Supplementary Information

Comprehensive Two-Step Supercritical Fluid Extraction for Green Isolation of Volatiles and Phenolic Compounds from Plant Material

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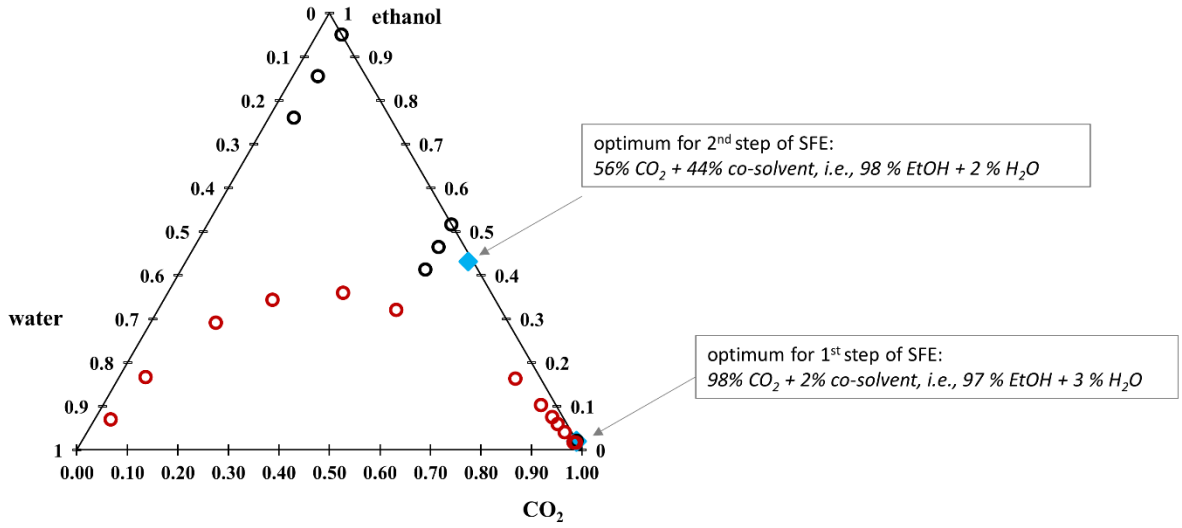


Figure S1: Phase diagram of a ternary system composed of CO_2/EtOH/H_2O. [1] The red circles mark the bubble point/dew point curve, i.e., the boundary between a single liquid phase (above the curve) and two phases (vapor/liquid) at 60 °C and 142 bar. The black circles mark the conditions investigated within the method optimization. The blue squares mark the optimal conditions for individual steps of optimized methods.

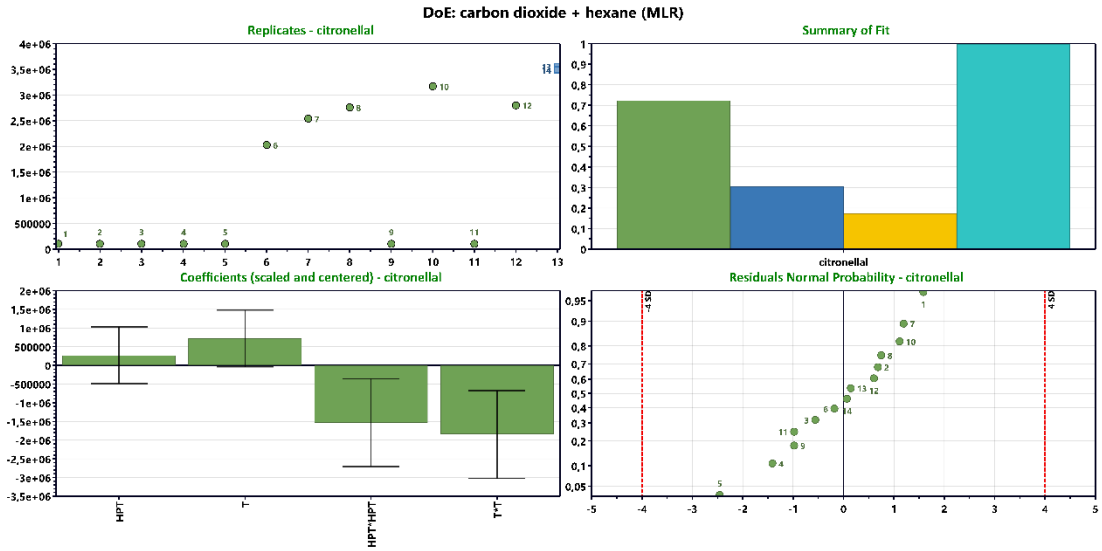


Figure S2: Model summary for by CO_2/hexane extracted citronellal.

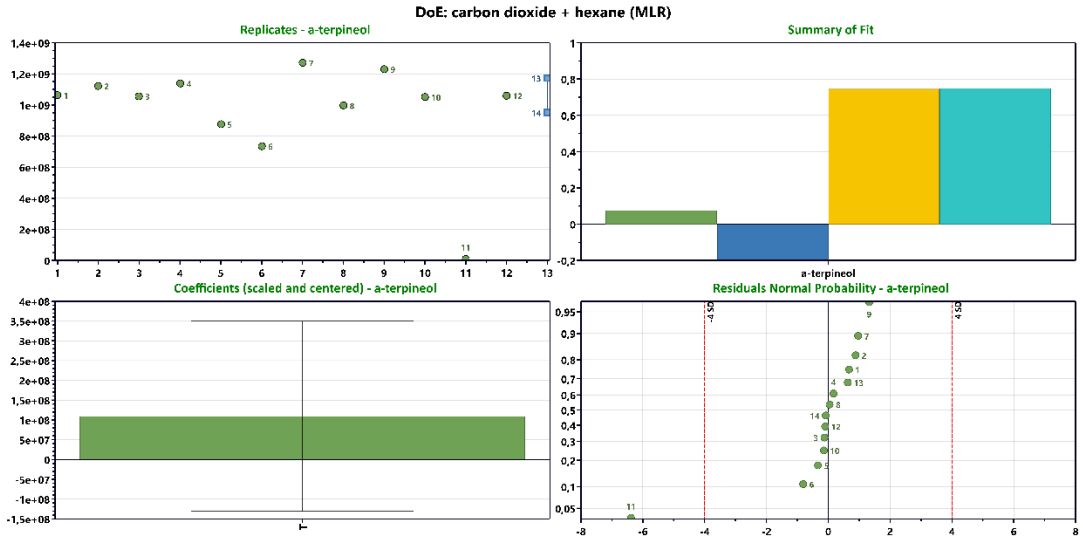


Figure S3: Model summary for terpineol extracted by CO_2/hexane.

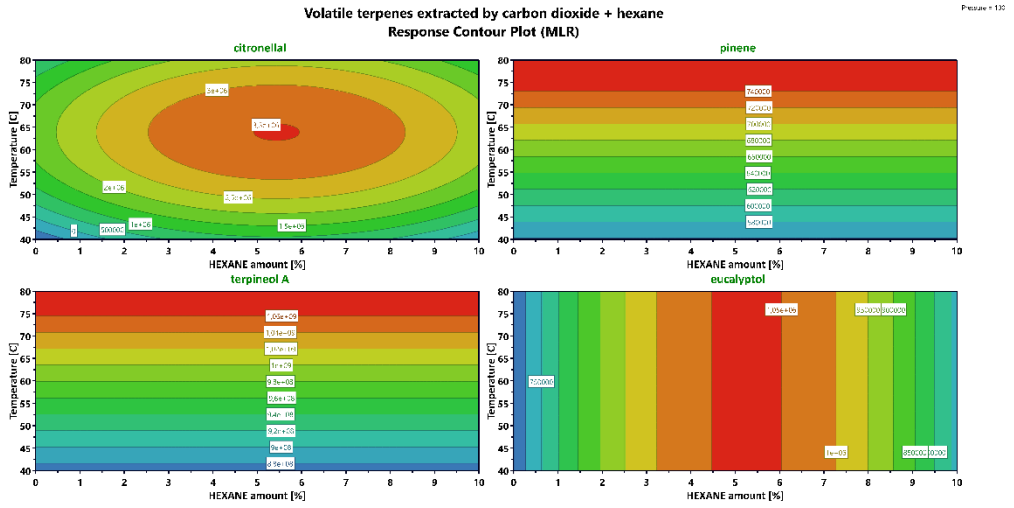


Figure S4: Response contour plot (MLR), volatile terpenes extracted by CO_2/hexane.

