SUPPLEMENTARY MATERIAL

Lavandin (*Lavandula x intermedia* Emeric ex Loiseleur) essential oil from Spain: determination of aromatic profile by gas chromatography – mass spectrometry, antioxidant and lipoxygenase inhibitory bioactivities.

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Abstract

Lavandin (*Lavandula x intermedia* Emeric ex Loiseleur) essential oils (EOs), from Abrial, Super and Grosso cultivars, cultivated and extracted in the South East of Spain, were analysed by GC/MS to determine their composition, in both relative (peak area) and absolute (using standard curves) concentrations. Linalool (34-47%), linalyl acetate (17-34%), camphor (4-9%) and eucalyptol (3-7%) were determined as the main molecules. This characterisation was completed with the enantioselective gas chromatography, where (-)-linalool, (+)-camphor and (-)-linalyl acetate were determined as the main components. Antioxidant activity was evaluated positively by several methods: activity against free radicals, chelating and reducing power, probably due to linalool and linalyl acetate. Mild inhibitory activity on lipoxygenase (LOX) was observed supporting potential anti-inflammatory activity, mainly due to linalool and camphor. These properties support the potential use of *L. x intermedia* EOs as natural cosmetic and natural pharmaceutical ingredient to fight several skin diseases.

Keywords: *Lavandula hybrida*; *Lavandula x intermedia*; essential oil; GC-MS; enantiomeric ratio; antioxidant; LOX inhibitory activity

Experimental

Plant material

Five samples of *Lavandula x intermedia* (300 g) were obtained from organic farming fields dedicated to growing plants for industrial extraction of EOs through steam distillation, certifying that all the plants were grown in the South East of Spain. The species were identified and authenticated by Dr Pedro Sanchez Gomez, professor of Botany in the Plant Biology department of Murcia University and voucher specimens were prepared and deposited at the herbarium of the department of Biochemistry and Molecular Biology-A. The identification numbers of the voucher specimens were BMBA120901, BMBA120902, BMBA120903, BMBA120904 and BMBA120905 for Abrial1, Super1, Super2, Grosso1, Grosso2, respectively.

The main changes among the five samples were the different cultivars *i.e.* Sample Abrial1 is Abrial cultivar, Samples Super1 and Super2 are Super cultivar and Samples Grosso1 and Grosso2 are Grosso cultivar. Also, Abrial1, Super1 and Grosso1 were grown in Supra Mediterranean bioclimatic zone and Super2 and Grosso2 were grown in Upper Meso-Mediterranean bioclimatic zones (Rivas-Martínez 1987).

Chemicals

The following compounds were purchased from Sigma-Aldrich Spain: pure compounds used as standard substances for GC identification and determination, pure terpenes tested for lipoxygenase inhibition, linoleic acid and soybean lipoxygenase, fluorescein, AAPH [2,2'-Azobis(2-methylpropionamidine dihydrochloride)] and Trolox [6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid], DPPH [2,2-diphenyl-1-picrylhydrazyl], ABTS [2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)], potassium persulphate, potassium ferricyanide, trichloroacetic acid and iron (III) chloride. Analytic grade solvents and buffers were acquired from Merck Spain. Deionised laboratory water type I (18 M Ω ·cm) was produced with a Millipore MilliQ-Reference device.

Extraction of the essential oil

The dry plants of each sample of *L. x intermedia* were separately subjected to steam distillation. The EO collected was dried over anhydrous sodium

sulphate obtaining strong smelling pale yellow oil which was stored at -20°C until used.

Fast gas chromatography-mass spectrometry (FGC/MS)

FGC/MS analyses of the EOs were conducted using an Agilent GC7890 chromatograph, coupled with an Agilent MS5975 mass spectrometer as detector, with electronic impact ionisation and single quadrupole analyser. To enhance repeatability in sampling, the analysis device was equipped with a Gerstel automatic multi-purpose sampler MPS-2XT, which is able to perform sandwich injection consisting in 0.2 µL air, 0.2 µL isooctane, 0.2 µL air, 0.3 µL sample and 0.2 µL air, described from plunger to needle.

Several consumables were used in this chromatography to improve the performance: Certified low bleed injector septum, single taper inlet Focus-Liner packed with glass wool and high temperature O-Ring purchased from Supelco, 1.5 mL amber glass vials, silicone/polytetrafluoroethylene (PTFE) septums for screw caps and crimp seals (PTFE/silicone/PTFE) for long-lasting samples, mandrel-interior glass inserts with polymer feet for samples up to 300 µL from Agilent. All the samples were managed with glass gas tight micro-syringes purchased from Hamilton. All samples were filtered with Agilent PTFE syringe micro filters (0.2 µm)

The analysis was performed on a low bleed capillary fused-silica column, SLB-5ms from Supelco (15m length x 0.1mm i.d. x 0.1µm film thickness). The carrier gas used was hydrogen (flow rate constant: 0.8 mL/min, starting column head pressure: 46.345 psi), produced *ad hoc* with an electrolytic Parker-Domnik-Hunter generator, fed with type I laboratory water. The maximum capacity of hydrogen generation exceeds 80 ml/min at a pressure of 6 bar.

The above mentioned equipment was controlled by ChemStation software and analysed using ChemStation, MS-Search, AMDIS and the mass spectral databases NIST 08 and Wiley 7.

The injector temperature was held at 300 °C, the septum purge was set to 3 mL/min and the split valve was set to 1:100. The column temperature started at 60 °C and increased to 300 °C following the temperature programme as follows: rate 20 °C/min to 142 °C and rate 40 °C/min to 300 °C and then held for 0.5 min. For a better chromatographic resolution, some temperature ranges increased at

a rate of 2 °C/min, the temperature ranges were: 92-94 °C, 121-123 °C, 133-135 °C.

MS conditions were as follows: Temperature of the transfer line 280 °C, electronic impact ionisation energy 70 eV, mass range 30-300 atomic mass units, scan rate 21.035 scan/s (assuring at least 15 points in the smallest of the peaks, minimum for stable quantitation), electron-multiplier voltage 1129, ion source temperature 230 °C, quadrupole temperature 150 °C. The EO compounds were identified based on retention time, retention index and mass spectra of the pure compounds (standards) using MSD Chemstation Data Analysis (Agilent Technologies, Santa Clara, CA). Tentative identification for each component not available commercially was attempted comparing the retention index and mass spectra against NIST and Wiley spectral databases using NIST MS Search 2.0 (NIST, Gaithersburg, MD). All the chromatograms were acquired with the Trace Ion Detection software filter activated, ensuring minimum noise interference. Further determination was done with the AMDIS algorithm to ensure that all peaks corresponded to pure compounds.

