Repurposing orange peel waste for limonene extraction using *deep* eutectic solvents for cosmetic applications

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Table S1. Database of solvents used for the COSMO-RS calculations, along with their corresponding numbers and chemical families. Solvents in bold writing were used as HBDs.

Number	Chemical family	Name
1	Alcohols	1-propanol
2	Alcohols	1-decanol
3	Alcohols	1-dodecanol
4	Alcohols	1-hexadecanol
5	Alcohols	1-hexanol
6	Alcohols	1-octanol
7	Alcohols	1-tetradecanol
8	Alcohols	2-phenoxyethanol
9	Alcohols	Cyclohexanol
10	Alcohols	Furfuryl alcohol
11	Alcohols	*p*-hydroxybenzyl alcohol
12	Polyols	1,10-decanediol
13	Polyols	1,15-pentadecanediol
14	Polyols	1,2-propanediol
15	Polyols	1,3-butanediol
16	Polyols	1,4-butanediol
17	Polyols	1,5-pentanediol
18	Polyols	1,6-hexanediol
19	Polyols	1,7-heptanediol
20	Polyols	1,8-octanediol
21	Polyols	1,9-nonanediol
22	Polyols	2,3-butanediol
23	Polyols	Diethylene glycol
24	Polyols	Erythritol
25	Polyols	Ethylene glycol
26	Polyols	Glycerol
27	Polyols	Inositol
28	Polyols	Mannitol
29	**Polyols**	**Sorbitol**
30	Polyols	Triethylene glycol
31	Polyols	Xylitol
32	Carboxylic Acids	3-phenyl-propionic acid
33	Carboxylic Acids	4-phenyl-butyric acid
34	Carboxylic Acids	5-phenyl-valeric acid
35	Carboxylic Acids	Acetic acid
36	Carboxylic Acids	Acetylsalicylic acid
37	Carboxylic Acids	Aconitic acid
38	Carboxylic Acids	Ascorbic acid
39	Carboxylic Acids	Benzoic acid
40	Carboxylic Acids	Butyric acid
41	Carboxylic Acids	Caproic acid
42	Carboxylic Acids	Citric acid
43	Carboxylic Acids	Formic acid
44	Carboxylic Acids	Fumaric acid
45	**Carboxylic Acids**	**Gallic Acid**
46	Carboxylic Acids	Geranic acid
47	Carboxylic Acids	Glutaric acid
48	Carboxylic Acids	Glycolic acid
49	Carboxylic Acids	Itaconic acid
85	Sugars	Mannose
86	Sugars	Raffinose
87	Sugars	Rhamnose
88	Sugars	Sorbose
89	Sugars	Sucrose
90	Sugars	Trehalose
91	Sugars	Xylose
92	Phenols	2,4,6-trimethyl phenol
93	Phenols	3,4-dimethyl phenol
94	Phenols	4-chloro phenol
95	Phenols	4-methoxy phenol
96	Phenols	α-naftol
97	Phenols	Catechol
98	Phenols	Chimaphilin
99	Phenols	Coumarin
100	Phenols	Dihydroquercetin
101	Phenols	Guaiacol
102	Phenols	Hydroquinone
103	Phenols	*o*-cresol
104	Phenols	Paeonol
105	Phenols	Phenol
106	Phenols	Quercetin
107	Phenols	Resorcinol
108	Phenols	Salol
109	Phenols	Vanillin
110	Molten Salts/ILs	Acetylcholine chloride
111	Molten Salts/ILs	Ammonium acetate
112	Molten Salts/ILs	Carnitine hydrochloride
113	Molten Salts/ILs	Choline acetate
114	Molten Salts/ILs	Choline bitartrate
115	Molten Salts/ILs	Choline chloride
116	Molten Salts/ILs	Choline dihydrogen citrate
117	Molten Salts/ILs	Choline dihydrogen phosphate
118	Molten Salts/ILs	Ethylammonium chloride
119	Molten Salts/ILs	Guanidine hydrochloride
120	Molten Salts/ILs	Sodium acetate
121	Molten Salts/ILs	Sodium propionate
122	Molten Salts/ILs	Tetrabutylammonium bromide
123	Molten Salts/ILs	Tetrabutylammonium chloride
124	Molten Salts/ILs	Tetraethylammonium chloride
125	Molten Salts/ILs	Tetramethylammonium bromide
126	Molten Salts/ILs	Tetramethylammonium chloride
127	Molten Salts/ILs	Tetrapropylammonium bromide
128	Molten Salts/ILs	Tetrapropylammonium chloride
129	Amino Acids	Alanine
130	Amino Acids	Arginine
131	Amino Acids	Aspartic acid
132	Amino Acids	Betaine
133	Amino Acids	Citrulline