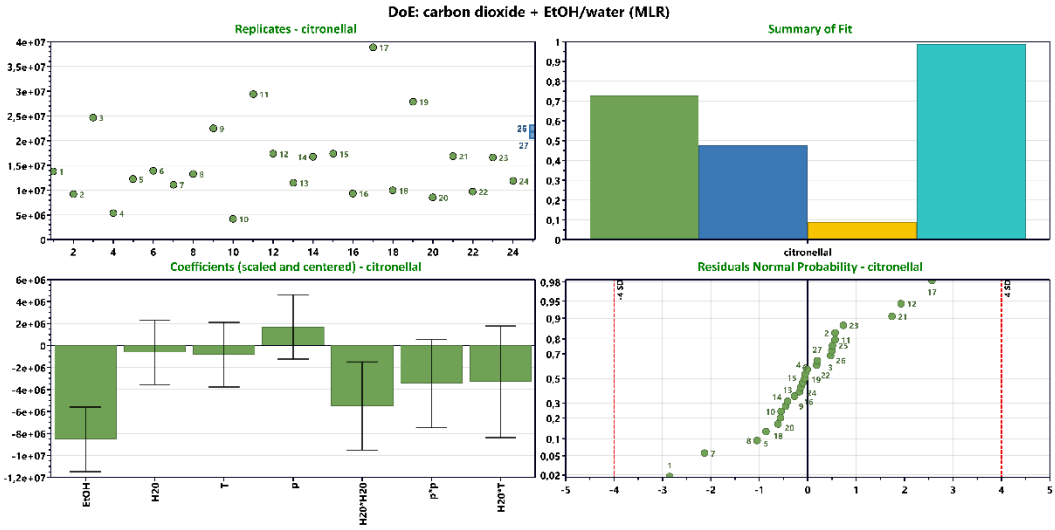


Figure S5: Model summary for citronellal extracted by CO_2/EtOH/H_2O.

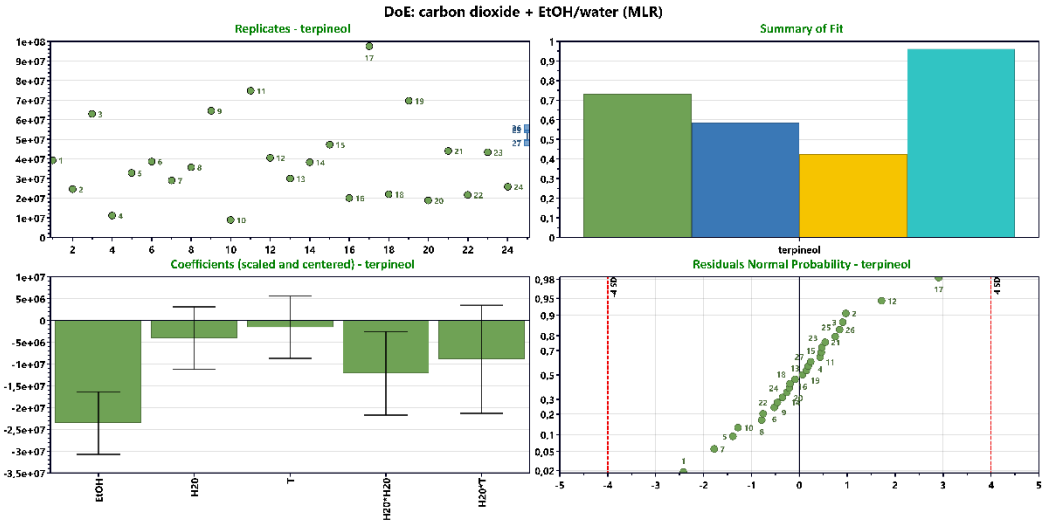


Figure S6: Model summary for terpineol extracted by CO_2/EtOH/H_2O

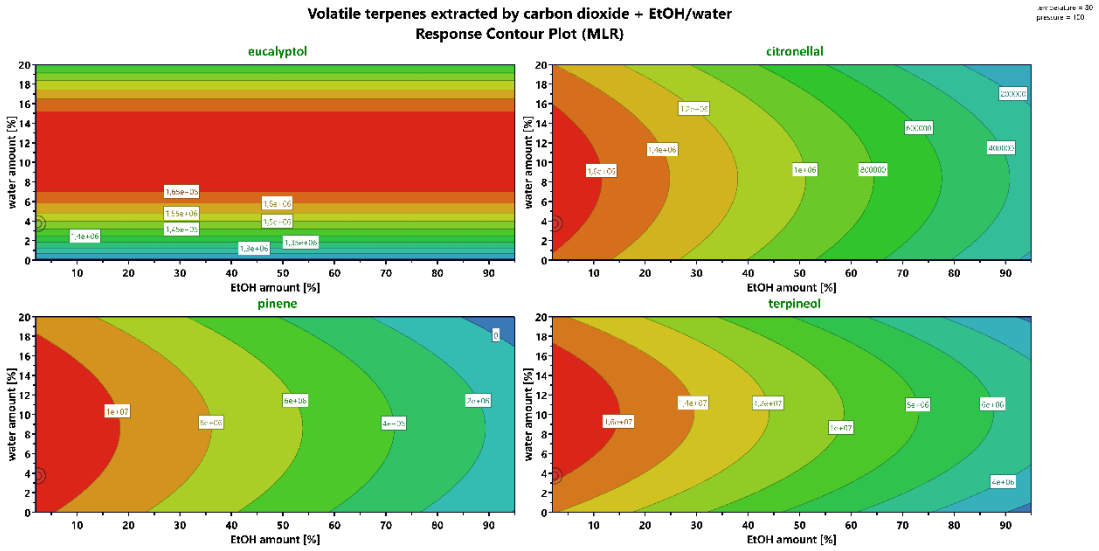


Figure S7: Response contour plot (MLR), volatile terpenes extracted by CO_2/EtOH/H_2O.