The quantitative determination was carried out based on calibration curves of each of the commercially available components of the essential oils. Those curves were made using nonane (MS **43**, 57, 71, 85), tetradecane (MS 43, **57**, 71, 85) and hexadecane (MS 41, 43, **57**, 71) as internal standards, calibration ranges and suppliers for all substances are listed in (Table S1). Each curve consisted of 10 concentration levels, each level of the calibration curve was injected and analysed in triplicate as well as the samples. The calibration curves are expressed as response ratio $\left(\frac{\text{analyte response}}{\text{internal standard response}} \right)$ vs. concentration ratio $\left(\frac{\text{analyte concentration}}{\text{internal standard concentration}} \right)$, thus, correction factors of each analyte are embedded in the calibration curves. Each sample was evaluated in two different dilutions in isooctane, 1:10 and 1:1000 in order to determine exact concentrations of compounds. In all the chromatograms, corresponding to samples and calibration, the integration intervals for peaks were manually selected to ensure accuracy in the method. The repeatability of five detections of 3mM samples is shown in RSD column for all standards. The limit of detection (LOD) was calculated by a signal-to-noise ratio of 3, and the limit of

quantitation (LOQ) was determined by a signal-to-noise ratio of 10 (European-Pharmacopoeia 2011).

In the case of non-commercially available compounds, the percentages of peak areas of the total ion countering (TIC) chromatogram were evaluated. Retention indices (van Den Dool & Dec. Kratz 1963) (LRIs) were calculated using a homologous series of C7-C30 n-alkanes standard solutions from Supelco, following the IUPAC recommendations (IUPAC 1997) for linear retention indices.

Each EO is described with two columns (Table S2). The first column determines the exact concentration of the compounds expressed in mM (commercially available standards only, >90% of the total area). In the second column, the total area of each compound present in the chromatogram was integrated (>99% of the total area).

Thanks to the first column, it becomes clear when an EO has been diluted with any kind of not detectable solvent by GC. The absolute concentration is not based on area percentages alone, but on calibration straights too, with commercial reagents as standards.

Enantioselective gas chromatography-mass spectrometry (EsGC/MS)

The same analytical device described above was used with hydrogen as carrier gas (flow rate constant: 2.5 mL/min, starting column head pressure: 8 psi), this time equipped with an Astec Chiraldex B-DM column (30 m length x 0.25 mm i.d. x 0.12 µm film thickness) from Supelco. This capillary column was made of fused silica with non-bonded 2,3-di-O-methyl-6-t-butyl silyl derivative of β-cyclodextrin. Performing under milder conditions, this column provided chiral chromatograms of the essential oils, where the chiral compounds were determined by retention time of the pure enantiomers commercially available, and double checked with the NIST spectral database. The peak areas of the triplicates were integrated and percentages of levorotatory (-) and dextrorotatory (+) enantiomers were determined.

Conditions: injector temperature 200 °C, transfer line temperature 200 °C, split 1:100, sandwich injection volumes: 0.2 µL air, 0.2 µL acetone, 0.2 µL air, 0.5 µL sample, 0.2 µL air, temperature programme as follows: starting at 35 °C, the temperature increased to 170 °C at a rate of 4 °C/min, then the temperature decreased to 35 °C again at a rate of 15 °C/min.

Antioxidant activity

The antioxidant potential of EOs can be determined using a representative selection of different antioxidant methods, *i.e.* ORAC (Oxygen Radical Absorbance Capacity) method to evaluate the scavenging capacity of free oxygen (peroxyl) radicals, ABTS or DPPH methods to measure the ability of reducing nitrogen radical cations, Fe^{2+} chelating power and Fe^{3+} reducing power methods, to account for the ability to neutralise oxidant metal ions.

ORAC assay

The ORAC values account for the ability of the samples to scavenge the peroxyl radical ($\text{ROO}\cdot$). ORAC values were determined by the slightly modified method of Ou et al. (Ou et al. 2001), as described below. In this assay, peroxyl radicals produced by a controlled source, AAPH, oxidise fluorescein to a non-fluorescent product, this reaction is registered by a fluorometer in a decay curve. The antioxidants able to scavenge these peroxyl radicals result in a higher value of area under the decay curve (AUC). The AUC was calculated using Equation (1).

$$\text{AUC} = 1 + f_1/f_0 + f_2/f_0 + \dots + f_n/f_0 \quad (1)$$

Where f_0 is the initial fluorescence reading at 0 min and f_i is the fluorescence reading at time i , up to n data points (usually $n = 50 - 200$). The net AUC was obtained by subtracting the AUC of the blank (antioxidant not present) from that of the sample. Trolox, a water soluble analogue of vitamin E, was used as a control standard.

This assay was performed at 37 °C during 60 min, in a Molecular Devices Gemini XPS fluorometer controlled by the software SoftMaxPro, using a 96-well plate. Each sample was evaluated in triplicate using $\lambda_{\text{ex}}=485$ nm and $\lambda_{\text{em}}=530$ nm. Each assay consisted of pH 7.5, 10 mM phosphate buffer, 1 μM fluorescein, 200 mM AAPH and antioxidant sample in several concentrations. Organic solvent was 1% ethanol. Trolox was used as a reference antioxidant.

ORAC values were expressed as Trolox equivalents (mol Tx/mol compound), using the widespread Trolox Equivalent Antioxidant Capacity (TEAC) units. TEAC units used for essential oils were “quantity TE per volume of EO”. This relative ORAC value was calculated as Equation (2). Proceeding this way Trolox was determined to be 1.00 ± 0.05 TEAC.

$$\text{ORAC} = \left(\frac{(\text{AUC}_{\text{Sample}} - \text{AUC}_{\text{Blank}})}{(\text{AUC}_{\text{T}_x} - \text{AUC}_{\text{Blank}})} \right) \times \left(\frac{[\text{T}_x]}{[\text{Sample}]} \right) \quad (2)$$

Determination of ABTS radical cation scavenging capacity

The ABTS radical cation (ABTS^{•+}) bleaching assay was carried out using the method reported in the literature (Re et al. 1999) with slight modifications. ABTS^{•+} was produced by reacting 3.5 mM ABTS with 1.25 mM potassium persulphate and leaving the mixture in the dark at room temperature for 12-16 h before use. The ABTS^{•+} solution was diluted (1:100) with ethanol to 0.035 mM with an absorbance of 0.7 ± 0.02 at 734 nm.