50	Carboxylic Acids	Lactic acid	134	Amino Acids	Glutamic acid
51	**Carboxylic Acids**	**Levulinic acid**	135	Amino Acids	Glycine
52	Carboxylic Acids	Maleic acid	136	Amino Acids	Histidine
53	Carboxylic Acids	Malic acid	137	Amino Acids	Leucine
54	Carboxylic Acids	Malonic acid	**138**	**Amino Acids**	**Lysine**
55	Carboxylic Acids	Mandelic acid	139	Amino Acids	Ornithine
56	Carboxylic Acids	Nicotinic acid	**140**	**Amino Acids**	**Proline**
57	Carboxylic Acids	Oxalic acid	141	Amino Acids	Serine
58	Carboxylic Acids	p-coumaric acid	142	Amino Acids	Threonine
59	Carboxylic Acids	Phenylacetic acid	143	Amines/Amides	Acetamide
60	Carboxylic Acids	*p*-hydroxy benzoic acid	144	Amines/Amides	Benzamide
61	Carboxylic Acids	Propionic acid	145	Amines/Amides	Diethanolamine
62	Carboxylic Acids	*p*-toluenesulfonic acid	146	Amines/Amides	Dimethylurea
63	Carboxylic Acids	Pyruvic acid	147	Amines/Amides	Ethanolamine
64	Carboxylic Acids	Ricinoleic acid	148	Amines/Amides	N,N-dimethylformamide
65	Carboxylic Acids	Salicylic acid	149	Amines/Amides	Nicotinamide
66	Carboxylic Acids	Succinic acid	150	Amines/Amides	N-methylurea
67	Carboxylic Acids	Tartaric acid	**151**	**Amines/Amides**	**Urea**
68	Carboxylic Acids	Valeric acid	152	Ethers/Esters	2-hydroxypropanoicacidethylester
69	Carboxylic Acids	Vanillic acid	153	Ethers/Esters	2-methyltetrahydrofuran
70	Fatty Acids	Decanoic acid	154	Ethers/Esters	Cyclopentyl-methyl-ether
71	Fatty Acids	Dodecanoic acid	155	Ethers/Esters	Dimethylcarbonate
72	Fatty Acids	Hexadecanoic acid	156	Ethers/Esters	Isopropylacetate
73	Fatty Acids	Nonanoic acid	157	Ethers/Esters	PEG400
74	Fatty Acids	Octanoic acid	158	Ethers/Esters	PPG400
75	Fatty Acids	Oleic acid	159	Terpenes	Camphor
76	Fatty Acids	Tetradecanoic acid	160	Terpenes	Menthol
77	Sugars	Arabinose	161	Terpenes	Thymol
78	**Sugars**	**D-Glucose**	162	Others	2-methylimidazole
79	Sugars	D-Ribose	163	Others	Cyrene
80	Sugars	Fructose	164	Others	Imidazole
81	Sugars	Fucose	165	Others	Pyrrole
82	Sugars	Galactose	166	Others	Thiourea
83	Sugars	L-Glucose	167	Others	Trioctylphosphine oxide
84	Sugars	Maltose			

Table S2. Water content of the pure compounds used in the DES preparation.

Name of the compound	Water content (wt%)
Polyethylene glycol 200	0.13
Polyethylene glycol 600	0.14
Polypropylene glycol 400	0
D-glucose	0.20
D(–)-fructose	0.17
D(–)-xylose	0.17
D-sorbitol	0.42
Xylitol	0.10
L-proline	0.66
L-lysine	2.12
Glycine	0.25
L-(+)-arginine	0.51
Gallic acid	3.12
Levulinic acid	0.65
DL-tartaric acid	0.38
Citric acid	1.25
L-ascorbic acid	0

Myristic acid	0.13
Palmitic acid	0
Stearic acid	0
Myristyl alcohol	0
Urea	0.32

Optimization of sample pre-treatment and extraction procedures:

Solid-liquid extraction (SLE)

Various pretreatment methods were tested and optimized for the extraction of limonene from orange peel in order to determine the most suitable method: (i) the orange peels were frozen with liquid nitrogen and crushed with a mortar and pestle, (ii) the fresh peels were simply cut into small pieces or (iii) to mimic the beverage industry, the oranges were cut in half and squeezed with a citrus press, dried in an oven and crushed with a blender. By removing water from the biomass, the last method resulted in a higher concentration of limonene *per* gram of biomass and improved the stability of the biomass before further processing. This pre-treatment method was therefore selected as the optimal approach for the process.

To determine the optimal duration of solid-liquid extraction (SLE), an experiment was conducted to analyze the amount of extracted limonene for each solvent — methanol, ethanol, acetone, ethyl acetate and heptane — at eight different time points (30, 60, 90, 120, 150, 180, 210 and 240 min). The results showed that 120 min was sufficient, as the concentration of extracted limonene did not increase beyond this time point for any of the solvents tested. Based on these results, the extraction time was set at 120 min.

Liquid-liquid extraction (LLE)

Preliminary experiments identified heptane as the optimal organic solvent for LLE from the screening of ethyl acetate, methanol, ethanol, hexanol, butanol, acetone and heptane, as it successfully formed two phase systems with each of tested *D*ES. Different temperatures (30, 40 and 50 °C), extraction times (30 or 60 min) and number of cycles were tested during the LLE optimisation. In addition, two methods for mixing the immiscible phases during LLE were evaluated: stirring with a magnetic stirrer and using a vertical rotation device. The aim was to achieve thorough mixing of the two phases to facilitate the efficient mass transfer of limonene from the *D*ES-rich phase to the heptane-rich phase. The experimental results showed that the vertical rotation device provided more effective mixing compared to magnetic stirring. It was also found that an extraction temperature of 40 °C, a duration of 30 min and a single LLE cycle were sufficient to efficiently recover limonene in the heptane-rich phase.

Soxhlet extraction

Based on preliminary analysis, Soxhlet extraction parameters were optimised for each organic solvent (methanol, ethanol, acetone and ethyl acetate) by adjusting the temperature to complete six cycles within approximately 120 min, which was the time optimised for SLE. The extraction temperatures were set at 130 °C for methanol, 140 °C for ethanol, 100 °C for acetone and 125 °C for ethyl acetate.

Quantification of limonene concentration in DES extracts considering LLE

Due to the non-volatile nature of *D*ES, direct GC-MS analysis cannot be used for the quantification of limonene in the extract. Therefore, the LLE step is required to transfer limonene from *D*ES into a GC-MS-compatible organic solvent. The efficiency of the LLE process was determined using a limonene standard and subsequently applied to calculate the concentration of limonene extracted from orange peels using *D*ES.

$$LLE\ efficiency\ (\%) = \left(\frac{measured\ c_{standard,heptane}}{total\ c_{standard,heptane}}\right) * 100 \quad (1)$$

where *measured* $c_{standard,heptane}$ is concentration of limonene standard in heptane-rich phase of LLE-system determined by GC-MS and *total* $c_{standard,heptane}$ is total theoretical concentration of limonene standard in the LLE system.

$$c_{limonene,DES} = \frac{c_{limonene,heptane}}{LLE\ efficiency\ (\%)} \quad (2)$$

where $c_{limonene,(D)ES}$ and $c_{limonene,heptane}$ are the limonene concentration in *D*ES and in the heptane-rich phase of LLE system determined by GC-MS, respectively.

$$m_{limonene} = c_{limonene,DES} * m_{(D)ES} \quad (3)$$

where $m_{limonene}$ is the extracted mass of limonene and $m_{(D)ES}$ is mass of *D*ES used for the extraction.

$$Y = \frac{m_{limonene}}{m_{OP}} \quad (4)$$

where *Y* stands for extraction yield of limonene and m_{OP} for the mass of dried orange peels used for the extraction.