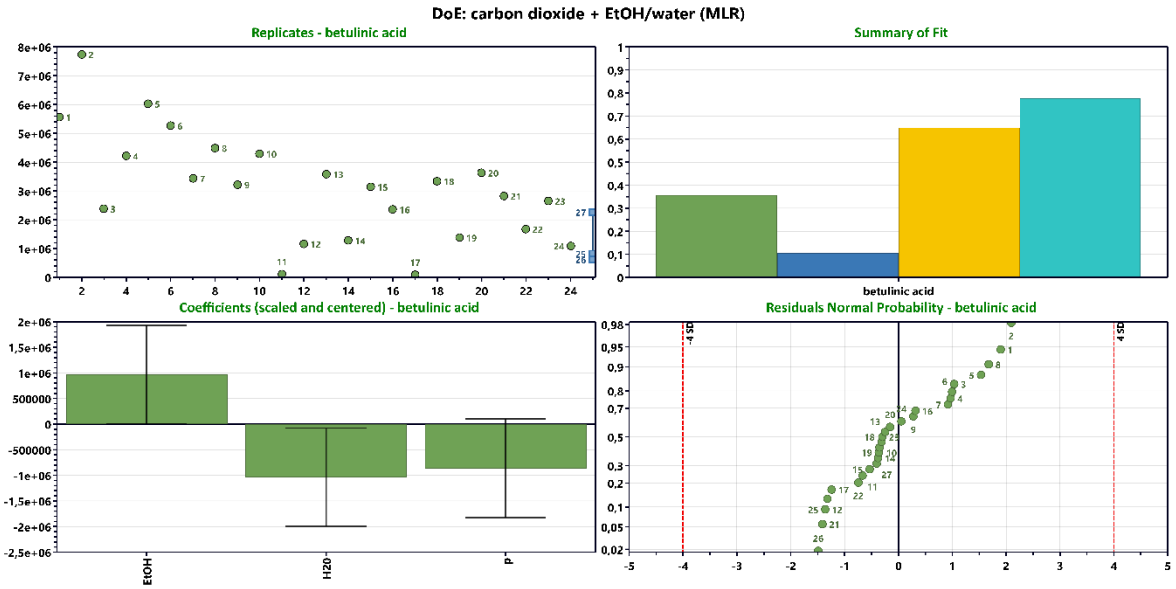


Figure S8: Model summary for betulinic acid extracted with CO_2/EtOH/H_2O.

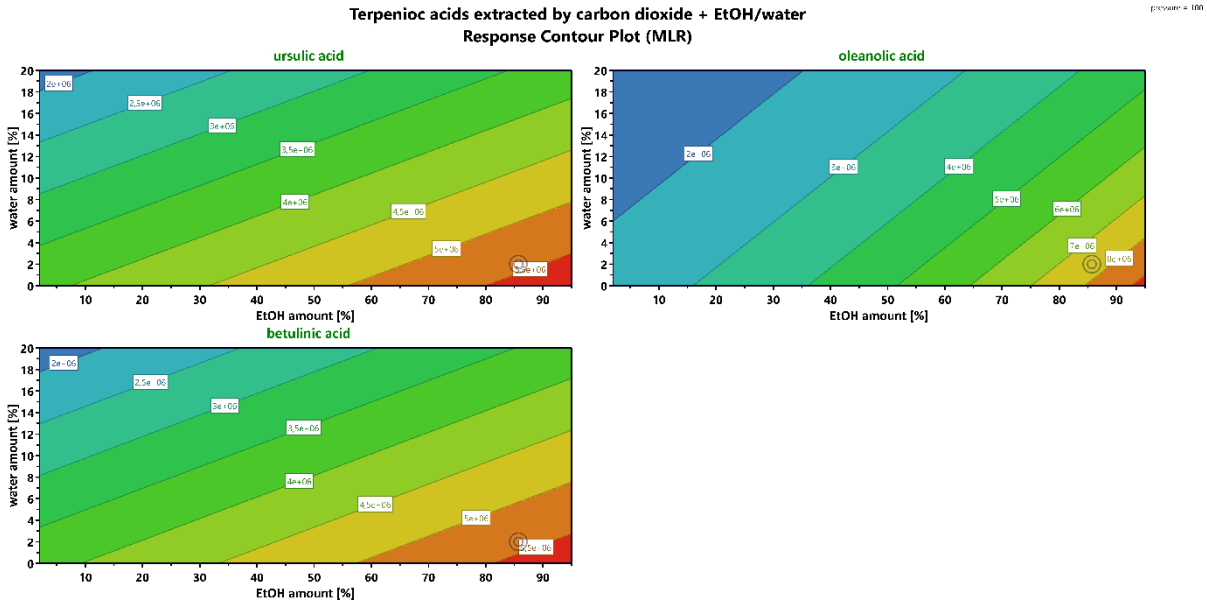


Figure S9: Response contour plot (MLR), terpenoic acids extracted by CO_2/EtOH/H_2O.

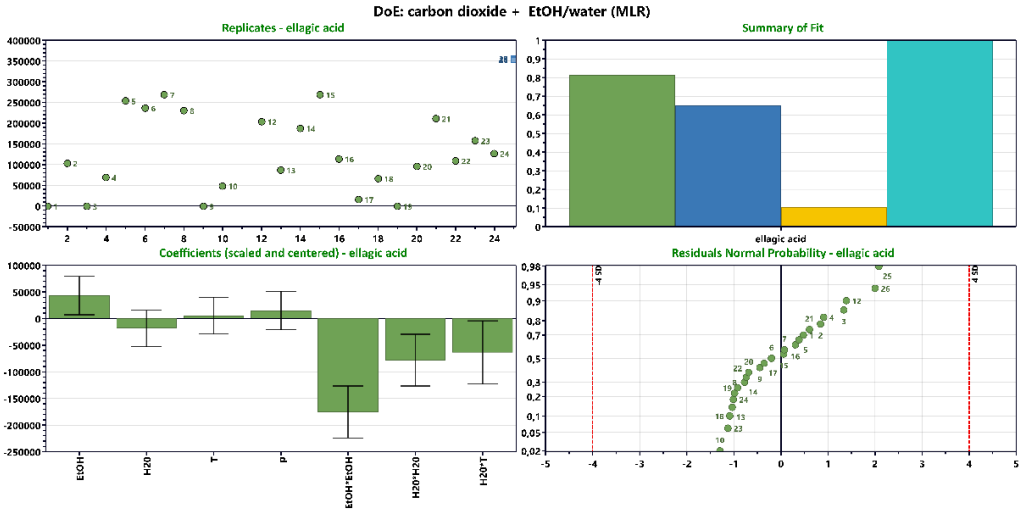


Figure S10: Model summary for ellagic acid extracted with CO_2/EtOH/H_2O.

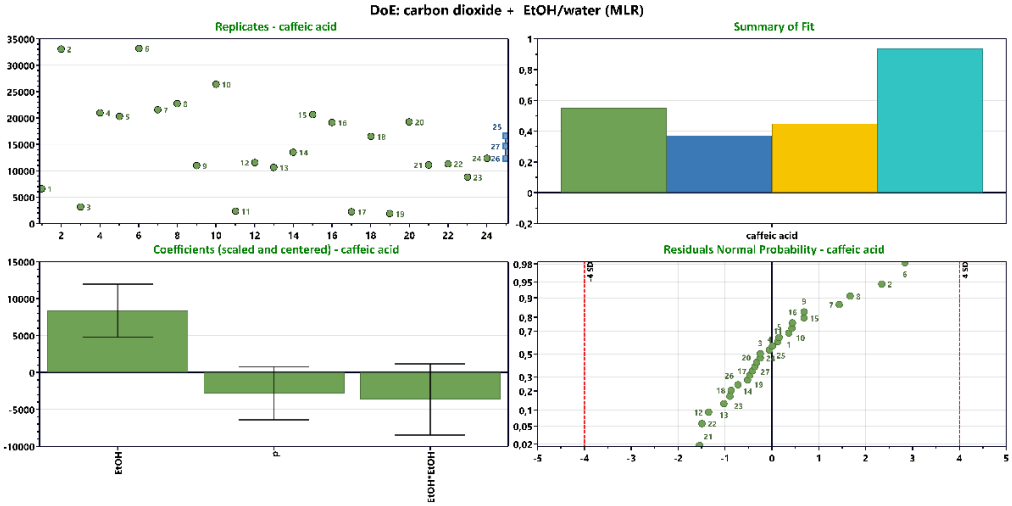


Figure S11: Model summary for caffeic acid extracted with CO_2/EtOH/H_2O.