Ethanol solutions of the EOs at various concentrations (0 - 0.5 mL/L) were mixed (1:3) with the prepared ABTS^{•+} solution. After reaction at room temperature for 6 min, the absorbance at 734 nm was measured using a Molecular Devices Spectramax 340PC spectrophotometer controlled by the software SoftMaxPro, using a 96-well plate. Lower absorbance of the reaction mixture indicates higher ABTS^{•+} scavenging activity. The ability to reduce the ABTS^{•+} was calculated using Equation (3).

$$\text{scavenging activity (\%)} = \frac{A_0 - A_1}{A_0} \times 100 \quad (3)$$

Where A_0 is the absorbance of the control (without sample) and A_1 is the absorbance in the presence of the sample. Trolox was used as a reference to express the results in TEAC units, for triplicate assays.

Free radical scavenging activity (DPPH[•])

A methanolic stock solution of each sample at different concentrations was mixed (1:3) with 100 μM stock methanolic solution of DPPH[•] (Brandwilliams et al. 1995). Absorbance measurements were made at 517 nm, after 60 min of reaction in the dark, at room temperature. The triplicate values of scavenging activity were reported in TEAC units, following the same process shown in ABTS assay.

Chelating power (ChP)

The degree of chelation of ferrous ions by essential oils and their major components was evaluated according to Miguel *et al.* (Miguel et al. 2010). Briefly, samples were incubated 1:1 with 2 mM FeCl_2 . The addition of the same volume of 5 mM ferrozine initiated the reaction, and after 10 min, the

absorbance at 562 nm was measured. An untreated sample served as negative control. The percentage of chelating ability was determined following the same procedure as in ABTS. EDTA was used as positive control, expressing the results in (quantity of EDTA equivalents / volume of EO), for triplicate assays.

Reducing power (RdP)

Each EO sample (300 μ L) was mixed with sodium phosphate buffer (2.5 mL, 0.2 M, pH 6.6) and potassium ferricyanide $K_3[Fe(CN)_6]$ (2.5 mL, 1% w/v) (Oyaizu 1986). The mixture was incubated at 50 °C for 20 min. Afterwards, 2.5 mL of 10% (w/v) trichloroacetic acid was added to the mixture, which was then centrifuged for 10 min at 3000 rpm. The upper layer of the solution (2.5 mL) was mixed with distilled water (2.5 mL) and with 0.5 mL, 0.1% (w/v) $FeCl_3$, and the absorbance was measured at 700 nm. Ascorbic acid was used as standard for this test, expressing the results in (quantity of Ascorbic acid equivalents / volume of EO), for triplicate assays.

Lipoxygenase inhibition

Lipoxygenase (LOX) (linoleate:oxygen oxidoreductase, EC 1.13.11.12) was assayed by the slightly modified method found in literature (Christop.J et al. 1970) based on absorption at 234 nm of the hydroperoxyde conjugated dienes ($\epsilon = 25000 \text{ M}^{-1} \text{ cm}^{-1}$) formed when linoleic acid (18:2, used as substrate) was oxidised in the presence of oxygen and LOX.

LOX was purchased from Sigma as lipoxidase preparation from *Glycine max* (soybean) and was certified as a homodimer of 108 kDa with a pI of 5.65. The enzyme was characterised in terms of substrate specificity, being the substrate a *cis*, *cis*-1,4-pentadiene system.

The assay was performed in a double beam Perkin-Elmer Lambda 35 spectrophotometer at 25 °C, controlled with the software UV-Winlab. The spectrophotometer was equipped with a pair of quartz cuvettes QS quality certified for wavelengths from 195 nm and longer, 10 mm lightpath, 1 mL volume, one used for the automatic reference subtraction and the other for the sample. The reference contained all components with the exception of substrate and inhibitors. Non-enzymatic assays were carried out, and their rates were subtracted from the steady state rates of the respective enzymatic reactions. All samples were evaluated in triplicate assays. The activity of the enzyme was

measured based on the slope of the initial linear portion (steady state rate) of the progress curve for the enzyme reaction.

Linoleic acid was dissolved using acetonitrile as cosolvent with chromatographic gradient -210 quality. This acetonitrile was used as cosolvent due to its lack of absorbance at 234 nm, and it was proved not to interfere significantly in the enzyme reaction at the low proportions used. Both enzyme and substrate solutions had to be kept on ice during the assays, to slow down their degradation (Whent et al. 2010).

The reaction mixture contained pH 9.0, 40 mM borate buffer, 4mM NaOH, variable concentration of inhibitor, 20 μ M Linoleic acid, 6% acetonitrile and the reaction was started with LOX addition. LOX was prepared to obtain 6.24 mU/mL, considering as one international unit (U) for enzyme activity, the amount of enzyme that catalyses the conversion of 1 μ mol of linoleic acid as substrate per minute. The K_M of the enzyme was determined using the assay conditions, obtaining $K_M = 40 \pm 6 \mu$ M.

Once the activity values at different concentrations of inhibitor were obtained, the inhibition degree (ID) was calculated using Equation (4).

$$ID(\%) = \frac{v_0 - v_i}{v_0} \times 100 \quad (4)$$

Where v_0 and v_i are the steady state rates in the absence and presence of inhibitor, respectively.

The main compounds of the EOs were studied to determine their IC_{50} values. Data of activity against 8 different inhibitor concentrations were plotted, and fitted by non-linear regression to a two parameters single rectangular hyperbola. Equation (5).

$$y = \frac{ax}{b + x} \quad (5)$$

The parameter b represents the IC_{50} , using a Gauss-Newton algorithm, implemented in the Sigma Plot software.

Statistical analysis.

