

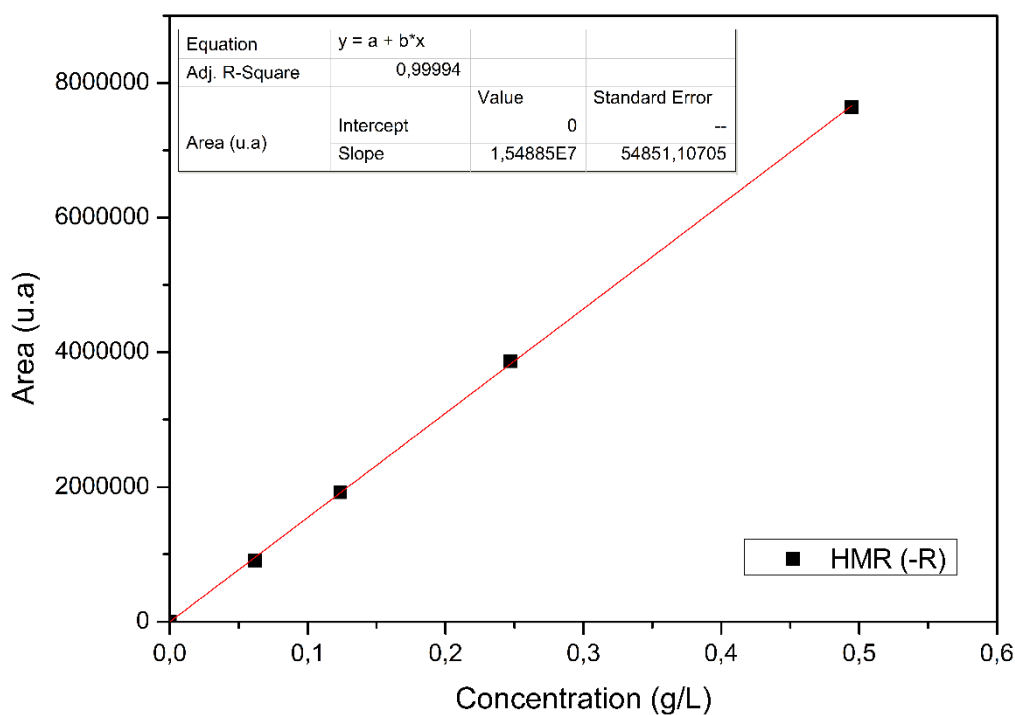
1 **Supplementary Material**

2 **Extraction processes of high added value molecules from wood**
3 **waste: overview and comparison of processes for an eco-friendly**
4 **recovery from paper industry by-product**

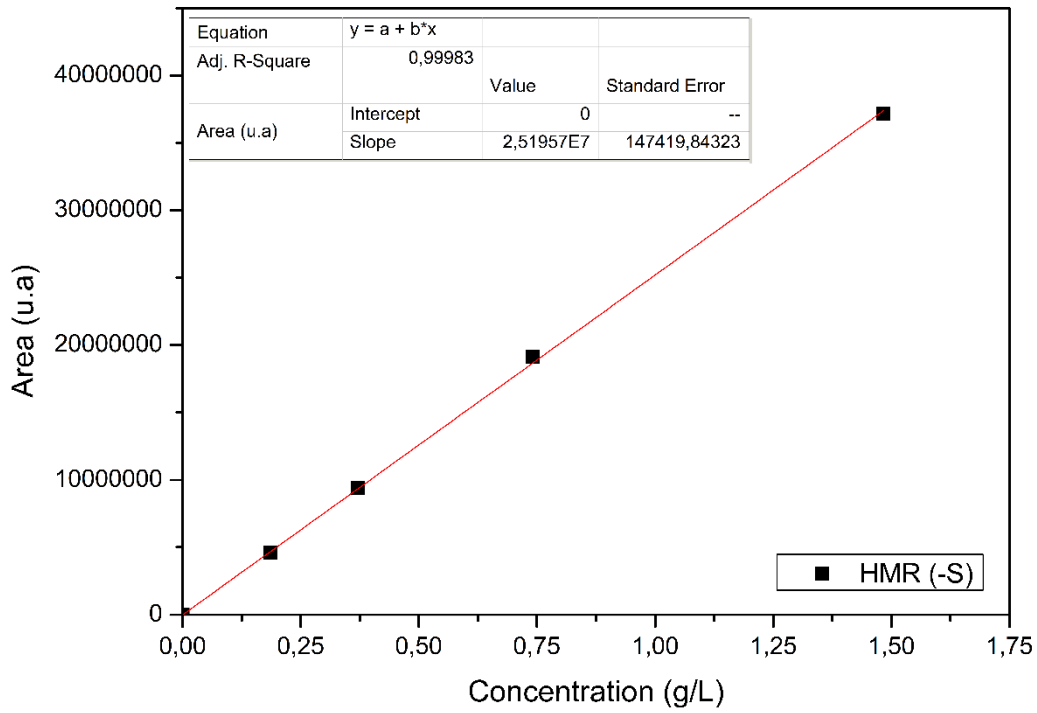
5 Renan RAVETTI DURAN, Laurence MUHR, Danielle BARTH*