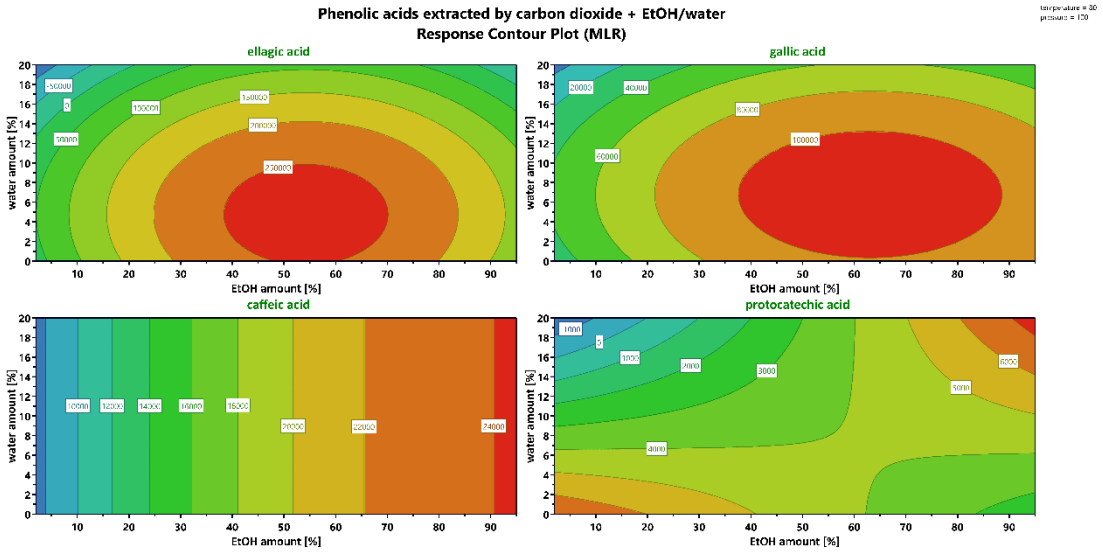


Figure S12: Response contour plot (MLR), phenolic acids extracted by CO_2/EtOH/H_2O.

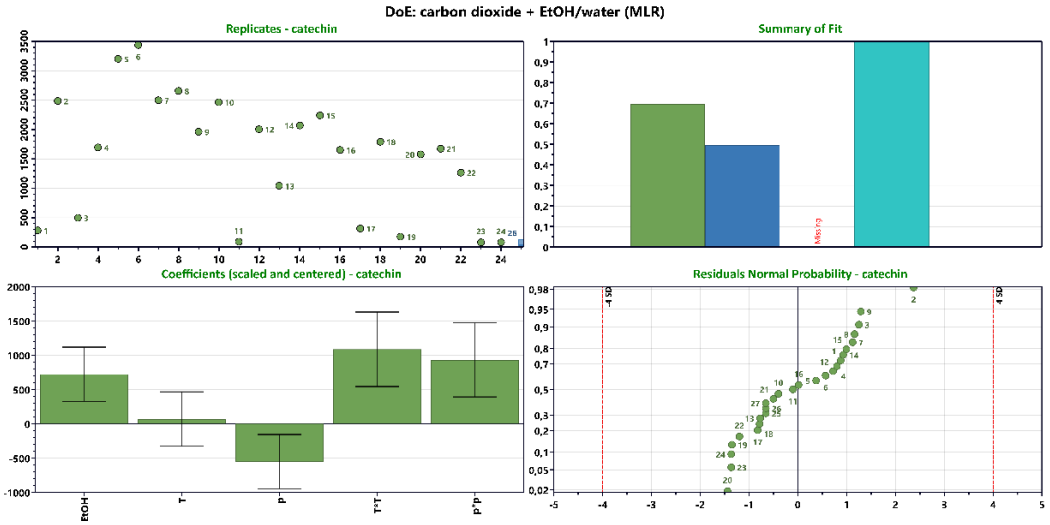


Figure S13: Model summary for epicatechin extracted with CO_2/EtOH/H_2O.

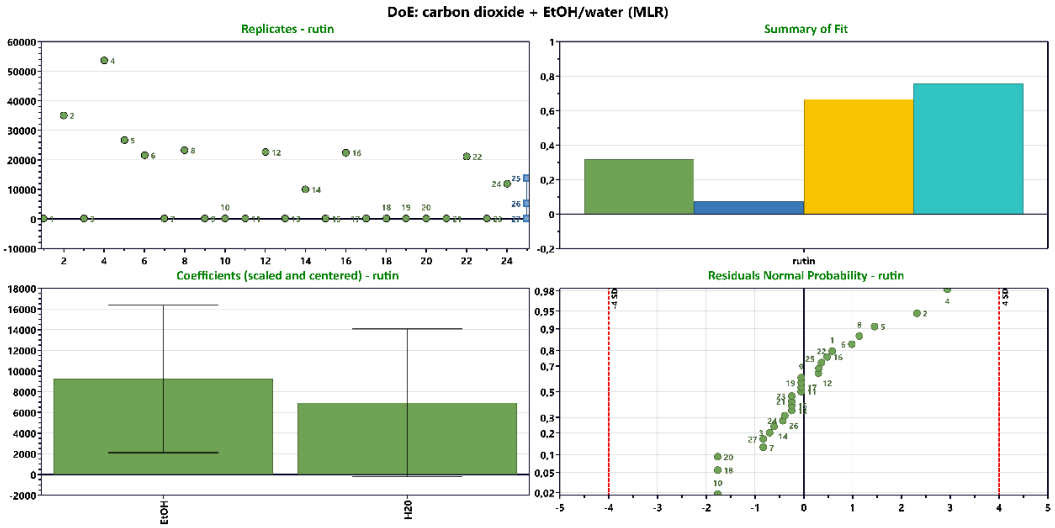


Figure S14: Model summary for rutin extracted with CO_2/EtOH/H_2O.

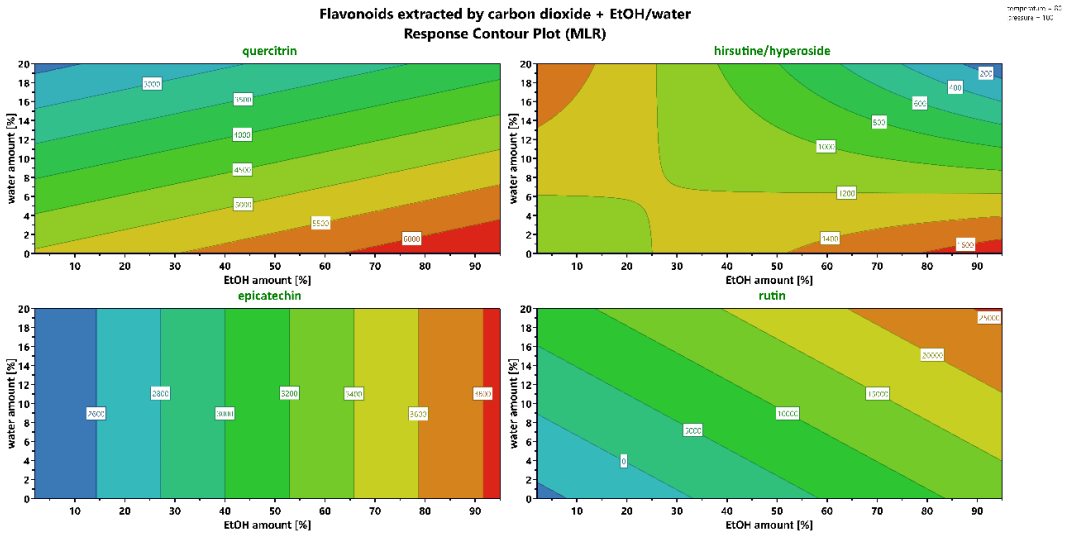


Figure S15: Response contour plot (MLR), flavonoids extracted with CO_2/EtOH/H_2O