All data was recorded as mean $\pm$ standard deviation of triplicate determinations. Each error value is magnified using the corresponding error propagation rules for arithmetic operations. Data quality was analysed by ANOVA (Sokal & Rohlf 2012), and means were separated using Tukey's HSD

considering significant differences for $p < 0.05$. Agglomerative hierarchical clustering based on Euclidean distance was performed using each EO as starting cluster to decide which ones are similar. Statistical analyses were conducted using SPSS (Chicago, SPSS Inc).

Table S1. Parameters of FGC-EI/MS calibration

Analyte	Calibration curve*	R ²	Calibration range (mM)	RSD (%)	LOD (mM)	LOQ (mM)	Standard source	Product Reference
<i>Nonane</i>	<i>Internal standard</i>						SAFC	442694
(-)- α -Pinene	$y = 0.471x - 0.018$	0.997	0.25 - 10.06	4.5	0.08	0.25	Fluka	80599
(+)-Camphene	$y = 0.272x - 0.008$	0.995	0.66 - 10.51	0.4	0.14	0.44	SAFC	w222909
Sabinene	$y = 0.460x - 0.026$	0.998	0.24 - 9.78	0.9	0.07	0.21	Extrasynthese	5062 S
(-)- β -Pinene	$y = 0.400x - 0.016$	0.995	0.26 - 10.29	3.7	0.09	0.26	Fluka	80609
3-Octanone	$y = 0.309x - 0.031$	0.996	2.56 - 10.24	4.1	0.64	1.95	SAFC	w280305
Myrcene	$y = 0.188x - 0.024$	0.993	2.24 - 8.97	3.5	0.56	1.70	Fluka	64643
Hexyl acetate	$y = 0.452x - 0.057$	0.992	2.40 - 9.59	1.7	0.32	0.96	Fluka	25539
(+)-Limonene	$y = 0.246x - 0.008$	0.995	0.60 - 9.55	0.9	0.12	0.36	Fluka	62118
Z- β -Ocimene	$y = 0.218x - 0.011$	0.996	0.70 - 6.97	2.2	0.16	0.48	SAFC	w353901
Eucalyptol	$y = 0.233x - 0.008$	0.995	2.39 - 9.55	8.7	0.60	1.82	SAFC	w246506
γ -Terpinene	$y = 0.366x - 0.017$	0.995	0.62 - 9.87	2.8	0.12	0.37	Aldrich	223190
Sabinene hydrate	$y = 0.268x - 0.007$	0.996	0.63 - 10.00	2.1	0.18	0.56	Fluka	96573
(-)-Linalool	$y = 0.214x - 0.008$	0.994	0.88 - 8.80	4.9	0.22	0.67	Fluka	74856
(+)-Camphor	$y = 0.181x - 0.024$	0.994	0.99 - 9.85	1.5	0.25	0.76	Alfa Aesar	A10708
(-)-Borneol	$y = 0.266x - 0.020$	0.998	0.57 - 9.06	4.4	0.19	0.57	Alfa Aesar	A12684
(-)-Terpinen-4-ol	$y = 0.241x - 0.003$	0.997	0.60 - 9.57	4.3	0.20	0.60	Aldrich	11584
Hexyl butyrate	$y = 0.332x - 0.034$	0.991	4.84 - 7.74	0.6	0.77	2.34	SAFC	w256811
(+)- α -Terpineol	$y = 0.175x - 0.003$	0.998	1.02 - 10.23	4.5	0.26	0.79	Fluka	83073
<i>Tetradecane</i>	<i>Internal standard</i>						SAFC	442708
(-)-Linalyl acetate	$y = 0.217x - 0.006$	0.998	0.72 - 7.18	0.2	0.18	0.55	SAFC	w263605
Neryl acetate	$y = 0.242x - 0.007$	0.999	0.73 - 7.31	3.8	0.18	0.55	SAFC	w277304
Geranyl acetate	$y = 0.249x - 0.009$	0.999	0.46 - 7.42	2.9	0.15	0.46	Aldrich	173495
<i>Hexadecane</i>	<i>Internal standard</i>						Fluka	52209
(-)-E- β -Caryophyllene	$y = 0.079x - 0.002$	0.998	4.41 - 7.05	6.6	0.71	2.16	Sigma	22075
α -Humulene	$y = 0.541x - 0.019$	0.999	0.40 - 6.35	2.2	0.13	0.40	Aldrich	53675
α -Bisabolene	$y = 0.111x - 0.043$	0.999	1.74 - 6.97	3.4	0.31	0.94	Alfa Aesar	A18724

*Response ratio vs. Concentration ratio, internal standard correction applied.

Each internal standard is reference compound for the analytes that follow.

Table S2A. FGC/MS determination of components in *L. x intermedia* Abrial and Super cultivars.