6 Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France
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9 **HPLC-PDA Standards**



10
11 **Figure S1: Calibration curve HMR (-R)**



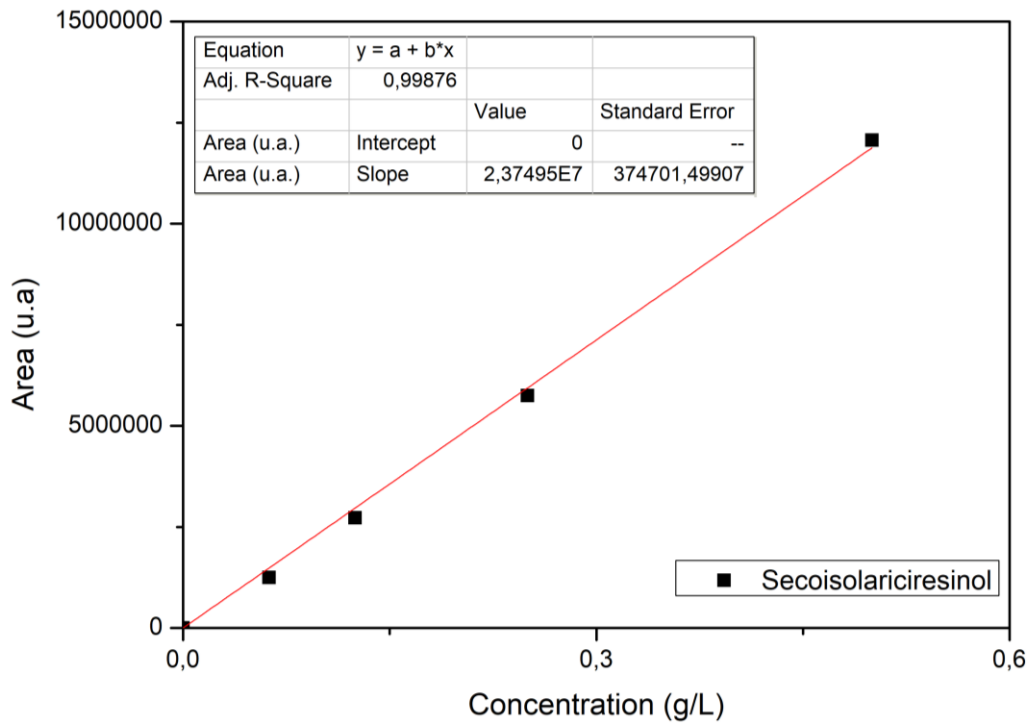
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Figure S2: Calibration curve **HMR (-S)**

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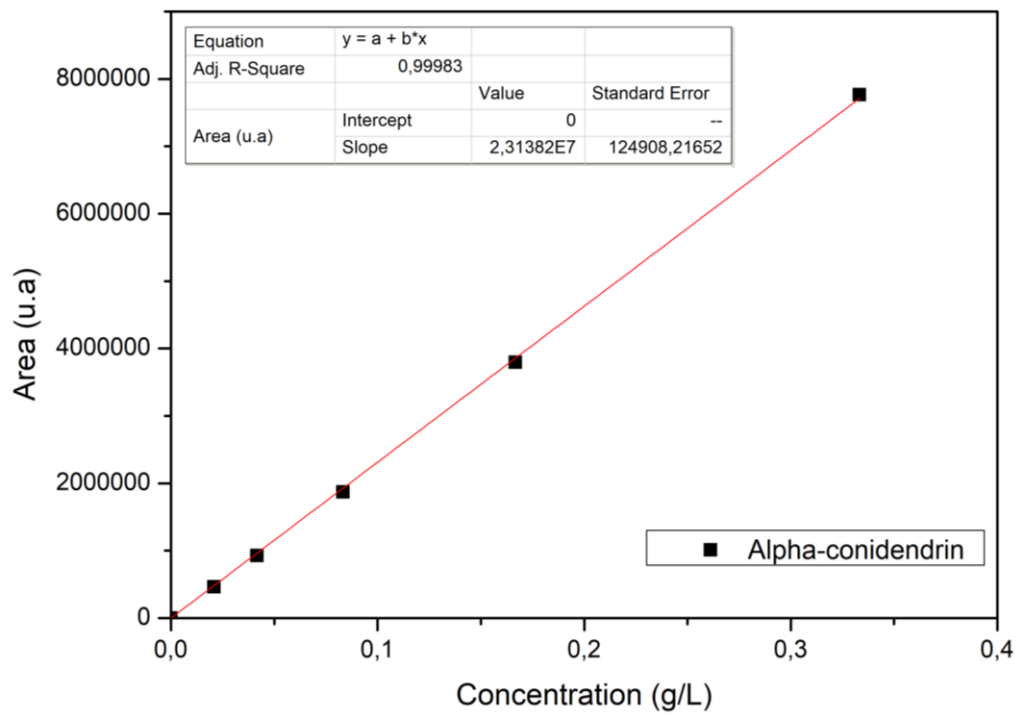
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Figure S3: Calibration curve **Secoisolariciresin**