AGREEprep

Analytical Greenness Metric
for Sample Preparation

18/12/2023 12:06:01

#	Criterion	Score	Weight
1.	**Sample preparation placement** Sample preparation placement: Ex situ	0.0	1
2.	**Hazardous materials** Mass [g] or volume [mL] of problematic materials: 0	1.0	5
3.	**Sustainability, renewability, and reusability of materials** > 75% of reagents and materials are sustainable or renewable	0.75	2
4.	**Waste** Mass [g] or volume [mL] of waste: 0.5	0.74	4
5.	**Size economy of the sample** Mass [g] or volume [mL] of the sample: 0.5	0.77	2
6.	**Sample throughput** Hourly sample throughput: 1	0.0	1
7.	**Integration and automation** No. of sample prep. steps: 2 steps or fewer; degree if automation: Fully automated systems	1.0	2
8.	**Energy consumption** Approximate energy consumption per analysis [W]: 11813	0.0	4
9.	**Post-sample preparation configuration for analysis** Liquid chromatography, gas chromatography with quadrupole detection, etc.	0.25	1
10.	**Operator's safety** No. of distinct hazards: 1 hazard	0.75	3

Figure S16: AGREEprep report.

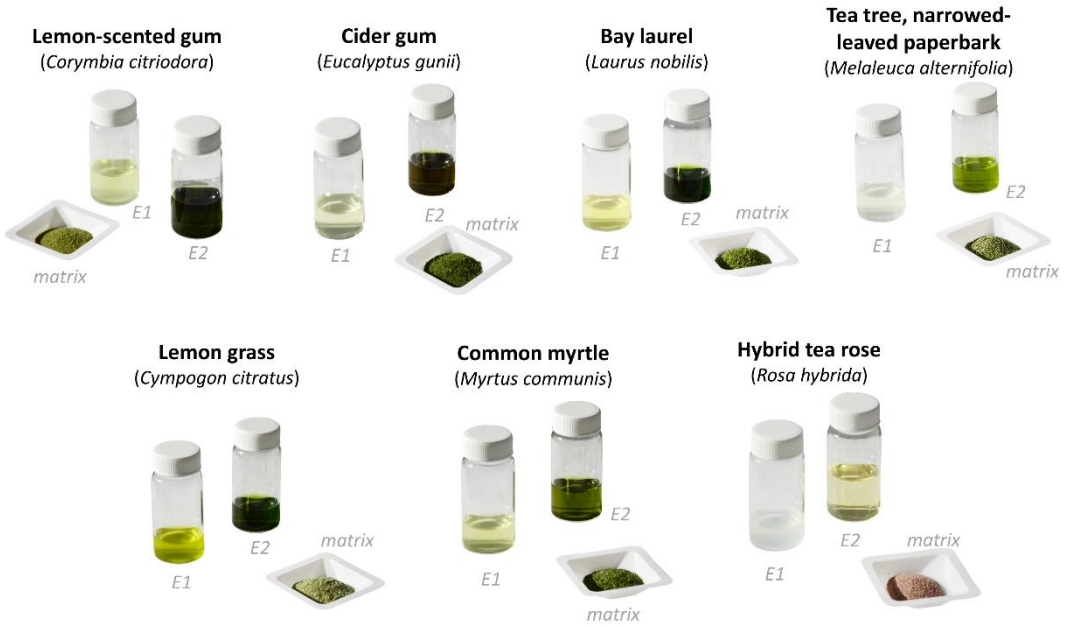
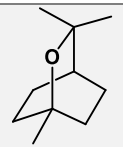
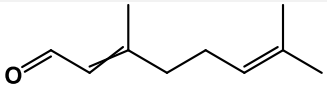
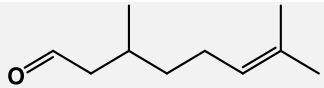
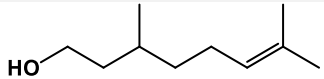
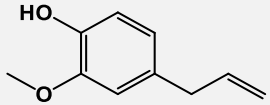
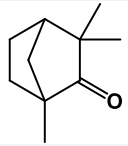
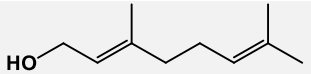
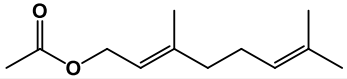
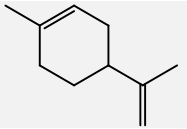
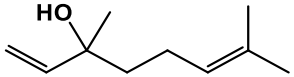
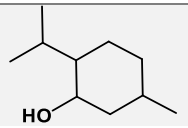
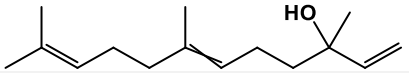
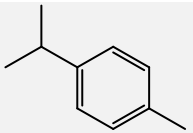
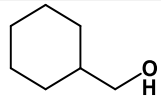
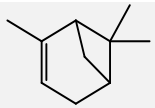
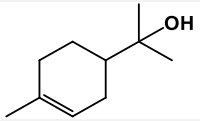
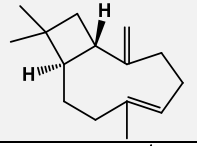
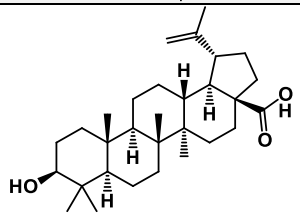
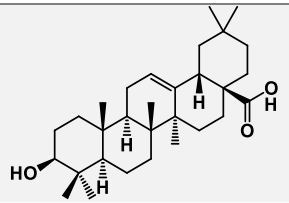
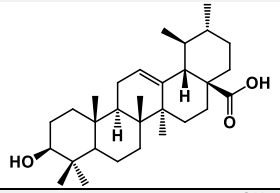
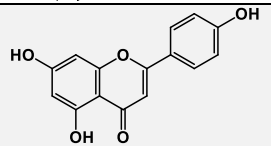
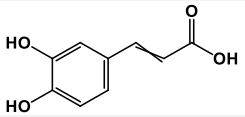
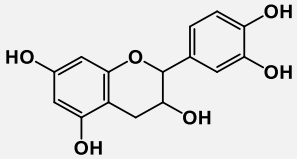
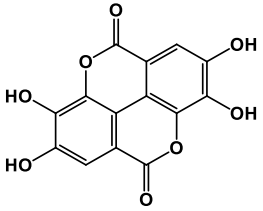


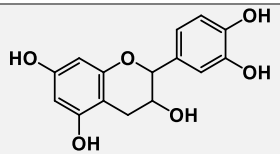
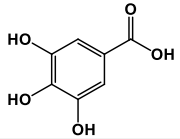
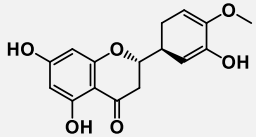
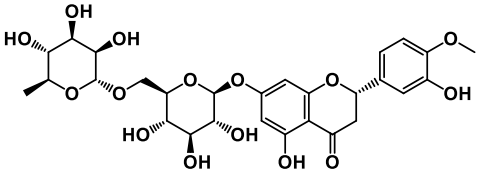
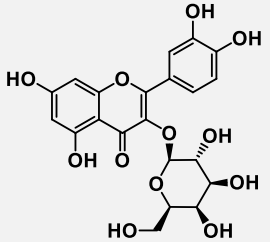
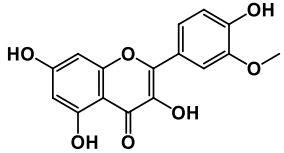
Figure S17: Summary of plant samples, including their botanical name, plant homogenized matrix, and extracts from step 1 (E1) and step 2 (E2) using the optimal conditions listed in the Experimental section.

