*R*)-4-(prop-1-en-2-yl)cyclohex-1-ene; **6**, 6-ethoxy-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene; **7**, 1-(diethoxymethyl)-1-methyl-3-(prop-1-en-2-yl)cyclopentane; **8**a/b, 2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one; **9**a/b, 1,2-diethoxy-1-methyl-(*R*)-4-(prop-1-en-2-yl)cyclohexane; **10**a/b, 1-[3-(prop-1-en-2-yl)cyclopentyl]ethan-1-one}.

GC−MS (EI, 70 eV) *m/z* (%): 165 (100), 93 (93), 137 (92), 107 (84), 91 (73), 94 (72), 43 (72), 109 (67), 79 (62), 77 (49), 180 (1) [M•+].

NMR and GC−MS Data of Compound 4a. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 5.48 (1H, m, H−C2), 4.80 (1H, m, H−C9), 4.76 (1H, m, H−C9), 3.84 (1H, m, H−C3), 3.58 (1H, dq, *J* = 9/7 Hz, H−C11), 3.47 (1H, dq, *J* = 9/7 Hz, H−C11), 2.22 (1H, ddd, *J* = 11/8/3 Hz, H−C4), 2.01 (1H, m, H−C6), 1.88 (1H, m, H−C6), 1.77 (3H, brs, H−C10), 1.72 (1H, m, H−C5), 1.68 (3H, brs, H−C7), 1.61 (1H, dddd, *J* = 13/11/10/5 Hz, H−C5), 1.17 (3H, t, *J* = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 147.5 (s (C−q), C8), 137.4 (s (C−q), C1), 122.6 (d (=CH), C2), 110.6 (t (=CH$_2$), C9), 77.1 (d (−O−CH), C3), 63.7 (t (−O−CH$_2$), C11), 46.8 (d (CH), C4), 29.8 (t (CH$_2$), C6), 26.6 (t (CH$_2$), C5), 23.3 (q (CH$_3$), C7), 21.0 (q (CH$_3$), C10), 15.7 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) *m/z* (%): 112 (100), 97 (89), 83 (80), 84 (42), 108 (35), 91 (19), 41 (18), 77 (14), 79 (12), 55 (11), 180 (1) [M•+].

NMR and GC−MS Data of Compound 4b. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 5.51 (1H, m, H−C2), 4.72 (2H, m, H−C9), 3.91 (1H, m, H−C3), 3.64 (1H, dq, *J* = 9/7 Hz, H−C11), 3.46 (1H, dq, *J* = 9/7 Hz, H−C11), 2.23 (1H, m, H−C4), 2.19 (1H, m, H−C5), 2.03 (1H, m, H−C6), 1.93 (1H, m, H−C6), 1.73 (3H, brs, H−C10), 1.72 (3H, m, H−C7), 1.46 (1H, ddd, *J* = 13/12/10 Hz, H−C5), 1.21 (3H, t, *J* = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 149.3 (s (C−q), C8), 135.5 (s (C−q), C1), 124.4 (d (=CH), C2), 108.9 (t (=CH$_2$), C9), 78.0 (d (−O−CH), C3), 63.8 (t (−O−CH$_2$), C11), 40.8 (d (CH), C4), 34.4 (t (CH$_2$), C5), 31.0 (t (CH$_2$), C6), 20.4 (q (CH$_3$), C10), 19.2 (q (CH$_3$), C7), 15.7 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) *m/z* (%): 84 (100), 112 (72), 134 (70), 119 (53), 55 (52), 79 (42), 41 (39), 95 (38), 77 (38), 83 (38), 180 (13) [M•+].

NMR and GC−MS Data of Compound 5. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.70 (1H, m, H−C2), 4.71 (2H, m, H−C9), 3.84 (2H, s, H−C7), 3.44 (2H, q, *J* = 7 Hz, H−C11), 2.16 (1H, m, H−C4), 2.15 (1H, m, H−C3), 2.10 (2H, m, H−C6), 1.97 (1H, m, H−C3), 1.84 (1H, m, H−C5), 1.74 (3H, brs, H−C10), 1.48 (1H, m, H−C5), 1.21 (3H, t, *J* = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 150.0 (s (C−q), C8), 134.9 (s (C−q), C1), 124.0 (d (=CH), C2), 108.6 (t (=CH$_2$), C9), 75.0 (t (−O−CH$_2$), C7), 65.2 (t (−O−CH$_2$), C11), 41.2 (d (CH), C4), 30.5 (t (CH$_2$), C3), 27.5 (t (CH$_2$), C5), 26.5 (t (CH$_2$), C6), 20.8 (q (CH$_3$), C10), 15.2 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) *m/z* (%): 93 (100), 91 (99), 119 (76), 79 (70), 137 (64), 67 (61), 83 (53), 92 (50), 68 (49), 134 (47), 180 (16) [M•+].