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Figure S4: Calibration curve **Alpha-conidendrin**

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Table S1: Retention time of Identified chemicals by HPLC-PDA

Retention time (min)	Chemical compounds
17.0	Isolariciresinol
17.6	Coniferyl alcohol
17.9	Hydroxymatairesinol
19.0	Hydroxymatairesinol
26.6	Lariciresinol
27.2	Secoisolariciresinol
28.0	Nortrachelogenin
32.9	Guaiacol
34.7	α -conidendrin
41.3	Pinoresinol
42.6	Matairesinol
42.7	Enterodiol
43.3	Enterolactone

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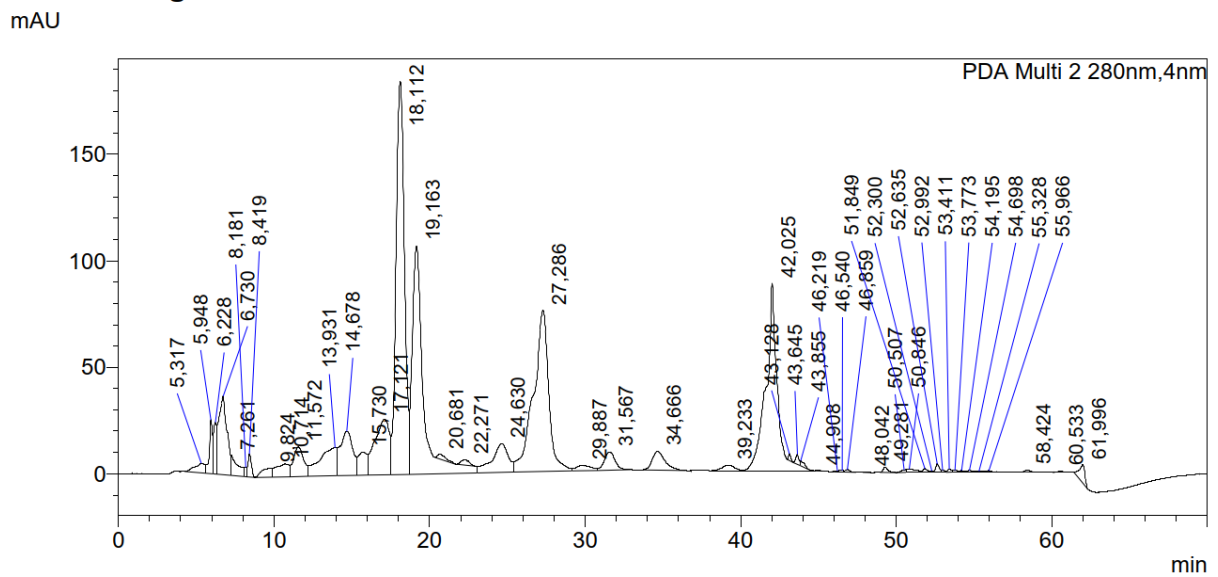
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HPLC-UV Extracts