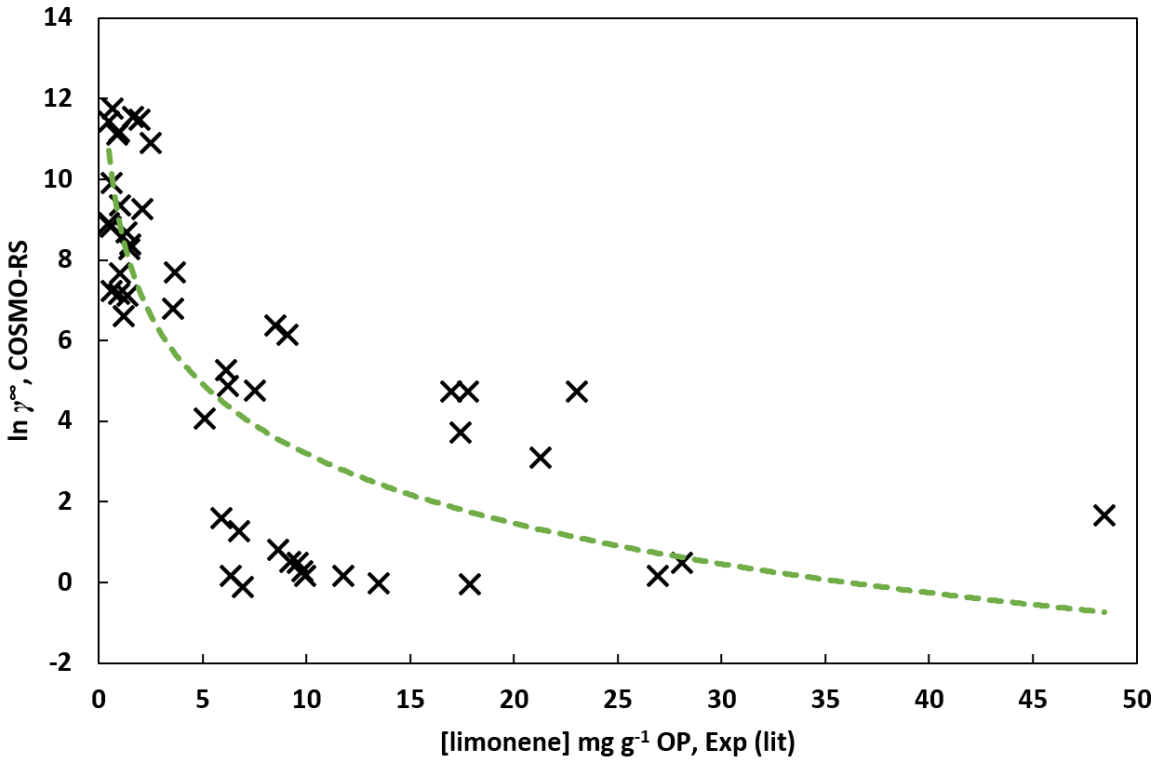

Fig. S1. Qualitative comparison between COSMO-RS predicted activity coefficients at infinite dilution and literature experimental data[19–24] on limonene extraction from orange peel. The green line serves as a visual aid to highlight the overall trend.