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Abrial 1		Super 1		Super 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
1.01	825	Hexyl methyl ether	45, 56, 69, 84		0.1d ± 0.0		0.1e ± 0.0			LRI, MS
1.15	860	4-Hexen-1-ol	31, 41, 55, 67						0.1 ± 0.0	LRI, MS
1.20	873	Hexyl alcohol	43, 56, 69, 82		0.1d ± 0.0		0.1d ± 0.0		0.2e ± 0.0	LRI, MS
1.47	929	Tricyclene	79, 93, 121, 136		0.1d ± 0.0		tr e			LRI, MS
1.53	939	α-Pinene	39, 91, 93 , 77	29.5a ± 0.3	0.5d ± 0.0	16.9b ± 0.5	0.3e ± 0.0	13.4c ± 0.2	0.2f ± 0.0	LRI, MS, std
1.63	957	Camphene	67, 79, 93 , 121	31.3a ± 0.4	0.4d ± 0.0	18.7b ± 0.6	0.3e ± 0.0	14.2c ± 0.3	0.2f ± 0.0	LRI, MS, std
1.75	978	Sabinene	41, 77, 91, 93	10.2 ± 0.0	0.1d ± 0.0		0.1e ± 0.0		0.1f ± 0.0	LRI, MS, std
1.78	983	β-Pinene	41, 69, 79, 93	27.9a ± 0.3	0.6d ± 0.0	12.8b ± 0.4	0.2e ± 0.0	13.6b ± 0.3	0.3f ± 0.0	LRI, MS, std
1.81	989	3-Octanone	43 , 57, 71, 99	15.7a ± 0.5	0.1d ± 0.0	35.4b ± 1.7	0.4e ± 0.0	18a ± 0.5	0.1f ± 0.0	LRI, MS, std
1.83	992	β-Myrcene	39, 41 , 69, 93	89.1a ± 2.0	0.8d ± 0.0	62.4b ± 1.4	0.6e ± 0.0	77.1c ± 1.4	0.7f ± 0.0	LRI, MS, std
1.89	1002	3-Octanol	41, 59, 83, 101				0.1 ± 0.0			LRI, MS
1.97	1011	Hexyl acetate	43 , 56, 84, 61	21.0a ± 0.3	0.2d ± 0.0	37.9b ± 0.6	0.4e ± 0.0	16.6c ± 0.5	0.1f ± 0.0	LRI, MS, std
1.98	1012	3-Carene	77, 79, 91, 93		tr d		0.1e ± 0.0			LRI, MS
2.04	1019	2-Carene	77, 93, 121, 136		0.1 ± 0.0					LRI, MS
2.11	1026	p-Cymene	77, 91, 119, 134		0.1d ± 0.0		0.1d ± 0.0		0.1e ± 0.0	LRI, MS
2.16	1032	Limonene	67, 68 , 79, 93	62.4a ± 2.0	1.0d ± 0.0	44.1b ± 0.9	0.7e ± 0.0	39.8c ± 0.5	0.6f ± 0.0	LRI, MS, std
2.17	1034	Z-β-Ocimene	41, 79, 91, 93	218.9a ± 18.9	2.9d ± 0.3	144.5b ± 2.3	1.5e ± 0.0	122.7b ± 3.9	1.4e ± 0.1	LRI, MS, std
2.19	1036	Eucalyptol	43 , 67, 81, 93	536.7a ± 17.9	7.6d ± 0.2	355.3b ± 28.9	3.9e ± 0.0	362.5b ± 18.0	4.8f ± 0.1	LRI, MS, std
2.26	1044	E-β-Ocimene	41, 79, 93, 121		6.1d ± 0.0		2.0e ± 0.0		1.9f ± 0.0	LRI, MS
2.40	1060	γ-Terpinene	77, 91, 93 , 136	10.0a ± 0.2	0.1d ± 0.0			8.6b ± 0.2	0.1e ± 0.0	LRI, MS, std
2.53	1074	Sabinene hydrate	77, 91, 93 , 121	6.5a ± 0.2	0.2d ± 0.0	6.1a ± 0.2	0.2d ± 0.0		0.2d ± 0.0	LRI, MS, std
2.66	1089	Terpinolene	93, 105, 121, 136		0.4d ± 0.0		0.2e ± 0.0		0.3f ± 0.0	LRI, MS
2.83	1108	Linalool	41, 55, 69, 93	2079.2a ± 61.0	37.0d ± 0.0	2168.7a ± 37.1	39.4e ± 0.1	2439.7b ± 31.4	45.8f ± 0.1	LRI, MS, std
2.97	1122	E-2-Nonenal	41, 55, 70, 83				0.1 ± 0.0			LRI, MS
3.08	1133	allo-Ocimene	91, 105, 121, 136		0.2d ± 0.0		0.1e ± 0.0		0.1e ± 0.0	LRI, MS
3.25	1151	n-Hexyl isobutyrate	43, 56, 71, 89		0.1d ± 0.0		0.1d ± 0.0		0.1d ± 0.0	LRI, MS
3.33	1159	Camphor	41, 81, 95 , 108	808.4a ± 31.2	9.0d ± 0.0	642.0b ± 4.7	4.8e ± 0.0	711.5c ± 3.3	7.6f ± 0.0	LRI, MS, std
3.46	1172	Lavandulol	41, 69, 111, 123		0.7d ± 0.0		0.2e ± 0.0		0.8f ± 0.0	LRI, MS

Table S2A. Continued

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Abrial 1		Super 1		Super 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
3.55	1181	1-Butenylidene cyclohexane	79, 93, 107, 136		0.1d ± 0.0				0.1d ± 0.0	LRI, MS
3.60	1186	Borneol	41, 93, 95 , 121	164.0a ± 4.2	1.9d ± 0.0	183.1b ± 4.9	2.3e ± 0.0	390.2c ± 8.7	2.7f ± 0.0	LRI, MS, std
3.63	1189	Terpinen-4-ol	71, 77, 91, 93	61.9a ± 2.9	1.0d ± 0.0	24.1b ± 1.6	0.4e ± 0.0	96.9c ± 1.4	1.5f ± 0.0	LRI, MS, std
3.69	1196	Hexyl butyrate	43 , 56, 71, 89	25.6a ± 0.6	0.3d ± 0.0	46.1b ± 1.5	0.7e ± 0.0	34.8c ± 1.3	0.5f ± 0.0	LRI, MS, std
3.71	1198	p-Cymenene	65, 91, 117, 132		0.1 ± 0.0					LRI, MS
3.77	1204	α-Terpineol	59, 68, 79, 93	66.1a ± 0.3	1.0d ± 0.0	45.9b ± 5.0	0.7e ± 0.0	104.1c ± 2.7	1.6f ± 0.0	LRI, MS, std
4.03	1231	Perillol	68, 79, 93, 121		0.1d ± 0.0		0.1d ± 0.0		0.2e ± 0.0	LRI, MS
4.05	1232	Isobornyl formate	93, 95, 121, 136		0.1d ± 0.0		0.1e ± 0.0		0.1e ± 0.0	LRI, MS
4.06	1234	Hexyl 2-methylbutyrate	41, 57, 85, 103				0.1d ± 0.0		0.1d ± 0.0	LRI, MS
4.12	1240	Hexyl valerate	43, 56, 85, 103		0.1d ± 0.0		0.1d. e ± 0.0		0.1e ± 0.0	LRI, MS
4.21	1249	Linalyl acetate	41, 69, 93 , 121	1215.6a ± 19.8	19.4d ± 0.1	2107.0b ± 30.7	34.5e ± 0.1	1198.9a ± 30.2	19.8f ± 0.1	LRI, MS, std
4.27	1255	Geraniol	41, 69, 93, 121		0.4d ± 0.0		0.5e ± 0.0		0.6f ± 0.0	LRI, MS
4.54	1284	Lavandulyl acetate	43, 69, 93, 121		1.5d ± 0.0		1.2e ± 0.0		1.2e ± 0.0	LRI, MS
5.04	1331	6-Undecanol	41, 55, 83, 101		0.1d ± 0.0		0.1e ± 0.0		0.1f ± 0.0	LRI, MS
5.34	1359	Neryl acetate	41, 69, 79, 93	12.8a ± 0.4	0.2d ± 0.0	13.3a ± 0.4	0.3d ± 0.0	19.9b ± 0.4	0.4e ± 0.0	LRI, MS, std
5.54	1379	Geranyl acetate	41, 69 , 79, 93	23.2a ± 0.5	0.4d ± 0.0	23.1a ± 1.1	0.4d ± 0.0	35.6b ± 0.8	0.7e ± 0.0	LRI, MS, std
5.57	1381	β-Cubebene	91, 105, 120, 161		0.1d ± 0.0				0.1e ± 0.0	LRI, MS
5.65	1389	α-Bergamotene	69, 93, 105, 119		0.1d ± 0.0				0.1d ± 0.0	LRI, MS
5.82	1405	α-Cedrene	93, 105, 119, 204		0.1d ± 0.0		0.1e ± 0.0		0.1e ± 0.0	LRI, MS
6.03	1426	α-Santalene	41, 94, 161, 189		0.4d ± 0.0				0.2e ± 0.0	LRI, MS
6.06	1429	E-β-Caryophyllene	41, 69, 79, 93	169.2a ± 4.4	2.0d ± 0.1	101.3b ± 0.9	1.2e ± 0.0	144.1c ± 1.3	1.8f ± 0.0	LRI, MS, std
6.17	1441	E-α-Bergamotene	41, 69, 93, 119		0.2d ± 0.0		0.1e ± 0.0		0.1f ± 0.0	LRI, MS
6.29	1453	β-Farnesene	41, 69, 93, 133		tr d		tr d			LRI, MS
6.37	1461	Z-β-Farnesene	41, 69, 93, 133		0.7d ± 0.0		0.7d ± 0.0		1.2e ± 0.0	LRI, MS
6.43	1467	α-Humulene	41, 67, 80, 93	5.2a ± 0.3	0.1d ± 0.0	4.0b ± 0.0	0.1e ± 0.0	5.1a ± 0.1	0.1d ± 0.0	LRI, MS, std
6.57	1481	α-Amorphene	105, 119, 161, 204		0.1 ± 0.0					LRI, MS