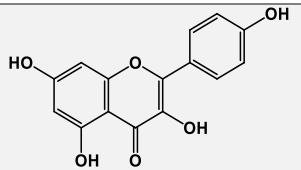
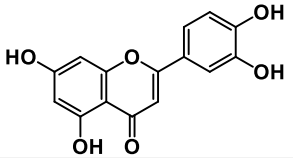
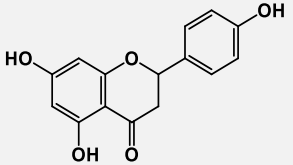
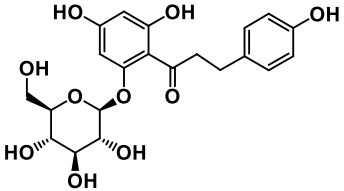
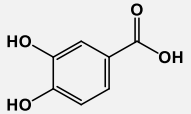
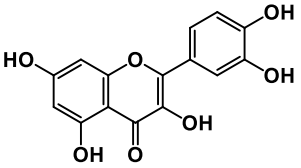
Table S1: List of analytes, including vendor, purity, and physicochemical properties. Summary formula, LogP, and pKa were obtained from the SciFinder database. Structure and exact mass were obtained using ChemDraw software.

ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
1,8-CINEOLE (EUCALYPTOL)	Sigma-Aldrich	99.3	$C_{10}H_{18}O$	154.1358	2.795±0.267	N/A		EtOH
CITRAL	Sigma-Aldrich	≥ 97	$C_{10}H_{16}O$	152.1201	3.127±0.359	N/A		EtOH
CITRONELLAL	Sigma-Aldrich	95.9	$C_{10}H_{18}O$	154.1358	3.297±0.259	N/A		EtOH
CITRONELLOL	Sigma-Aldrich	99.5	$C_{10}H_{20}O$	156.1514	3.239±0.235	15.13±0.10		EtOH
EUGENOL	Sigma-Aldrich	99.7	$C_{10}H_{12}O_2$	164.0837	2.403±0.236	10.29±0.18		EtOH
FENCHONE	Sigma-Aldrich	≥ 99.5	$C_{10}H_{16}O$	152.1201	2.089±0.300	N/A		EtOH
GERANIOL	Sigma-Aldrich	98.7	$C_{10}H_{18}O$	154.1358	2.942±0.271	14.45±0.10		EtOH
GERANYL ACETATE	Sigma-Aldrich	98.3	$C_{12}H_{20}O_2$	196.1463	3.904±0.315	N/A		EtOH
LIMONENE	Sigma-Aldrich	99.5	$C_{10}H_{16}$	136.1252	4.552±0.241	N/A		EtOH
LINALOOL	Sigma-Aldrich	98.9	$C_{10}H_{18}O$	154.1358	2.795±0.263	14.51±0.29		EtOH

ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
MENTHOL	Sigma-Aldrich	99.3	$C_{10}H_{20}O$	156.1514	3.216±0.204	15.30±0.60		EtOH
NEROLIDOL (MIXTURE A + B)	Sigma-Aldrich	99.3	$C_{15}H_{26}O$	222.1984	4.682±0.295	14.44±0.29		EtOH
P-CYMENE	Sigma-Aldrich	99.7	$C_{10}H_{14}$	134.1096	4.014±0.189	N/A		EtOH
T-TERPIN	Sigma-Aldrich	99.5	$C_{7}H_{14}O$	114.1045	1.056±0.242	15.18±0.29		EtOH
A-PINENE	Sigma-Aldrich	99.5	$C_{10}H_{16}$	136.1252	4.321±0.237	N/A		EtOH
A-TERPINEOL	Sigma-Aldrich	98	$C_{10}H_{18}O$	154.1358	2.708±0.236	15.09±0.29		EtOH
B-CARYOPHYLLENE	Sigma-Aldrich	N/A	$C_{15}H_{24}$	204.1878	6.416±0.248	N/A		EtOH
BETULINIC ACID	Sigma-Aldrich	≥99.3	$C_{30}H_{48}O_{3}$	456.3603	7.38	4.75		MeOH

ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
OLEANOLIC ACID	Sigma-Aldrich	≥99.9	$C_{30}H_{48}O_3$	456.3603	7.47	X		MeOH/ACN (50/50)
URSOLIC ACID	MedChem Express	≥98	$C_{30}H_{48}O_3$	456.3603	7.33	4.74		MeOH/ACN (50/50)
APIGENIN	Sigma-Aldrich	99	$C_{15}H_{10}O_5$	270.0528	2.127±0.452	6.53±0.40		MeOH/ACN (50/50)
CAFFEIC ACID	Sigma-Aldrich	99.4	$C_9H_8O_4$	180.0423	0.663±0.286	4.58±0.10		MeOH/ACN (50/50)
CATECHIN	Sigma-Aldrich	99	$C_{15}H_{14}O_6$	290.0790	0.610±0.454	9.54±0.10		ACN
ELLAGIC ACID	Sigma-Aldrich	97.4	$C_{14}H_6O_8$	302.0063	0.239±1.553	5.02±0.20		MeOH

ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
EPICATECHIN	Sigma-Aldrich	96.1	$C_{15}H_{14}O_6$	290.0790	0.610±0.454	9.54±0.10		MeOH/ACN (50/50)
GALLIC ACID	Sigma-Aldrich	100	$C_7H_6O_5$	170.0215	0.531±0.325	4.33±0.10		MeOH/ACN (50/50)
HESPERETIN	Sigma-Aldrich	99	$C_{16}H_6O_6$	304.0947	1.938±0.471	7.49±0.40		MeOH
HESPERIDIN	Sigma-Aldrich	95.9	$C_{28}H_{34}O_{15}$	610.1898	-1.212±0.819	7.15±0.40		MeOH
HIRSUTRIN	MedChem Express		$C_{21}H_{20}O_{12}$	464.0955	-0.111±1.370	6.17±0.40		MeOH
ISORHAMNETIN	Extrasynthese	≥99	$C_{16}H_{12}O_7$	316.0583	2.787±0.822	6.31±0.40		MeOH

ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
KAEMPFEROL	Sigma-Aldrich	97.8	$C_{15}H_{10}O_6$	286.0477	2.685±0.812	6.34±0.40		MeOH/ACN (50/50)
LUTEOLIN	Sigma-Aldrich	99.4	$C_{15}H_{10}O_6$	286.0477	2.695±0.554	6.50±0.40		MeOH/ACN (50/50)
NARINGENIN	Sigma-Aldrich	98.9	$C_{15}H_{12}O_5$	272.0685	2.628±0.406	7.52±0.40		ACN
PHLORIDZIN	Sigma-Aldrich	99	$C_{21}H_{24}O_{10}$	436.1369	-0.365±0.385	7.15±0.40		MeOH/ACN (50/50)
PROTOCATECHUIC ACID	Sigma-Aldrich	99.9	$C_7H_6O_4$	154.0266	1.010±0.237	4.45±0.10		ACN
QUERCETIN	MedChem Express	≥98	$C_{15}H_{10}O_7$	302.0427	1.989±1.075	6.31±0.40		MeOH