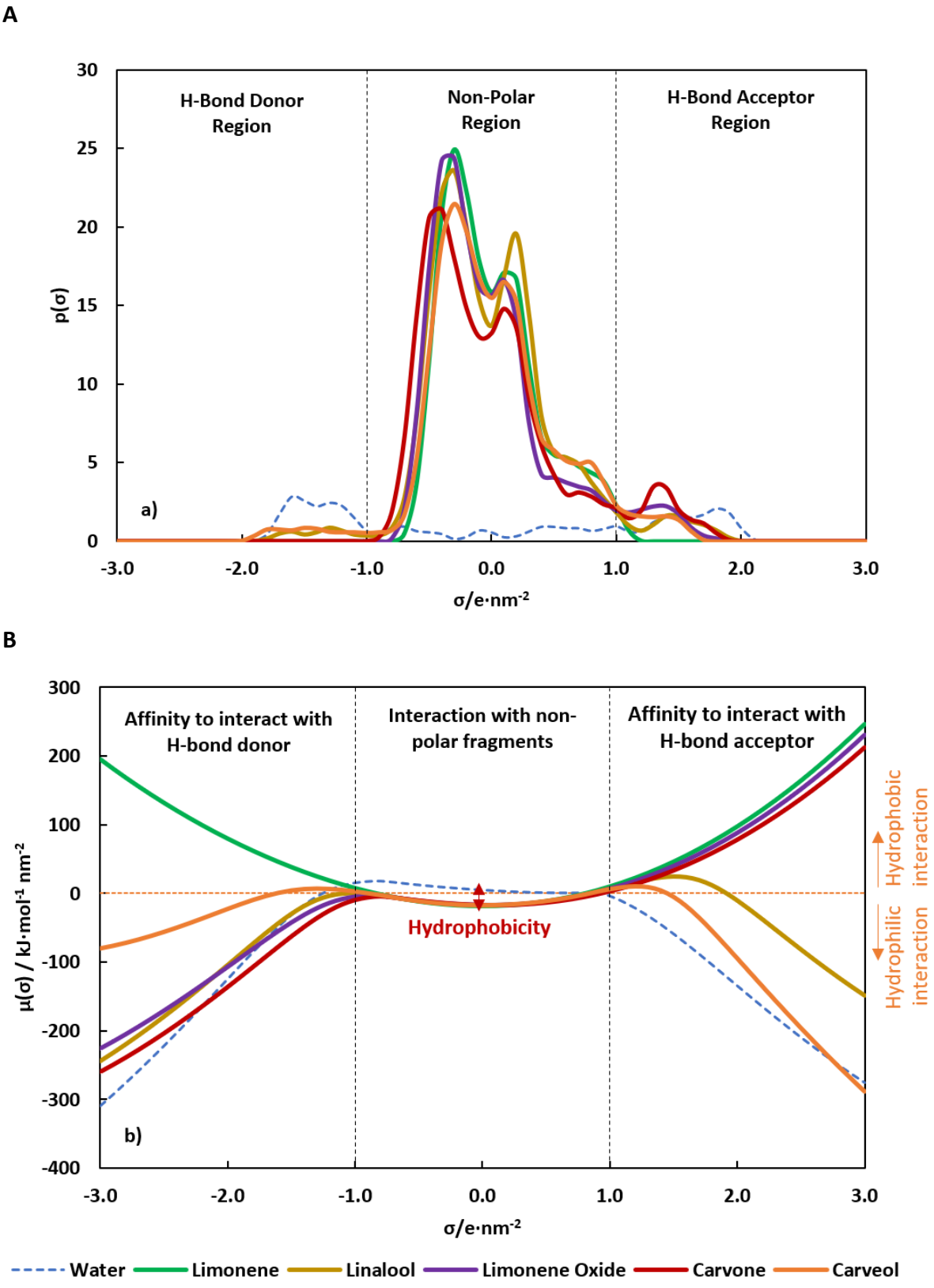

Fig. S2. Sigma profile (A) and sigma potential (B) of limonene, linalool, limonene oxide, carvone, carveol, and water predicted by COSMO-RS.

Table S3. LOD and LOQ for the measured analytes.

Analyte	Method*	Retention time (min)	LOD (μg mL^{-1})	LOQ (μg mL^{-1})
Epicatechin	HPLC	10.5	0.2	0.5
Caffeic acid		11.4	0.05	0.2
Hesperidin		14.0	0.06	0.2
Quercetin		16.4	0.7	1.4
Naringenin		17.0	0.03	0.08
Bergapten		18.1	0.008	0.03
Limonene	GC-MS	12.2	10	30
Linalool		13.5	15	40
Limonene oxide 1**		14.1	25	70
Limonene oxide 2**		14.2	20	55
Carveol 1**		15.3	25	65
Carveol 2**		15.5	30	75
Carvone		15.7	20	45

*The LODs and LOQs for GC-MS measurements are reported for the scan mode. Even lower LODs could be achieved when extracting specific ion.
** Limonene oxide and carveol standards contained a mixture of *cis* and *trans* isomers.
*** Manual dilution before the HPLC measurement is not considered in reported values. In case of bergapten, even when considering the samples dilution, the LOD is low enough (*i.e.* 0.8 μg mL^{-1}) to meet the regulations (limit is 15 μg mL^{-1}).

Table S4. Allowed concentrations of different chemicals in cosmetic products.

Name of the compound	Max. used concentration (%)*	Name of the compound	Max. used concentration (%)*
1,10-decanediol	0.01	D-Ribose	0.05
1,5-pentanediol	39.9	Fructose	20
Inositol	2	Maltose	0.5
Mannitol	60.5	Mannose	5
Sorbitol	70	Rhamnose	10
Triethylene glycol	0.2	Sucrose	65
Xylitol	14	Trehalose	2
Acetic acid	0.3	Xylose	1
Ascorbic acid	10	Hydroquinone	0.02
Benzoic acid	5	Resorcinol	5
Caproic acid	0.011	Sodium acetate	0.5
Citric acid	39	Alanine	0.1
Formic acid	0.2	Arginine	18
Fumaric acid	5	Aspartic acid	1
Glycolic acid	50	Betaine	8.7
Lactic acid	30	Glutamic acid	2
Levulinic acid	4.5	Glycine	4
Maleic acid	0.004	Histidine	0.05
Malic acid	50	Leucine	0.001

Salicylic acid	30	**Lysine**	0.7
Succinic acid	26	**Proline**	2
Capric acid	4	Serine	2
Lauric acid	18	Threonine	0.05
Palmitic acid	21	Diethanolamine	0.3
Caprylic acid	4	Ethanolamine	18
Oleic acid	20.9	**Urea**	10
Myristic acid	28.7	Thymol	0.25
D-Glucose	97.8		

*The data was provided by Cosmetic Ingredient Review (https://www.cir-safety.org/).

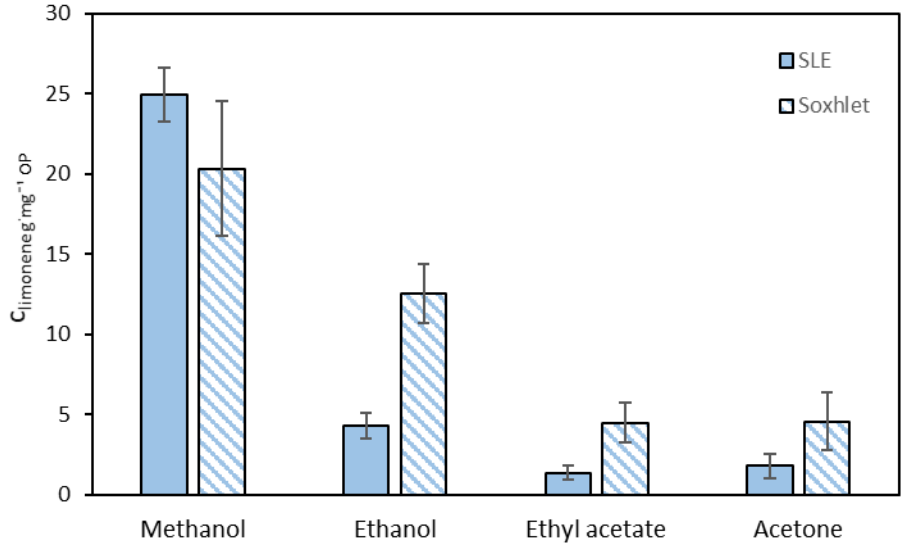

Fig. S3: Limonene concentration obtained with SLE and Soxhlet extraction using different organic solvents.