Table S2A. Continued

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Abrial 1		Super 1		Super 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
6.65	1489	γ-Murolene	105, 119, 161, 204		0.4d ± 0.0		0.3e ± 0.0		0.4f ± 0.0	LRI, MS
6.78	1504	α-Selinene	161, 175, 189, 204		0.1d ± 0.0		0.1e ± 0.0		0.1d ± 0.0	LRI, MS
6.80	1507	α-Farnesene	41, 93, 107, 121		0.1d ± 0.0		0.1e ± 0.0		0.1e ± 0.0	LRI, MS
6.84	1514	Bergamotene	41, 77, 93, 119						0.1 ± 0.0	LRI, MS
6.89	1521	Germacrene D	105, 119, 161, 204		0.1d ± 0.0		tr e		0.1d ± 0.0	LRI, MS
7.05	1549	α-Bisabolene	41, 79, 93 , 119					35.5 ± 0.3	0.3 ± 0.0	LRI, MS, std
7.32	1593	Caryophyllene oxide	41, 79, 91, 105		tr d		0.1d ± 0.0		0.1d ± 0.0	LRI, MS
7.61	1657	Cadinol	105, 119, 161, 204		tr					LRI, MS
7.77	1695	α-Bisabolol	41, 69, 93, 119		0.1d ± 0.0		0.2e ± 0.0		0.1f ± 0.0	LRI, MS
		Oxygenated terpenes:								
		Alcohol			42.0		43.4		53.0	
		Ketone			9.0		4.8		7.6	
		Aldehyde			0.0		0.0		0.0	
		Ester			21.6		36.5		22.2	
		Ether			7.6		3.9		4.9	
		Monoterpene hydrocarbons			14.1		6.6		6.6	
		Oxygenated monoterpenes			80.1		88.4		87.4	
		Sesquiterpene hydrocarbons			4.7		2.7		4.6	
		Oxygenated sesquiterpenes			0.1		0.3		0.1	
		Total terpene hydrocarbons			18.7		9.3		11.2	
		Total oxygenated terpenes			80.2		88.6		87.5	
		Non isoprenoid components			1.0		2.1		1.3	

LRI = Linear Retention Index obtained using the homologous series of n-alkanes (C7-C30). *Quantitation ions are shown in bold. SD = standard deviation. MS = tentatively identified by NIST 08 & Wiley 7. std = identified by comparison with reference standards. Results are expressed as mean ± standard deviation of three determinations.

a, b, c Different letters in the same compound concentration mean statistically significant differences with $p < 0.05$. d, e, f Different letters in the same compound area mean statistically significant differences with $p < 0.05$. Areas in bold mean "biomolecular marker" of the EO biochemotype, tr = traces (<0.1%)

Table S2B. FGC-MS determination of components in *L. x intermedia* Grosso cultivar.