NMR and GC−MS Data of Compound 6. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 5.60 (1H, m, H−C2), 4.73 (2H, m, H−C9), 3.68 (1H, dq, *J* = 9/7 Hz, H−C11), 3.60 (1H, m, H−C6), 3.43 (1H, dq, *J* = 9/7 Hz, H−C11), 2.36 (1H, m, H−C4), 2.15 (1H, m, H−C3), 2.05 (1H, m, H−C5), 1.81 (1H, m, H−C3), 1.77 (1H, m, H−C7), 1.74 (3H, brs, H−C10), 1.40 (1H, ddd, *J* = 14/13/4 Hz, H−C5), 1.23 (3H, t, *J* = 7 Hz, H−C12).

^{13}C NMR (CDCl$_3$ with 0.05% v/v TMS, 150 MHz): δ 149.9 (s (C−q), C8), 133.2 (s (C−q), C1), 125.5 (d (=CH), C2),

108.6 (t (=CH$_2$), C9), 76.0 (d (−O−CH), C6), 64.8 (t (−O−CH$_2$), C11), 35.5 (d (CH), C4), 32.1 (t (CH$_2$), C5), 31.1 (t (CH$_2$), C3), 21.0 (q (CH$_3$), C7), 21.0 (q (CH$_3$), C10), 15.8 (q (CH$_3$), C12).

GC−MS (EI, 70 eV) *m/z* (%): 137 (100), 84 (94), 91 (76), 119 (66), 109 (63), 93 (61), 55 (47), 77 (46), 112 (45), 83 (42), 180 (18) [M•+].

NMR and GC−MS Data of Compound 7. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 4.69 (1H, m, H−C8), 4.65 (1H, m, H−C8), 4.11 (1H, s, H−C10), 3.81 (1H, m, H−C11 or H−C12), 3.81 (1H, m, H−C11 or H−C12), 3.54 (1H, m, H−C11 or H−C12), 3.54 (1H, m, H−C11 or H−C12), 2.52 (1H, m, H−C3), 1.96 (1H, ddd, *J* = 13/8/1 Hz, H−C2), 1.75 (1H, m, H−C5), 1.75 (1H, m, H−C4), 1.72 (3H, brs, H−C9), 1.50 (1H, m, H−C4), 1.37 (1H, m, H−C5), 1.22 (3H, t, *J* = 7 Hz, H−C13 or H−C14), 1.22 (3H, t, *J* = 7 Hz, H−C13 or H−C14), 1.11 (1H, dd, *J* = 13/11 Hz, H−C2), 1.03 (3H, s, H−C6).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 149.0 (s (C−q), C7), 110.72 (d (−O−CH−O−), C10), 107.8 (t (=CH$_2$), C8), 65.9 (t (−O−CH$_2$), C11 or C12), 65.7 (t (−O−CH$_2$), C11 or C12), 47.4 (d (CH), C3), 47.2 (s (C−q), C1), 41.0 (t (CH$_2$), C2), 35.4 (t (CH$_2$), C5), 30.7 (t (CH$_2$), C4), 24.6 (q (CH$_3$), C6), 21.3 (q (CH$_3$), C9), 15.6 (q (CH$_3$), C13 or C14), 15.5 (q (CH$_3$), C13 or C14).

GC−MS (EI, 70 eV) *m/z* (%): 103 (100), 75 (40), 47 (33), 99 (13), 107 (9), 93 (8), 43 (8), 71 (8), 41 (7), 55 (7), 226 (1) [M•+].