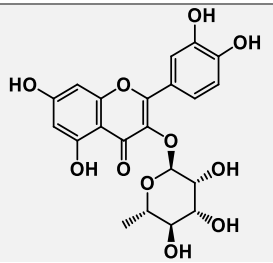
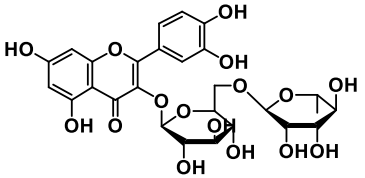
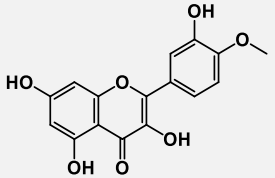
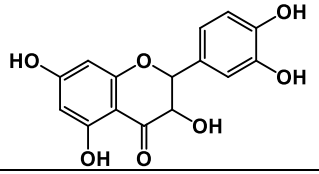
ANALYTE	VENDOR	PURITY [%]	FORMULA	EXACT MASS [DA]	LOG P	PKA	STRUCTURE	SOLVENT
QUERCITRIN	MedChem Express	99.24	$C_{21}H_{20}O_{12}$	448.1006	0.579±1.358	6.17±0.40		MeOH
RUTIN	Extrasynthese	≥99	$C_{27}H_{30}O_{16}$	610.1534	-0.903±1.416	6.17±0.40		MeOH
TAMARIXETIN	Extrasynthese	≥98	$C_{16}H_{12}O_{7}$	316.0583	2.670±0.822	6.31±0.40		MeOH
TAXIFOLIN	MedChem Express	≥99.5	$C_{15}H_{12}O_{7}$	304.0583	1.569±0.555	7.39±0.60		ACN

Table S2: List of conditions tested in the SFE optimization using the Box-Behnken design of experiments. Ethanol was used as a co-solvent.

Experiment	Run order	Cosolvent amount	Water [vol%]	Temperature [°C]	Pressure [bar]
N1	10	2	0	60	210
N2	24	95	0	60	210
N3	23	2	20	60	210
N4	3	95	20	60	210
N5	26	48.5	10	40	100
N6	15	48.5	10	80	100
N7	6	48.5	10	40	320
N8	27	48.5	10	80	320
N9	1	2	10	60	100
N10	18	95	10	60	100
N11	2	2	10	60	320
N12	8	95	10	60	320
N13	22	48.5	0	40	210
N14	4	48.5	20	40	210
N15	7	48.5	0	80	210
N16	16	48.5	20	80	210
N17	5	2	10	40	210
N18	21	95	10	40	210
N19	14	2	10	80	210
N20	13	95	10	80	210
N21	17	48.5	0	60	100
N22	20	48.5	20	60	100
N23	19	48.5	0	60	320
N24	11	48.5	20	60	320
N25	9	48.5	10	60	210
N26	25	48.5	10	60	210
N27	12	48.5	10	60	210

Table S3: List of conditions tested in SFE optimization using Box-Behnken design of experiments. Hexane was used as a co-solvent.

Experiment	Run order	Cosolvent amount	Temperature [°C]	Pressure [bar]
N1	4	0	40	210
N2	10	10	40	210
N3	5	0	80	210
N4	6	10	80	210
N5	14	0	60	100
N6	11	10	60	100
N7	13	0	60	320
N8	2	10	60	320
N9	12	5	40	100
N10	3	5	80	100
N11	9	5	40	320
N12	15	5	80	320
N13	8	5	60	210
N14	1	5	60	210
N15	7	5	60	210

Table S4: The suggested optimized conditions proposed by MODDE for the further optimization and final selection of the key parameters. Conditions in bold were suggested by the MODDE optimizer as the most suitable one. The conditions marked in orange were finally selected for the evaluation of the kinetic study.

Target analytes	Cosolvent	Cosolvent amount [%, v/v]	Water amount in cosolvent [%, v/v]	Temperature [°C]	Pressure [bar]	Probability of failure [%]
volatile terpenes	**hexane**	**8**	**0**	**45**	**221**	**25**
volatile terpenes	EtOH	2	4	80	178	5
volatile terpenes	EtOH	2	0	76	268	4.9
volatile terpenes	EtOH	4	0	79	313	5.4
volatile terpenes	EtOH	2	9	80	159	9
volatile terpenes	**EtOH**	**2**	**3**	**78**	**133**	**8.6**
terpenoic acids	**EtOH**	**86**	**2**	**76**	**122**	**0.64**
terpenoic acids	EtOH	64	1	44	102	0.8
terpenoic acids	EtOH	89	1	55	190	0.94
phenolic acids	EtOH	74	12	80	320	9.3
phenolic acids	**EtOH**	**44**	**1**	**80**	**108**	**10**
phenolic acids	EtOH	69	18	44	318	15
flavonoids	**EtOH**	**32**	**20**	**42**	**108**	**35**
flavonoids	EtOH	95	9	46	320	44
flavonoids	EtOH	22	20	40	248	51
polar analytes	*EtOH*	*93*	*7*	*80*	*320*	*54*

Table S5: Chromatographic conditions of UHPSFC method 2 for the analysis of flavonoids, adopted from Plachká et al. [2].

time (min)	CO_2 (%)	organic modifier (%)	flow rate (mL min^{-1})	BPR psi (bar)
0	100	0	1.5	1885 (130)
0.5	100	0	1.5	1885 (130)
0.7	97	3	1.5	1885 (130)
5.0	96	4	1.5	1885 (130)
5.5	80	20	1.5	1885 (130)
7.0	80	20	1.5	1885 (130)
8.5	77	23	1.5	1885 (130)
10.0	77	23	1.5	1885 (130)
12.0	30	70	1.5	1885 (130)
13.0	10	90	0.7	1494 (103)
14.0	10	90	0.7	1494 (103)
14.5	100	0	1.5	1494 (103)
15.0	100	0	1.5	1885 (130)
15.5	100	0	1.5	1885 (130)

Table S6: SRM transitions selected for each target analyte together along their optimal collision energy. RT – retention time, CE – collision energy, ESI – electrospray ionization, ESCi – multimodal ionization. Adopted from Plachká et al. [2]