Table S5. Statistics from comparing the effect of organic solvents and *D*ES with ANOVA and Tukey HSD posthoc test.

Group 1	Group 2	Null value	Estimate	CI low	CI high	Adjusted p-value	Significance level
Acetone	Ethyl acetate	0	-0.29	-0.54	-0.04	0.0129	*
Acetone	Ethanol	0	-0.41	-0.65	-0.16	0.0002	***
Acetone	Heptane	0	0.16	-0.09	0.40	0.5540	NS
Acetone	Methanol	0	-0.04	-0.29	0.21	1.0000	NS
Acetone	PEG200-Gall.A-H_2O	0	-0.49	-0.74	-0.24	9.23e-06	****
Acetone	PEG200-Glu-H_2O	0	-0.98	-1.23	-0.73	5.29e-12	****
Acetone	PEG200-Lev.A-H_2O	0	0.14	-0.10	0.39	0.6550	NS
Acetone	PEG200-Lys-H_2O	0	-0.17	-0.42	0.08	0.4030	NS
Acetone	PEG200-Pro-H_2O	0	-0.19	-0.44	0.06	0.2530	NS
Acetone	PEG200-Sor-H_2O	0	-0.73	-0.98	-0.48	4.21e-09	****
Acetone	PEG200-Urea-H_2O	0	-0.79	-1.04	-0.54	6.58e-10	****
Ethyl acetate	Ethanol	0	-0.12	-0.37	0.13	0.8730	NS
Ethyl acetate	Heptane	0	0.44	0.20	0.69	4.48e-05	****
Ethyl acetate	Methanol	0	0.25	0.00	0.50	0.0447	*
Ethyl acetate	PEG200-Gall.A-H_2O	0	-0.20	-0.45	0.05	0.2130	NS
Ethyl acetate	PEG200-Glu-H_2O	0	-0.69	-0.94	-0.44	1.17e-08	****
Ethyl acetate	PEG200-Lev.A-H_2O	0	0.43	0.18	0.68	6.63e-05	****
Ethyl acetate	PEG200-Lys-H_2O	0	0.12	-0.13	0.37	0.8770	NS
Ethyl acetate	PEG200-Pro-H_2O	0	0.10	-0.15	0.34	0.9640	NS
Ethyl acetate	PEG200-Sor-H_2O	0	-0.44	-0.69	-0.19	5.62e-05	****
Ethyl acetate	PEG200-Urea-H_2O	0	-0.50	-0.75	-0.25	5.45e-06	****
Ethanol	Heptane	0	0.56	0.31	0.81	7.53e-07	****
Ethanol	Methanol	0	0.37	0.12	0.62	0.0007	***
Ethanol	PEG200-Gall.A-H_2O	0	-0.08	-0.33	0.17	0.9890	NS
Ethanol	PEG200-Glu-H_2O	0	-0.58	-0.82	-0.33	4.71e-07	****