NMR and GC−MS Data of Compound 8a. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.76 (1H, m, H−C9), 4.73 (1H, m, H−C9), 2.45 (1H, dt, *J* = 11/2 Hz, H−C6), 2.38 (1H, m, H−C2), 2.36 (1H, m, H−C5), 2.28 (1H, m, H−C6), 2.13 (1H, m, H−C3), 1.94 (1H, m, H−C4), 1.74 (3H, brs, H−C10), 1.65 (1H, m, H−C4), 1.38 (1H, qd, *J* = 13/4 Hz, H−C3), 1.04 (3H, d, *J* = 7 Hz, H−C7).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 212.7 (s (C=O), C1), 147.7 (s (C−q), C8), 109.6 (t (=CH$_2$), C9), 47.0 (d (CH), C5), 46.9 (t (CH$_2$), C6), 44.8 (d (CH), C2), 34.9 (t (CH$_2$), C3), 30.8 (t (CH$_2$), C4), 20.5 (q (CH$_3$), C10), 14.4 (q (CH$_3$), C7).

GC−MS (EI, 70 eV) *m/z* (%): 67 (100), 95 (79), 68 (52), 81 (48), 82 (46), 109 (42), 41 (40), 69 (36), 55 (28), 39 (27), 152 (18) [M•+].

NMR and GC−MS Data of Compound 8b. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.83 (1H, m, H−C9), 4.69 (1H, m, H−C9), 2.60 (1H, m, H−C5), 2.55 (1H, m, H−C6), 2.42 (1H, m, H−C6), 2.40 (1H, m, H−C2), 1.85 (1H, m, H−C3), 1.85 (2H, m, H−C4), 1.73 (3H, brs, H−C10), 1.60 (1H, m, H−C3), 1.09 (3H, d, *J* = 7 Hz, H−C7).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 214.0 (s (C=O), C1), 146.9 (s (C−q), C8), 111.5 (t (=CH$_2$), C9), 44.6 (d (CH), C2), 44.1 (t (CH$_2$), C6), 44.0 (d (CH), C5), 30.7 (t (CH$_2$), C3), 26.4 (t (CH$_2$), C4), 26.4 (q (CH$_3$), C10), 21.5, 15.6 (q (CH$_3$), C7).

GC−MS (EI, 70 eV) *m/z* (%): 67 (100), 95 (92), 68 (52), 82 (45), 41 (41), 69 (37), 81 (36), 152 (31) [M•+], 55 (29), 39 (27).

NMR and GC−MS Data of Compound 9a. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 4.70 (1H, m, H−C9), 4.68 (1H, m, H−C9), 3.61 (1H, dq, *J* = 9/7 Hz, H−C12), 3.37 (1H, m, H−C12), 3.37 (2H, m, H−C11), 3.23 (1H, brs, H−C2), 2.18 (1H, tt, *J* = 12/2 Hz, H−C4), 1.73 (1H, m, H−C3), 1.72 (3H, brs, H−C10), 1.67 (1H, m, H−C6), 1.53 (1H, m, H−C6), 1.44 (1H, m, H−C5), 1.37 (1H, m, H−C5), 1.26 (1H, m, H−

C3), 1.17 (3H, t, J = 7 Hz, H−C14), 1.16 (3H, t, J = 7 Hz, H−C13), 1.16 (3H, s, H−C7).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 150.8 (s (C−q), C8), 108.1 (t (=CH$_2$), C9), 79.8 (d (−O−CH), C2), 74.8 (s (−O−C), C1), 64.7 (t (−O−CH$_2$), C12), 55.5 (t (−O−CH$_2$), C11), 37.7 (d (CH), C4), 30.2 (t (CH$_2$), C6), 29.6 (t (CH$_2$), C3), 26.3 (t (CH$_2$), C5), 21.5 (q (CH$_3$), C7), 20.9 (q (CH$_3$), C10), 16.1 (q (CH$_3$), C13), 15.7 (q (CH$_3$), C14).

GC−MS (EI, 70 eV) m/z (%): 99 (100), 71 (36), 43 (19), 58 (11), 140 (8), 108 (7), 100 (7), 86 (6), 41 (6), 93 (6), 226 (1) [M$^{•+}$].