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Grosso 1		Grosso 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
1.15	860	4-Hexen-1-ol	31, 41, 55, 67		tr			LRI, MS
1.20	873	Hexyl alcohol	43, 56, 69, 82		tr c		0.3d ± 0.0	LRI, MS
1.47	929	Tricyclene	79, 93, 121, 136		0.1 ± 0.0			LRI, MS
1.53	939	α-Pinene	39, 91, 93 , 77	24.2a ± 1.0	0.4c ± 0.0	19.6b ± 1.5	0.5c ± 0.0	LRI, MS, std
1.63	957	Camphene	67, 79, 93 , 121	20.4a ± 0.6	0.3c ± 0.0	16.1b ± 1.0	0.3d ± 0.0	LRI, MS, std
1.75	978	Sabinene	41, 77, 91, 93	9.4a ± 0.5	0.1c ± 0.0	51.1b ± 0.5	0.1d ± 0.0	LRI, MS, std
1.78	983	β-Pinene	41, 69, 79, 93	24.3a ± 1.0	0.6c ± 0.0	14.2b ± 0.2	0.3d ± 0.0	LRI, MS, std
1.83	992	β-Myrcene	39, 41 , 69, 93	75.8a ± 5.7	0.7c ± 0.0	49.7b ± 2.1	0.8d ± 0.0	LRI, MS, std
1.97	1011	Hexyl acetate	43 , 56, 84, 61	15.3a ± 0.8	0.1c ± 0.0	15.9a ± 0.2	0.2d ± 0.0	LRI, MS, std
1.99	1013	3-Carene	77, 79, 91, 93		0.1c ± 0.0		0.1c ± 0.0	LRI, MS
2.04	1019	2-Carene	77, 93, 121, 136		0.1c ± 0.0		0.1d ± 0.0	LRI, MS
2.11	1026	p-Cymene	77, 91, 119 , 134	5.8a ± 0.2	0.1c ± 0.0	6.1a ± 0.1	0.1d ± 0.0	LRI, MS, std
2.16	1032	Limonene	67, 68 , 79, 93	49.4a ± 3.0	0.8c ± 0.0	55.1a ± 5.8	0.9d ± 0.0	LRI, MS, std
2.17	1034	Z-β-Ocimene	41, 79, 91, 93	79.6a ± 5.3	1.1c ± 0.1	52.1b ± 1.6	0.5d ± 0.0	LRI, MS, std
2.19	1036	Eucalyptol	43 , 67, 81, 93	428.5a ± 33.1	6.1c ± 0.2	214.3b ± 9.5	4.5d ± 0.1	LRI, MS, std
2.26	1044	E-β-Ocimene	41, 79, 93, 121		0.4c ± 0.0		0.7d ± 0.0	LRI, MS
2.39	1059	γ-Terpinene	77, 91, 93 , 136	10.3a ± 0.2	0.1c ± 0.0	16.9b ± 0.3	0.3d ± 0.0	LRI, MS, std
2.53	1074	Sabinene hydrate	77, 91, 93 , 121	7.6a ± 0.6	0.2c ± 0.0	7.0a ± 0.2	0.2c ± 0.0	LRI, MS, std
2.66	1089	Terpinolene	93, 105, 121, 136		0.3c ± 0.0		0.4d ± 0.0	LRI, MS
2.83	1108	Linalool	41, 55, 69, 93	1886.1a ± 41.4	34.1c ± 0.3	4283.2b ± 28.5	47.3d ± 0.0	LRI, MS, std
3.08	1133	allo-Ocimene	91, 105, 121, 136		0.1c ± 0.0		0.1c ± 0.0	LRI, MS
3.25	1151	n-Hexyl isobutyrate	43, 56, 71, 89		0.1c ± 0.0		0.2d ± 0.0	LRI, MS
3.33	1159	Camphor	41, 81, 95 , 108	718.1a ± 17.8	7.1c ± 0.1	394.8b ± 18.7	7.1c ± 0.0	LRI, MS, std
3.46	1172	Lavandulol	41, 69, 111, 123		0.3c ± 0.0		1.4d ± 0.0	LRI, MS
3.55	1181	1-Butenylidene cyclohexane	79, 93, 107, 136		0.1 ± 0.0			LRI, MS
3.60	1186	Borneol	41, 93, 95 , 121	362.3a ± 3.3	2.0c ± 0.0	221.7b ± 0.1	3.9d ± 0.1	LRI, MS, std
3.63	1189	Terpinen-4-ol	71, 77, 91, 93	217.0a ± 17.4	3.0c ± 0.0	195.3a ± 1.5	4.7d ± 0.2	LRI, MS, std
3.69	1196	Hexyl butyrate	43 , 56, 71, 89	17.9a ± 1.1	0.2c ± 0.0	24.8b ± 0.7	0.4d ± 0.0	LRI, MS, std

Table S2B. Continued

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Grosso 1		Grosso 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
3.77	1204	α-Terpineol	59, 68, 79, 93	85.8a ± 2.2	1.3c ± 0.0	73.8b ± 1.8	1.4d ± 0.0	LRI, MS, std
4.03	1231	Perillol	68, 79, 93, 121		0.2c ± 0.0		0.2c ± 0.0	LRI, MS
4.12	1240	Hexyl valerate	43, 56, 85, 103		0.1c ± 0.0		0.2d ± 0.0	LRI, MS
4.21	1249	Linalyl acetate	41, 69, 93 , 121	1872.4a ± 34.9	30.7c ± 0.2	1074.6b ± 31.0	17.1d ± 0.0	LRI, MS, std
4.27	1255	Geraniol	41, 69, 93, 121		0.6c ± 0.0		0.6c ± 0.0	LRI, MS
4.54	1284	Lavandulyl acetate	43, 69, 93, 121		2.4c ± 0.1		1.3d ± 0.0	LRI, MS
5.04	1331	6-Undecanol	41, 55, 83, 101		0.1c ± 0.0		0.1d ± 0.0	LRI, MS
5.34	1359	Neryl acetate	41, 69, 79, 93	17.0a ± 0.3	0.3c ± 0.0	35.2b ± 0.2	0.3d ± 0.0	LRI, MS, std
5.54	1379	Geranyl acetate	41, 69 , 79, 93	30.8a ± 0.5	0.6c ± 0.0	25.4b ± 0.1	0.5c ± 0.0	LRI, MS, std
5.57	1381	β-Cubebene	91, 105, 120, 161		0.1c ± 0.0		0.1d ± 0.0	LRI, MS
5.65	1389	α-Bergamotene	69, 93, 105, 119		0.1c ± 0.0		0.1c ± 0.0	LRI, MS
5.82	1405	α-Cedrene	93, 105, 119, 204		0.1 ± 0.0			LRI, MS
6.03	1426	α-Santalene	41, 94, 161, 189		0.2 ± 0.0			LRI, MS
6.06	1429	E-β-Caryophyllene	41, 69, 79, 93	119.5a ± 3.0	1.4c ± 0.0	57.2b ± 0.2	1.1d ± 0.0	LRI, MS, std
6.17	1441	E-α-Bergamotene	41, 69, 93, 119		0.1c ± 0.0		0.1d ± 0.0	LRI, MS
6.25	1449	β-Farnesene	41, 69, 93, 133		tr			LRI, MS
6.37	1461	Z-β-Farnesene	41, 69, 93, 133		0.9c ± 0.0		0.7d ± 0.0	LRI, MS
6.43	1467	α-Humulene	41, 67, 80, 93	5.6 ± 0.2	0.1 ± 0.0			LRI, MS, std
6.57	1481	α-Amorphene	105, 119, 161, 204		0.1 ± 0.0			LRI, MS
6.65	1489	γ-Murolene	105, 119, 161, 204		0.6c ± 0.0		0.2d ± 0.0	LRI, MS
6.78	1504	α-Selinene	161, 175, 189, 204		0.2c ± 0.0		0.1c ± 0.0	LRI, MS
6.80	1507	α-Farnesene	41, 93, 107, 121		0.2c ± 0.0		0.1d ± 0.0	LRI, MS
6.84	1514	Bergamotene	41, 77, 93, 119		0.2c ± 0.0		0.1d ± 0.0	LRI, MS
6.89	1521	Germacrene D	105, 119, 161, 204		0.2 ± 0.0			LRI, MS
6.95	1532	β-Sesquiphellandrene	41, 69, 93, 161		0.1 ± 0.0			LRI, MS
7.32	1593	Caryophyllene oxide	41, 79, 91, 105		tr c		0.1d ± 0.0	LRI, MS