ANALYTE	RT (MIN)	IONIZATION MODE	SRM	CE (eV)
1,8-CINEOLE (EUCALYPTOL)	1.101	ESCi$^+$	155.3 > 137.2	10
CITRAL	3.175 + 3.525	ESCi$^+$	153.1 > 71.1	10
CITRONELLAL	2.347	ESCi$^+$	155.3 > 111.2 155.3 > 94.97	10
CITRONELLOL	2.737	ESCi$^+$	157.3 > 83.1 157.3 > 68.8	20
EUGENOL	5.242	ESCi$^+$	164.2 > 149.1 164.2 > 132.1	10
FENCHONE	1.056	ESCi$^+$	152.9 > 135.2 152. 9 > 109.1	10
GERANIOL	3.168	ESCi$^+$	155.3 > 137.3	10
GERANYL ACETATE	3.539	ESCi$^+$	196.2 > 181.2 181.2 > 163.2	10
LIMONENE	2.590	ESCi$^+$	136.9	x
LINALOOL	1.945	ESCi$^+$	137.0 > 81.1	10
MENTHOL	1.668	ESCi$^+$	171.0 > 135.0 157.3	10
NEROLIDOL A NEROLIDOL B	4.682 + 4.970	ESCi$^+$	205.2 > 121.1 205.2 > 135.0	10
p-CYMENE	2.102	ESCi$^+$	134.2 > 119.1	10
T-TERPIN	4.756	ESCi$^+$	136.9 > 81.0	10
α-PINENE	1.02	ESCi$^+$	137.3	x
α-TERPINEOL	3.365	ESCi$^+$	155.3 > 137.3 137.3 > 71.1	20
β-CARYOPHYLLENE	3.499	ESCi$^+$	205.4 > 149.1 205.4 > 121.1	10
BETULINIC ACID	4.151	ESI$^-$	455.4 > 455.4 455.4 > 407.1	10
OLEANOLIC ACID	4.32	ESI$^-$	455.4 > 455 4 455.4 > 407.1	10
URSOLIC ACID	4.589	ESI$^-$	455.4 > 455.4 455.4 > 407.1	10
APIGENIN	6.450	ESI$^-$	268.9 > 224.9 268.9 > 200.9	20
CAFFEIC ACID	6.621	ESI$^-$	178.9 > 135.0	20
CATECHIN	10.398	ESI$^-$	289.3 > 203.2 289.3 > 178.9	20
ELLAGIC ACID	7.771	ESI$^-$	301.0 > 163.1	10
EPICATECHIN	10.171	ESI$^-$	289.3 > 203.2 289.3 > 178.9	5
GALLIC ACID	7.965	ESI$^-$	168.9 > 124.9	10
HESPERETIN	6.201	ESI$^-$	301.0 > 241.9 301.0 > 199.1	20
HESPERIDIN	10.771	ESI$^-$	609.2 > 301.0	20
HIRSUTRIN	10.822	ESI$^-$	462.9 > 300.0	30
ISORHAMNETIN	6.576	ESI$^-$	315.1 > 299.9 315.1 > 271.0	20
KAEMPFEROL	6.851	ESI$^-$	285.2 > 150.9 285.2 > 228.9	30
LUTEOLIN	7.003	ESI$^-$	285.2 > 175.0 285.2 > 199.0	30
NARINGENIN	6.391	ESI$^-$	270.9 > 150.8 270.9 > 177.1	20
PHLORIDZIN	10.047	ESI$^-$	434.9 > 272.9	20
PROTOCATECHUIC ACID	6.634	ESI$^-$	153.0 > 108.8	10
QUERCETIN	8.071	ESI$^-$	301.0 > 179.0 301.0 > 245.0	20
QUERCITRIN	10.093	ESI$^-$	446.9 > 300.9 446.9 > 348.8	20

RUTIN	11.474	ESI^-	609.2 > 301.0 301.0 > 179.2	30
TAMARIXETIN	6.729	ESI^-	315.1 > 299.9 315.1 > 271.0	20
TAXIFOLIN	7.794	ESI^-	302.9 > 217.0 302.9 > 176.9	20

Table S7: The extracted amount of target compounds extracted during each extraction step for all extracted plant species expressed in %.

	Corymbia citriodora			*Eucalyptus gunii*			*Melaleuca alternifolia*			*Cympogon citratus*			*Myrtus communis*			*Laurus nobilis*			*Rosa hybrida*		
	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE
caryophyllene	100	0	0	98	2	0	79	4	17	0	0	0	0	0	0	98	2	0	100	0	0
citral	0	0	0	100	0	0	0	0	0	99	1	0	100	0	0	100	0	0	100	0	0
citronellal	97	3	0	100	0	0	51	0	49	100	0	0	100	0	0	0	0	0	100	0	0
citronellol	100	0	0	0	0	0	48	0	52	0	0	0	0	0	0	0	0	0	0	0	0
cymene	0	0	0	94	6	0	56	2	42	97	3	0	0	0	100	100	0	0	0	0	0
eucalyptol	0	0	0	97	3	0	56	0	44	0	0	0	0	0	0	100	0	0	0	0	0
eugenol	100	0	0	100	0	0	62	1	37	100	0	0	81	17	2	99	1	0	94	6	0
fenchon	0	0	0	98	2	0	57	0	43	100	0	0	0	0	0	100	0	0	0	0	0
geraniol	100	0	0	0	0	0	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0
geranyl acetate	97	3	0	95	4	1	77	4	19	0	0	0	100	0	0	0	0	0	0	0	0
limonene	89	11	0	0	0	0	0	0	0	0	0	0	100	0	0	100	0	0	0	0	0
linalool	97	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0	0
menthol	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
nerolidol A	95	3	2	100	0	0	81	13	7	78	18	4	55	35	10	96	1	3	47	8	44
nerolidol B	88	8	4	85	14	1	95	4	1	56	20	24	51	15	35	99	1	0	70	26	3
α-pinene	100	0	0	99	0	1	0	0	0	0	0	0	100	0	0	0	0	0	0	0	0
terpin	100	0	0	100	0	0	0	0	0	100	0	0	100	0	0	100	0	0	100	0	0
terpineol	100	0	0	0	0	0	54	0	46	0	0	0	0	0	0	0	0	0	0	0	0
apigenin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
catechin	0	65	35	0	31	69	0	13	87	0	0	100	0	0	100	0	0	0	0	0	100
epicatechin	0	0	0	0	0	0	0	100	0	0	0	0	0	0	0	26	29	45	0	0	0
hesperetin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
hesperidin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
hirsutrin	0	53	47	0	38	62	0	23	77	0	39	61	0	27	73	0	35	65	0	32	68
isorhamnetin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100
kaempfetol	0	0	0	0	0	100	0	0	100	0	0	0	0	0	0	0	0	0	0	100	0
luteolin	0	0	0	0	0	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0
naringenin	0	0	0	0	0	100	0	10	90	0	0	0	0	0	100	0	0	0	0	100	0
phloridzin	0	37	63	0	26	74	6	25	68	0	0	0	0	17	83	0	30	70	0	47	53
quercetin	0	0	0	0	0	100	0	23	77	0	0	0	0	0	0	0	0	0	0	0	100
quercitrin	0	72	28	0	50	50	0	26	74	0	40	60	0	18	82	0	39	61	0	44	56
rutin	0	100	0	0	36	64	0	100	0	0	0	0	0	0	0	0	31	69	0	26	74
tamarixetin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
taxifolin	0	0	0	0	0	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0
caffeic acid	28	39	33	26	26	48	0	19	81	16	57	27	18	26	56	39	27	34	0	43	57
ellagic acid	0	53	47	0	0	0	0	40	60	0	0	0	0	0	0	0	0	100	0	0	0

	Corymbia citriodora			*Eucalyptus gunii*			*Melaleuca alternifolia*			*Cympogon citratus*			*Myrtus communis*			*Laurus nobilis*			*Rosa hybrida*		
	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE	SFE step 1	SFE step 2	UAE
gallic acid	0	31	69	0	15	85	0	3	97	0	23	77	0	3	97	0	12	88	0	13	87
protocatechuic acid	43	23	33	31	26	43	7	20	73	0	54	46	18	29	54	55	14	31	22	36	42
betulinic acid	90	6	4	76	7	16	35	17	47	95	2	3	88	2	9	91	0	9	81	3	16
oleanolic acid	79	12	9	66	10	24	50	11	39	97	1	2	76	6	18	93	0	7	82	5	13
ursulic acid	42	37	21	58	14	27	30	16	54	97	1	2	48	13	39	92	3	5	65	11	24

RFERENCES

(1) Lim, J. S.; Lee, Y. Y.; Chun, H. S. *The Journal of Supercritical Fluids* **1994**, *7* (4), 219-230, DOI: https://doi.org/10.1016/0896-8446(94)90009-4

(2) Plachká, K.; Pilařová, V.; Kosturko, Š.; Škop, J.; Svec, F.; Nováková, L. *Analytical Chemistry* **2024**, DOI: https://doi.org/10.1021/acs.analchem.3c03599