NMR and GC−MS Data of Compound 9b. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.73 (1H, m, H−C9), 4.69 (1H, m, H−C9), 3.69 (1H, dq, J = 9/7 Hz, H−C12), 3.50 (1H, dq, J = 9/7 Hz, H−C11), 3.40 (1H, m, H−C11), 3.40 (1H, m, H−C12), 2.98 (1H, m, H−C2), 1.97 (1H, m, H−C6), 1.96 (1H, m, H−C4), 1.76 (2H, m, H−C3), 1.73 (3H, brs, H−C10), 1.42 (2H, m, H−C5), 1.23 (3H, s, H−C7), 1.18 (3H, t, J = 7 Hz, H−C14), 1.17 (3H, t, J = 7 Hz, H−C13), 1.12 (1H, m, H−C6).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.8 (s (C−q), C8), 108.6 (t (=CH$_2$), C9), 85.0 (d (−O−CH), C2), 74.6 (s (−O−C), C1), 65.4 (t (−O−CH$_2$), C12), 56.6 (t (−O−CH$_2$), C11), 44.6 (d (CH), C4), 34.6 (t (CH$_2$), C6), 31.2 (t (CH$_2$), C3), 26.2 (t (CH$_2$), C5), 21.5 (q (CH$_3$), C7), 20.6 (q (CH$_3$), C10), 16.2 (q (CH$_3$), C13), 15.6 (q (CH$_3$), C14).

GC−MS (EI, 70 eV) m/z (%): 99 (100), 71 (38), 43 (19), 58 (10), 100 (7), 140 (7), 108 (6), 86 (6), 41 (6), 93 (6), 226 (1) [M$^{•+}$].

NMR and GC−MS Data of Compound 10a. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 4.73 (1H, m, H−C9), 4.70 (1H, m, H−C9), 2.95 (1H, m, H−C3), 2.49 (1H, m, H−C5), 2.17 (3H, s, H−C2), 2.04 (1H, m, H−C4), 1.93 (1H, m, H−C7), 1.84 (1H, m, H−C7), 1.84 (1H, m, H−C6), 1.73 (3H, brs, H−C10), 1.61 (1H, ddd, J = 12/11/10 Hz, H−C4), 1.49 (1H, m, H−C6).

^{13}C NMR (CDCl$_3$, 150 MHz): δ 210.6 (s (C=O), C1), 147.4 (s (C−q), C8), 109.0 (t (=CH$_2$), C9), 51.9 (d (CH), C3), 47.7 (d (CH), C5), 31.2 (t (CH$_2$), C4), 30.5 (t (CH$_2$), C6), 28.8 (q (CH$_3$), C2), 27.3 (t (CH$_2$), C7), 21.0 (q (CH$_3$), C10).

GC−MS (EI, 70 eV) m/z (%): 43 (100), 109 (99), 67 (88), 137 (49), 71 (39), 41 (28), 79 (26), 93 (26), 55 (26), 82 (25), 152 (24) [M$^{•+}$].

NMR and GC−MS Data of Compound 10b. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.70 (2H, m, H−C9), 3.00 (1H, dtd, J = 10/8/5 Hz, H−C3), 2.47 (1H, m, H−C5), 2.16 (3H, s, H−C2), 2.06 (1H, dddd, J = 13/8/5/1 Hz, H−C4), 1.98 (1H, m, H−C7), 1.88 (1H, m, H−C6), 1.78 (1H, m, H−C7), 1.73 (3H, brs, H−C10), 1.65 (1H, dt, J = 13/10 Hz, H−C4), 1.48 (1H, dtd, J = 12/10/8 Hz, H−C6).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 210.9 (s (C=O), C1), 148.0 (s (C−q), C8), 108.7 (t (=CH$_2$), C9), 51.3 (d (CH), C3), 46.4 (d (CH), C5), 32.9 (t (CH$_2$), C4), 31.7 (t (CH$_2$), C6), 28.9 (q (CH$_3$), C2), 28.5 (t (CH$_2$), C7), 21.5 (q (CH$_3$), C10).

GC−MS (EI, 70 eV) m/z (%): 71 (100), 109 (99), 43 (78), 67 (67), 137 (65), 152 (44) [M$^{•+}$], 41 (26), 39 (23), 79 (22), 82 (21).

1a and **1b** are the $(Z)/(E)$-isomers of 1-ethoxy-6-methyl-(R)-3-(prop-1-en-2-yl)cyclohex-1-ene. Both isomers have not been described in the literature so far. The odor of both isomers was perceived as herbal, parsley root-like.