Table S2B. Continued

t _R (min)	LRI	Analyte (X)	Qualifying and quantitation ions* (m/z)	Grosso 1		Grosso 2		Identification methods
				Concentration (mM ± SD)	Area (% ± SD)	Concentration (mM ± SD)	Area (% ± SD)	
7.61	1658	Cadinol	105, 119, 161, 204		0.1c ± 0.0		0.1d ± 0.0	LRI, MS
7.77	1695	α-Bisabolol	41, 69, 93, 119		0.2 ± 0.0			LRI, MS
		Oxygenated terpenes:						
		Alcohol			41.2		59.1	
		Ketone			7.1		7.1	
		Aldehyde			0.0		0.0	
		Ester			34.0		19.3	
		Ether			6.2		4.5	
		Monoterpene hydrocarbons			5.9		5.8	
		Oxygenated monoterpenes			88.4		90.0	
		Sesquiterpene hydrocarbons			5.0		2.8	
		Oxygenated sesquiterpenes			0.0		0.1	
		Total terpene hydrocarbons			10.9		8.5	
		Total oxygenated terpenes			88.4		90.0	
		Non isoprenoid components			0.7		1.4	

LRI = Linear Retention Index obtained using the homologous series of n-alkanes (C7-C30). SD = standard deviation. tr = traces (<0.1%)

MS = tentatively identified by NIST 08 & Wiley 7. std = identified by comparison with reference standards. Results are expressed as mean ± standard deviation of three determinations. *Areas in bold mean "biomolecular marker" of the EO biochemotype. *Quantitation ions are shown in bold.

a, b Different letters in the same compound concentration mean statistically significant differences with p < 0.05. c,d Different letters in the same compound area mean statistically significant differences with p < 0.05.

Table S3. GC/MS determination of components in *L. x intermedia*, comparative with ISO normative.

Component (X)	Normative*		Abrial 1	Super 1	Super 2	Normative†		Grosso 1	Grosso 2
	Min (%)	Max (%)	Area X (%)	Area X (%)	Area X (%)	Min (%)	Max (%)	Area X (%)	Area X (%)
β-Myrcene						0.30	1.00	0.74	0.80
Limonene	0.50	1.50	1.10	0.72	0.69	0.50	1.50	0.83	0.99
Z-β-Ocimene	1.50	3.00	3.54	1.75	1.70	0.50	1.50	1.28	0.53
Eucalyptol	6.00	11.00	8.41	4.26	5.41	4.00	8.00	6.64	4.79
E-β-Ocimene	3.00	7.00	6.97	2.22	2.19	nd	1.00	0.39	0.75
Linalool	26.00	38.00	41.91	43.27	51.98	24.00	37.00	37.74	51.27
Camphor	7.00	11.00	10.29	5.23	8.60	6.00	8.50	7.86	7.68
Lavandulol	0.40	1.20	0.78	0.21	0.87	0.20	1.00	0.38	1.48
Borneol	1.50	3.50	2.17	2.51	3.12	1.50	3.50	2.26	4.33
Terpinen-4-ol	0.30	1.00	1.10	0.41	1.72	1.50	5.00	3.35	5.27
Hexyl butyrate						0.30	0.50	0.31	0.45
α-Terpineol						0.30	1.30	1.45	1.57
Linalyl acetate	20.00	29.00	21.99	38.09	22.39	25.00	38.00	34.15	18.60
Lavandulyl acetate	1.00	2.00	1.73	1.32	1.34	1.50	3.50	2.63	1.47

* ISO normative for lavandin Abrial (ISO 2001)

† ISO normative for lavandin Grosso (ISO 2009)

Table S4. EsGC/MS determination of components in *L. x intermedia*.

t _R (min)		Analyte (X)	Abrial 1		Super 1		Super 2		Grosso 1		Grosso 2	
(+) - X	(-) - X		(+) - [X]	(-) - [X]	(+) - [X]	(-) - [X]	(+) - [X]	(-) - [X]	(+) - [X]	(-) - [X]	(+) - [X]	(-) - [X]
			(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
7.79	7.52	α-Pinene	95	5	95	5	95	5	95	5	95	5
8.47	8.24	Camphene	35*	65*	30*	70*	14	86	19	81	5	95
8.89	9.16	β-Pinene	66*	34*	89*	11*	73*	27*	80*	20*	95	5
10.52	10.00	Limonene	95	5	95	5	95	5	95	5	80*	20*
15.73	15.57	Linalool	5	95	3	97	5	95	5	95	3	97
16.72	16.46	Camphor	95	5	95	5	95	5	95	5	95	5
18.32	18.51	Terpinen-4-ol	95	5	95	5	95	5	95	5	95	5
20.10	19.76	α-Terpineol	78*	22*	95	5	95	5	95	5	78*	22*
20.15	19.58	Borneol	95	5	95	5	95	5	95	5	95	5
23.92	22.81	E-β-Caryophyllene	5	95	5	95	5	95	5	95	5	95
-	28.81	Caryophyllene oxide	5	95	5	95	5	95	5	95	5	95

*Biomolecular marker of the EO biochemotype

Figure S5. Dendrogram for *L. x intermedia* samples.

The samples in X axis are: 1 = Abrial1, 2 = Super1, 3 = Super2, 4 = Grosso1, 5 = Grosso2.

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