Ethanol	PEG200-Lev.A-H_2O	0	0.55	0.30	0.80	1.08e-06	****
Ethanol	PEG200-Lys-H_2O	0	0.23	-0.02	0.48	0.0809	NS
Ethanol	PEG200-Pro-H_2O	0	0.21	-0.04	0.46	0.1470	NS
Ethanol	PEG200-Sor-H_2O	0	-0.32	-0.57	-0.07	0.0041	**
Ethanol	PEG200-Urea-H_2O	0	-0.39	-0.64	-0.14	0.0004	***
Heptane	Methanol	0	-0.19	-0.44	0.06	0.2570	NS
Heptane	PEG200-Gall.A-H_2O	0	-0.64	-0.89	-0.40	5.17e-08	****
Heptane	PEG200-Glu-H_2O	0	-1.14	-1.39	-0.89	2.01e-13	****
Heptane	PEG200-Lev.A-H_2O	0	-0.01	-0.26	0.24	1.0000	NS
Heptane	PEG200-Lys-H_2O	0	-0.33	-0.58	-0.08	0.0032	**
Heptane	PEG200-Pro-H_2O	0	-0.35	-0.60	-0.10	0.0015	**
Heptane	PEG200-Sor-H_2O	0	-0.88	-1.13	-0.63	6.08e-11	****
Heptane	PEG200-Urea-H_2O	0	-0.95	-1.20	-0.70	1.18e-11	****
Methanol	PEG200-Gall.A-H_2O	0	-0.45	-0.70	-0.20	3.42e-05	****
Methanol	PEG200-Glu-H_2O	0	-0.94	-1.19	-0.70	1.28e-11	****
Methanol	PEG200-Lev.A-H_2O	0	0.18	-0.07	0.43	0.3320	NS
Methanol	PEG200-Lys-H_2O	0	-0.14	-0.38	0.11	0.7340	NS
Methanol	PEG200-Pro-H_2O	0	-0.16	-0.40	0.09	0.5480	NS
Methanol	PEG200-Sor-H_2O	0	-0.69	-0.94	-0.44	1.25e-08	****
Methanol	PEG200-Urea-H_2O	0	-0.76	-1.00	-0.51	1.84e-09	****
PEG200-Gall.A-H_2O	PEG200-Glu-H_2O	0	-0.49	-0.74	-0.24	7.93e-06	****
PEG200-Gall.A-H_2O	PEG200-Lev.A-H_2O	0	0.63	0.38	0.88	7.27e-08	****
PEG200-Gall.A-H_2O	PEG200-Lys-H_2O	0	0.32	0.07	0.56	0.0049	**
PEG200-Gall.A-H_2O	PEG200-Pro-H_2O	0	0.30	0.05	0.54	0.0101	*
PEG200-Gall.A-H_2O	PEG200-Sor-H_2O	0	-0.24	-0.49	0.01	0.0694	NS
PEG200-Gall.A-H_2O	PEG200-Urea-H_2O	0	-0.30	-0.55	-0.06	0.0076	**
PEG200-Glu-H_2O	PEG200-Lev.A-H_2O	0	1.13	0.88	1.37	2.44e-13	****
PEG200-Glu-H_2O	PEG200-Lys-H_2O	0	0.81	0.56	1.06	4.2e-10	****
PEG200-Glu-H_2O	PEG200-Pro-H_2O	0	0.79	0.54	1.04	7.33e-10	****
PEG200-Glu-H_2O	PEG200-Sor-H_2O	0	0.25	0.01	0.50	0.0416	*
PEG200-Glu-H_2O	PEG200-Urea-H_2O	0	0.19	-0.06	0.44	0.2780	NS
PEG200-Lev.A-H_2O	PEG200-Lys-H_2O	0	-0.32	-0.57	-0.07	0.0047	**
PEG200-Lev.A-H_2O	PEG200-Pro-H_2O	0	-0.34	-0.59	-0.09	0.0023	**
PEG200-Lev.A-H_2O	PEG200-Sor-H_2O	0	-0.87	-1.12	-0.62	8.03e-11	****
PEG200-Lev.A-H_2O	PEG200-Urea-H_2O	0	-0.94	-1.19	-0.69	1.54e-11	****
PEG200-Lys-H_2O	PEG200-Pro-H_2O	0	-0.02	-0.27	0.23	1.0000	NS
PEG200-Lys-H_2O	PEG200-Sor-H_2O	0	-0.55	-0.80	-0.31	9.47e-07	****
PEG200-Lys-H_2O	PEG200-Urea-H_2O	0	-0.62	-0.87	-0.37	1.1e-07	****
PEG200-Pro-H_2O	PEG200-Sor-H_2O	0	-0.53	-0.78	-0.29	1.89e-06	****
PEG200-Pro-H_2O	PEG200-Urea-H_2O	0	-0.60	-0.85	-0.35	2.13e-07	****
PEG200-Sor-H_2O	PEG200-Urea-H_2O	0	-0.07	-0.31	0.18	0.9990	NS

Null value is the value representing the null hypothesis, Estimate is the observed difference in means of the groups compared, and CI low and high are limit levels of confidence interval. Significance levels are NS $p \geq 0.05$, *$p < 0.05$, ** $p < 0.01$, ***$p < 0.001$, ****$p < 0.0001$.

Table S6. Statistics from comparing the effect of water content in *D*ES with paired t-test.

HBD	Group 1	Group 2	t-value	df	p-value	Adjusted p-value	Significance level
Gallic acid	PEG200-Gall.A	PEG200-GallA-H_2O	23.11	2.82	0.0003	0.0008	***
Levulinic acid	PEG200-Lev.A	PEG200-Lev.A-H_2O	1.77	2.08	0.2130	0.2130	NS
Urea	PEG200-Urea	PEG200-Urea-H_2O	8.14	2.03	0.0140	0.0280	*

Significance levels are NS p ≥ 0.05, *p < 0.05, ** p < 0.01, ***p < 0.001, ****p < 0.0001. df are degrees of freedom.

Table S7. Statistics from comparing the effect of PEG molecular weight in *D*ES with paired t-test.

HBD	Group 1	Group 2	t-value	df	p-value	Adjusted p-value	Significance level
Proline	PEG200-Pro-H_2O	PEG600-Pro-H_2O	-41.96	2.38	0.0002	0.0007	***
Levulinic acid	PEG200-Lev.A	PEG600-Lev.A	0.70	2.03	0.5560	0.5560	NS
Urea	PEG200-Urea	PEG600-Urea	2.95	2.48	0.0760	0.2280	NS

Significance levels: NS p ≥ 0.05, *p < 0.05, ** p < 0.01, ***p < 0.001, ****p < 0.0001. df are degrees of freedom.

Table S8. Volume loss* after separation of *D*ES extract from the residual biomass.

***D*ES**	**Average volume loss (%)**
PEG200-Lys-H_2O	27
PEG200-Pro-H_2O	56
PEG200-Glu-H_2O	43
PEG200-Gall.A	51
PEG200-Gall.A-H_2O	40
PEG200-Lev.A.	21
PEG200-Lev.A-H_2O	36
PEG600-Lev.A	28
PEG200-Urea	28
PEG200-Urea-H_2O	40
PEG600-Urea	28

*The loss of the volume (initial volume of solvent used for the extraction subtracted with obtained volume of the extract after extraction) due to absorption/adsorption of solvent to the biomass.

Table S9. Statistics from testing stability of extracts with paired t-test.

*D*ES extract	Group 1	Group 2	t-value	df	p-value	Adjusted p-value	Significance level
PEG200-Gall.A	week 0	week 5	-5.405	2	0.033	0.263	NS
PEG200-Gall.A-H_2O	week 0	week 5	4.174	2	0.053	0.317	NS
PEG200-Lev.A	week 0	week 5	-3.097	2	0.090	0.327	NS
PEG200-Lev.A-H_2O	week 0	week 5	-3.716	2	0.065	0.327	NS
PEG200-Lys-H_2O	week 0	week 5	-1.708	2	0.230	0.327	NS
PEG200-Pro-H_2O	week 0	week 5	-11.016	2	0.008	0.090	NS
PEG200-Sor-H_2O	week 0	week 5	3.687	2	0.066	0.327	NS
PEG200-Urea	week 0	week 5	5.912	2	0.027	0.263	NS
PEG200-Urea-H_2O	week 0	week 5	12.102	2	0.007	0.088	NS
PEG600-Lev.A	week 0	week 5	-6.043	2	0.026	0.263	NS
PEG600-Pro-H_2O	week 0	week 5	-11.495	2	0.007	0.090	NS

Significance levels: NS $p \geq 0.05$, *$p < 0.05$, ** $p < 0.01$, ***$p < 0.001$, ****$p < 0.0001$. df are degrees of freedom.