2a and **2b** represent the $(Z)/(E)$-isomers of 2-ethoxy-1-methylidene-(R)-4-(prop-1-en-2-yl)cyclohexane, where **2a** is the (Z)-isomer and **2b** is the corresponding (E)-isomer. These compounds have been mentioned previously by Kergomard et al. while investigating the thermodynamics of the acetylation of carveol and by Gonçalves et al. while investigating the palladium-catalyzed oxidation of monoterpenes.[10,16] The recorded mass spectra are in accordance with those described in the literature, whereas the NMR data are only partly in accordance with those described in the literature for **2a**.[10,17] The ^{13}C values are identical to those described previously, but the assignment to the corresponding carbon atoms of the molecules made by Gonçalves et al. is not correct.[10] For both isomers, no odor impressions have been described in the literature. Furthermore, they have not yet been described in nature. In this study, the odor of **2a** was described as herbal, fresh, green, and dill-like and that of **2b** as herbal, spicy, earthy, and juniper-like.

3a and **3b** are the $(Z)/(E)$-isomers of 3-ethoxy-3-methyl-6-(prop-1-en-2-yl)cyclohex-1-ene. Both isomers have not been described in the literature yet. In this study, the odor of **3a** was described as sweetish, fruity, anise, and licorice-like and that of **3b** as spicy, anise, cinnamon, and clove-like.

4a and **4b** are the $(Z)/(E)$-isomers of 3-ethoxy-1-methyl-(R)-4-(prop-1-en-2-yl)cyclohex-1-ene, where **4a** represents the (E)-isomer and **4b** the (Z)-isomer. Both isomers have not been described in the literature yet. Because of the similarity in the structures of **4a** and **4b**, there is much similarity in the ^{1}H NMR spectra of the isomers. Unambiguous proton chemical-shift assignments of **4a** and **4b** were based on the multiplicity pattern of proton resonances and also on the use of homonuclear ^{1}H,^{1}H COSY spectra. The distinction between **4a** and **4b** was made mainly on the basis of the ^{1}H results, including the cross-peak between the methine protons 3-H and 4-H in the COSY spectra. The differentiation between **4a** and **4b** was based on rather different vicinal H−H couplings between the methine protons 3-H and 4-H. The magnitude of the vicinal coupling constant (J = 8 Hz) indicated a *trans*-diaxial relationship between 3-H and 4-H in the (E)-isomer **4a** and was fully consistent with the observed strong cross-peak in the COSY spectrum. The vicinal ^{1}H coupling constant is strongly dihedral angle-dependent. In order to determine dihedral angles for comparison of the different ^{1}H vicinal coupling constants in **4a** and **4b**, a conformer distribution analysis was performed to identify the low-lying conformations of **4a** with Spartan '20, Version 1.1.4, employing the Merck molecular force field.[18] The odor of **4a** was perceived as herbal, green, floral, and parsley root-like and that of **4b** as herbal, parsley root-like.

Analysis of NMR and mass spectrometric data revealed **5** as 1-(ethoxymethyl)-(R)-4-(prop-1-en-2-yl)cyclohex-1-ene. This compound has already been mentioned in the literature, but no NMR or MS data are available.[19,20] An odor impression could not be found in the literature as well. In this study, the odor was described as fruity, sweetish, green, and coriander-like.