Table S10: Liquid-liquid extraction efficiency (%) determined with the use of limonene standard for different *D*ES.

Name	LLE efficiency (%)
PEG200-Lys-H_2O	76 ± 2
PEG200-Pro-H_2O	75 ± 3
PEG600-Pro-H_2O	73 ± 6
PEG200-Sor-H_2O	63 ± 3
PEG200-Glu-H_2O	73 ± 11
PEG200-Gall.A	47 ± 3
PEG200-Gall.A-H_2O	76 ± 4
PEG200-Lev.A	84 ± 2
PEG200-Lev.A-H_2O	79 ± 1
PEG600-Lev.A	81 ± 1
PEG200-Urea	84 ± 2
PEG200-Urea-H_2O	71 ± 9
PEG600-Urea	76 ± 1

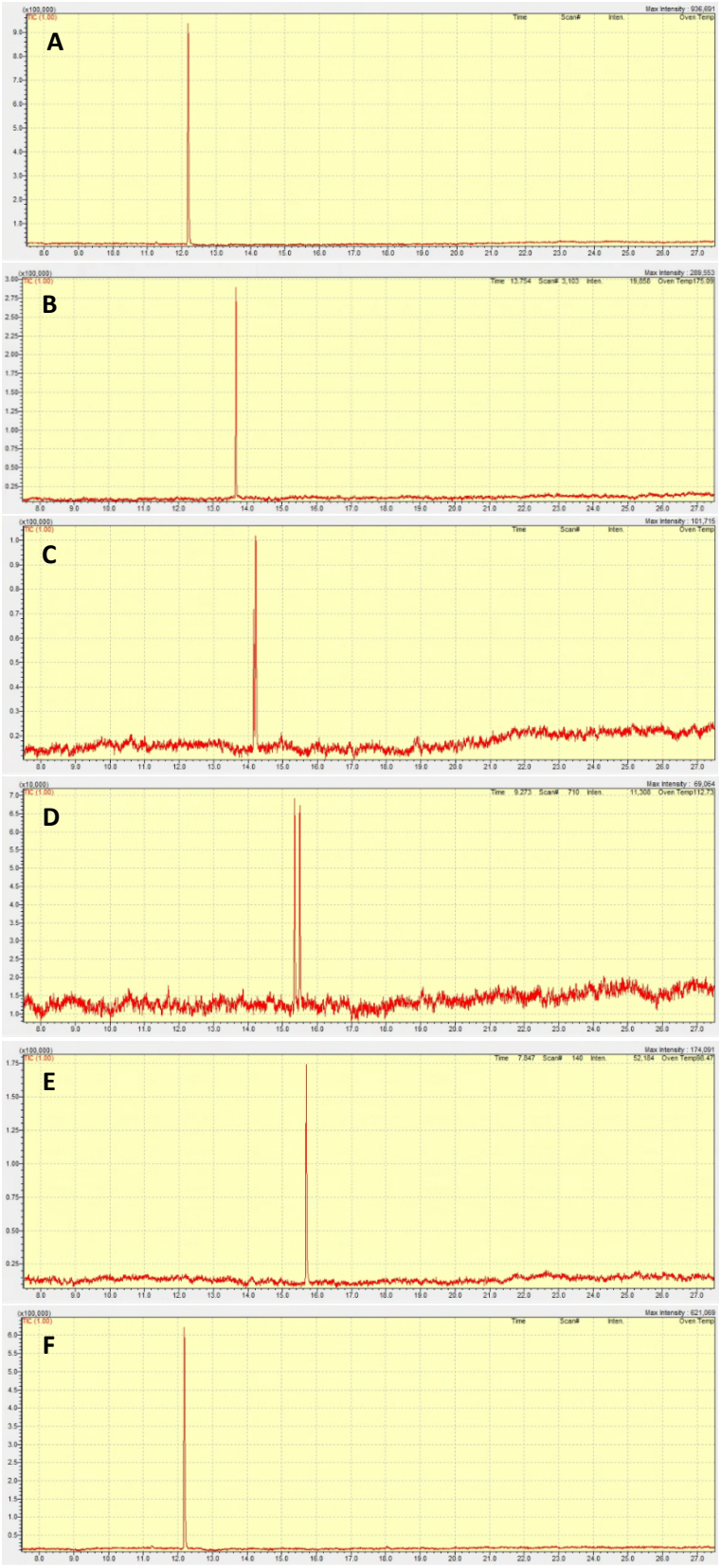

Fig. S4. GC-MS chromatogram in scan measuring mode. A) limonene, B) linalool, C) limonene oxide (*cis* and *trans*), D) carveol (*cis* and *trans*), E) carvone, F) sample (orange peels extract with PEG200-urea); retention times in **Table S**.