Analysis of NMR and mass spectrometric data indicated **6** to be 6-ethoxy-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene. By comparison of the NMR data with those described in the literature, **6** was identified as the (E)-isomer.[10] **6** was first mentioned by Kergomard et al.[16] The recorded mass spectra are in accordance with those described in the literature, whereas the NMR data are only partly in accordance with
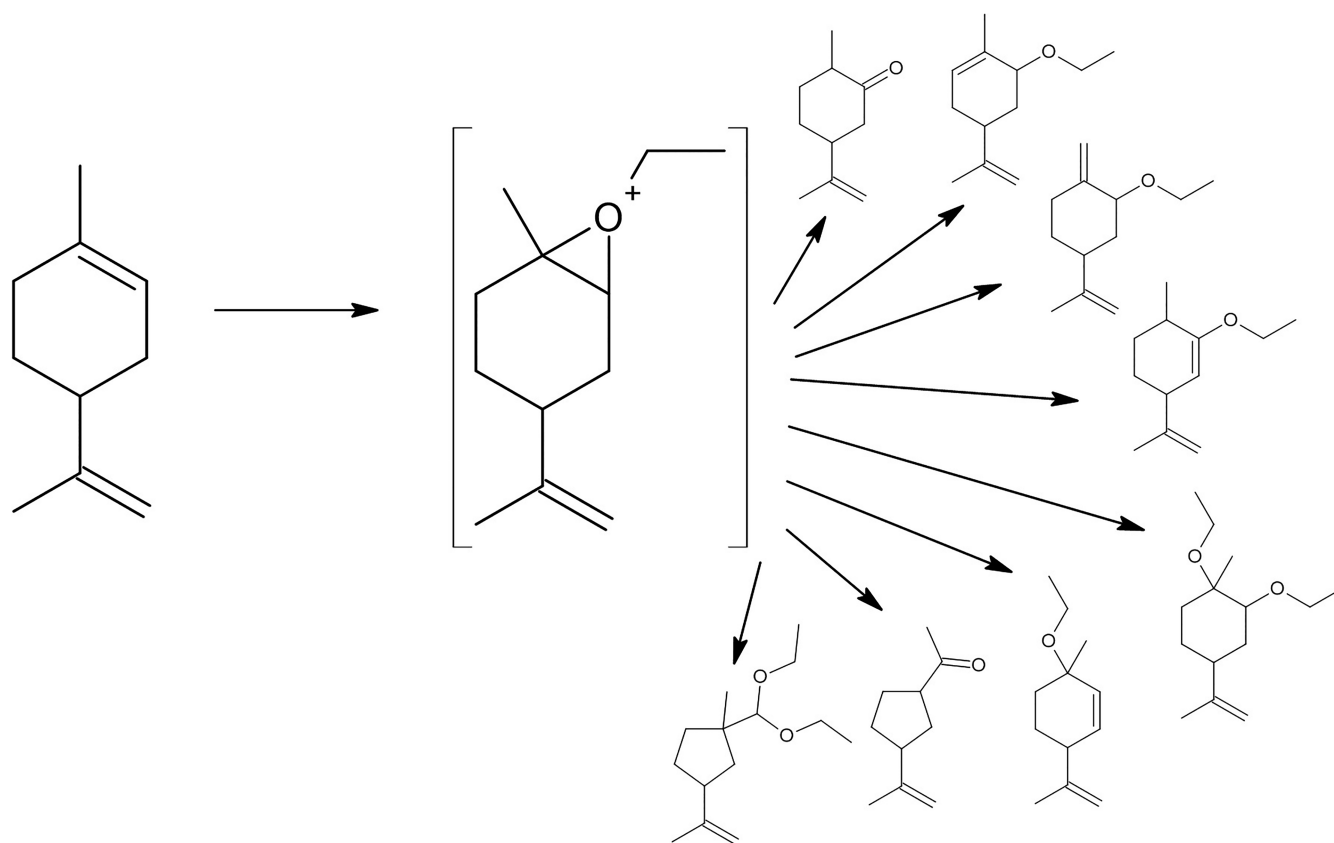
Figure 3. Proposed reaction for the formation of some of the isolated compounds.

those described in the literature studies.[10,21] The ^{13}C NMR data reported by Gonçalves et al. are approximately 1.1 ppm more positive, which may indicate an incorrect calibration in their experiments.[10] Additionally, the assignment to the corresponding carbon atoms of the molecules made by Gonçalves et al. is partly not correct. 6 represents one of the three isolated compounds for which an odor description has been reported in the literature previously. It has been described as carrot-like, parsley-like, herbal, earthy, and woody, which is in accordance with the olfactory impressions perceived in this study.[21] As indicated by the respective mass spectra, the other isomer was likely formed electrochemically as well, but it could not be isolated.

Analysis of NMR and mass spectra identified 7 as 1-(diethoxymethyl)-1-methyl-3-(prop-1-en-2-yl)cyclopentane. This compound has not been described in the literature yet. The odor of 7 was perceived as minerally, woody, earthy, and spicy.

8a and 8b represent the (Z)/(E)-isomers of 2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one (dihydrocarvone), where 8a is the (Z)-isomer and 8b is the corresponding (E)-isomer. The determined NMR and mass spectra are in accordance with those described in the literature as well as with the data obtained for the commercially available standard.[22,23] The odor of 8a has been described as musty and woody while that of 8b as minty and caraway-like, which is mostly in accordance with the olfactory impressions perceived in this study.[24−26]

Analysis of NMR and mass spectra showed that 9a and 9b are isomers of 1,2-diethoxy-1-methyl-(R)-4-(prop-1-en-2-yl)-cyclohexane. Both compounds have not been described in the literature previously. The odor of 9a was described here as

herbal, dill-like, and earthy and that of 9b as fresh, menthol-like, floral, and citrus-like.