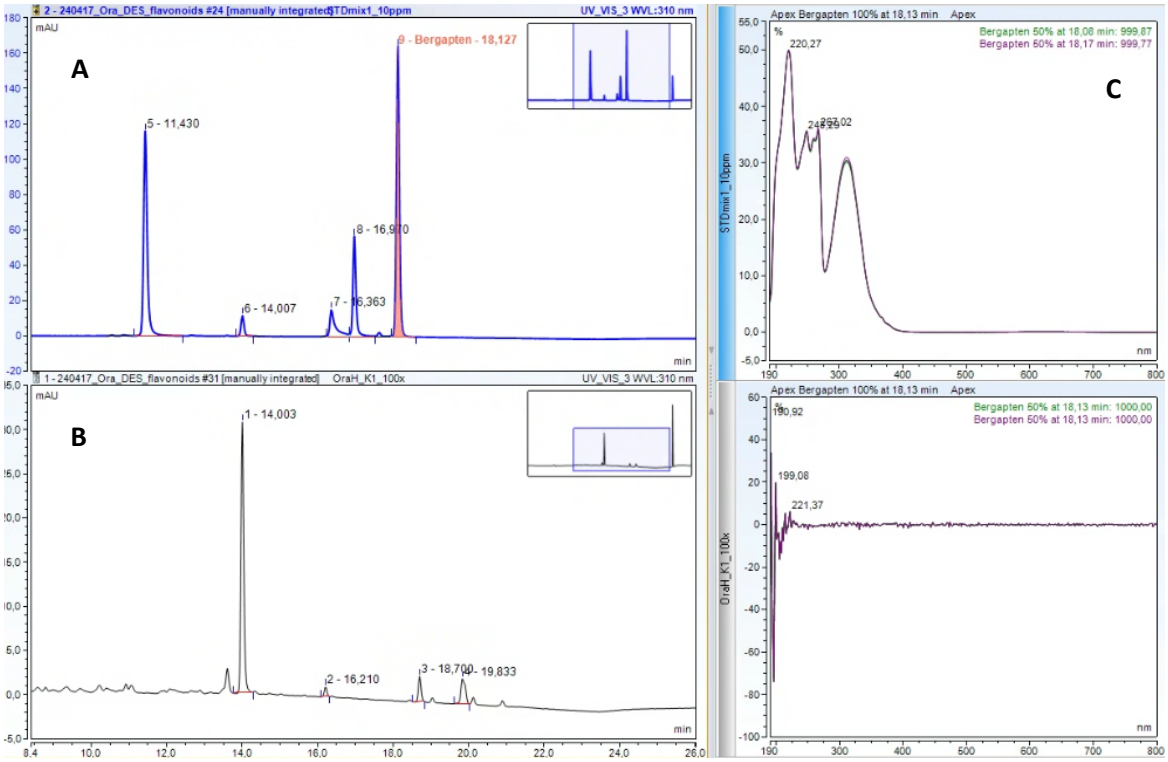

Fig. S5.HPLC chromatogram measured at 310 nm for detection of bergapten. A) mix of standards (epicatechin, caffeic acid, hesperidin, quercetin, naringenin, and bergapten; retention times listed in Table S9), B) sample (orange peel extract with PEG200-urea), C) UV-VIS spectra of bergapten standard.

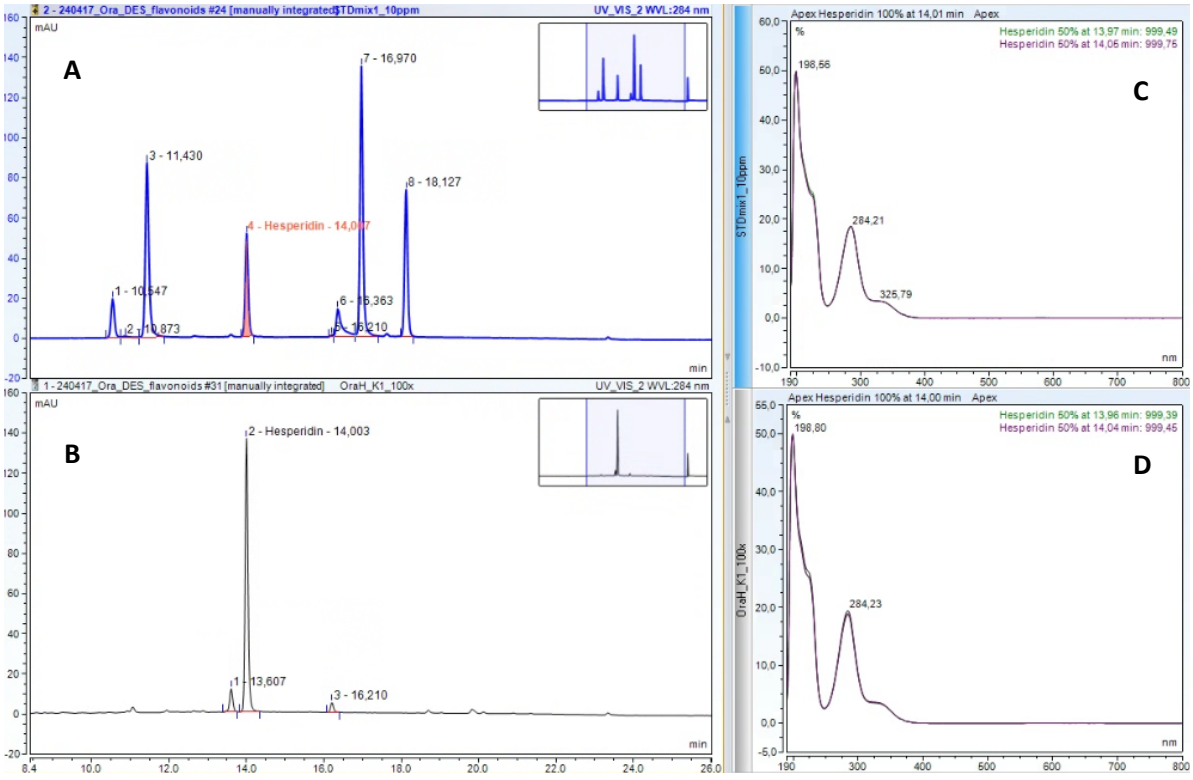

Fig. S6. HPLC chromatograms measured at 284 nm for detection of flavonoids. A) mix of standards (epicatechin, caffeic acid, hesperidin, quercetin, naringenin, and bergapten; retention times listed in **Table S**), B) sample (orange peel extract with PEG200-urea), C) UV-VIS spectra of hesperidin standard, D) UV-VIS spectra of hesperidin in the sample.