10a and 10b were identified by NMR and mass spectrometric data as isomers of 1-[3-(prop-1-en-2-yl)-cyclopentyl]ethan-1-one. 10a and 10b have been described in the literature as rearrangement products of limonene oxide, but neither analytical data nor an odor impression has been reported for them.[27−29] The perceived odor impressions for 10a are minty, tart, floral, fruity, fresh, and citrus-like and those of 10b are minty, tart, resinous-like, green, and spicy.

In summary, of the 17 compounds isolated in this study, the structures of 2a/b, 5, 6, 8a/b, and 10a/b have been mentioned in the literature previously. NMR data are only available for 2a, 6, and 8a/b, whereas MS data and odor descriptions are only given for 6 and 8a/b. The retention indices (RIs) have been determined for 8a.[25]

The electrochemical oxidation yields at first a radical cation.[9] It may be presumed that following this first step, the formation of a limonene oxide-like transition state (Figure 3) takes place. All of the isolated compounds, except for 4a, 4b, and 5, are likely products of such a limonene oxide-like transition state. 7, 8a, 8b, 10a, and 10b are products of an additional Meinwald rearrangement, where 8a and 8b are formed by a hydride shift and 7, 10a, and 10b by an alkyl shift (Figure 4).[29−31] 4a, 4b, and 5 are assumably formed after abstraction of a hydrogen in the α position to the double bond due to a slightly increased acidity.

As indicated above, only for three of the isolated compounds, an odor impression was found in the literature. For these three compounds, the odor impressions perceived in this study matched those described in the literature well (Table
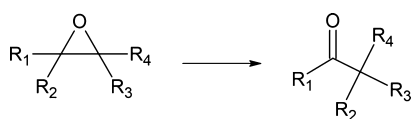
Figure 4. Meinwald rearrangement in a general reaction.

1). Unfortunately, there is a lack of systematically comparable compounds and their odor impressions in the literature. Thus, comparisons may only be made with few structurally similar compounds. For example, (R)-limonene is known for its typical orange-like odor, whereas carvone has a spearmint-like odor for the (R)-isomer and a caraway-like odor for the antipode. Linalool has a floral odor, estragole gives a licorice-like scent, and (+)-nootkatone is known for its grapefruit-like odor.[32−34]

On the basis of the semiquantitative analysis of the sample, it seems likely that products with lower steric hindrance, such as **4a** or **6**, are preferably formed, compared to those with higher steric hindrance, such as **4b**.

In general, oxidation of terpenes, either via natural processes or synthetically, represents a powerful tool to create novel aroma compounds with pleasing organoleptic properties. Some of the above-mentioned compounds are oxygenated terpenes which are well known and important aroma compounds that can be obtained from plants. Surprisingly, nonnatural, synthetically generated compounds were also revealed to have pleasant aroma properties in this study. The chemical oxidation may be performed either targeted to form specific compounds or nontargeted, like in this study, to generate a broad variety of compounds in just one step.[6,8]

An advantage of the electrochemical oxidation compared to other methods is the simple and efficient generation of new aroma compounds from inexpensive and easily available starting materials.[13] By altering some parameters such as the current density or the type of used electrodes, the composition of the created aroma compounds might be influenced. This needs to be further investigated in future studies.

Because of the pretty similar structures of the generated compounds, the preparative isolation of single compounds out of the mixture is difficult but, if necessary, can be achieved with the methods reported herein. Thus, a future industrial application of the generated mixture, after safety evaluation by the competent authorities, seems to be more likely.

Overall, 20 compounds could be structurally and sensorily characterized in electrochemically oxidized limonene, of which 11 had not been described in the literature before. In addition, a method for the sustainable production of aroma compounds is described that does not require the use of critical chemicals and which may quickly generate olfactorily appealing aroma mixtures.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.2c01301.

GC−FID chromatogram of the diluted sample determined on an Agilent HP-INNOWAX column (PDF)

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Notes
The authors declare no competing financial interest.

ABBREVIATIONS
FID, flame ionization detector; GC, gas chromatograph(y); HPLC, high-performance liquid chromatography; MS, mass spectrometry; NMR, nuclear magnetic resonance; O, olfactometry; TLC, thin-layer chromatography; TMS, tetramethylsilane.

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