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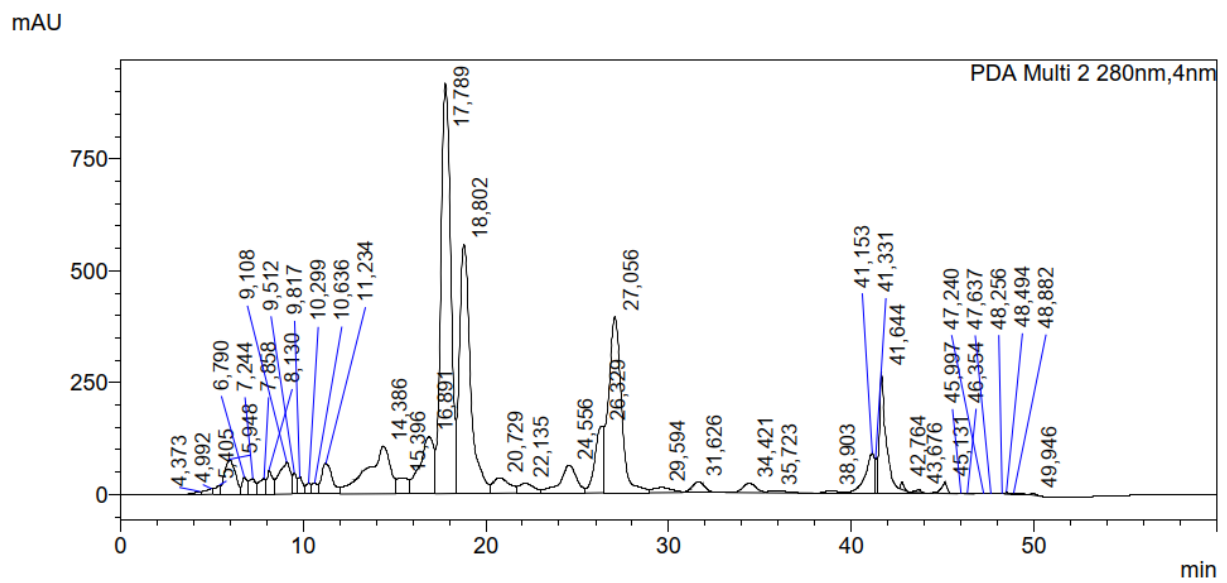
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Figure S5: Single batch extract (40 mL of solvent, ethanol 15%, 40 °C, 1 g of wood)

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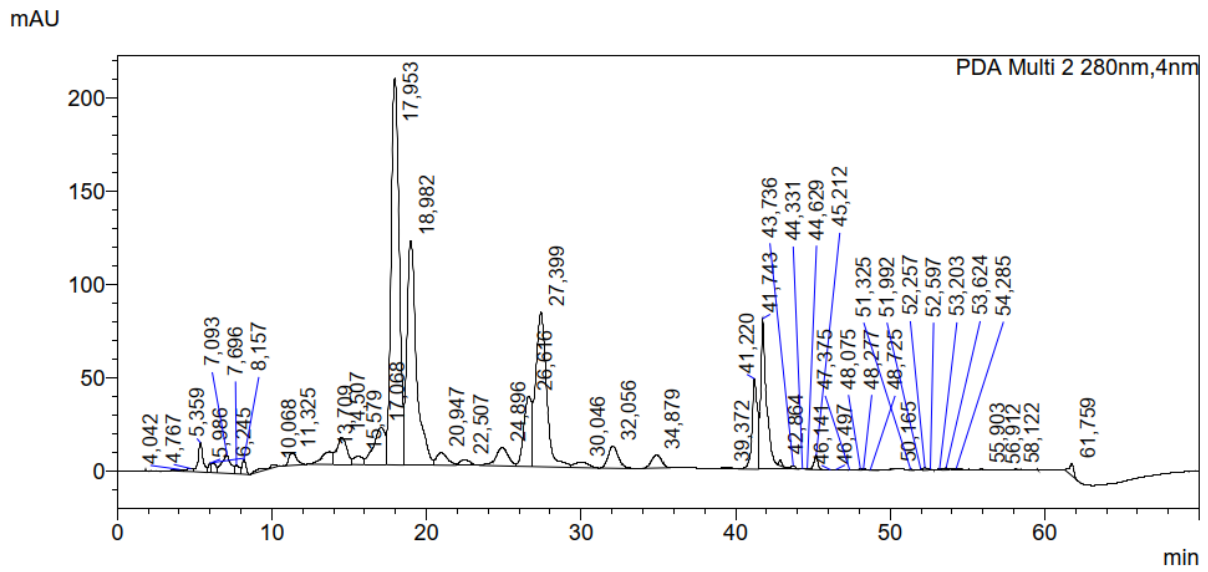


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Figure S6: Simulated countercurrent-Fraction CC41

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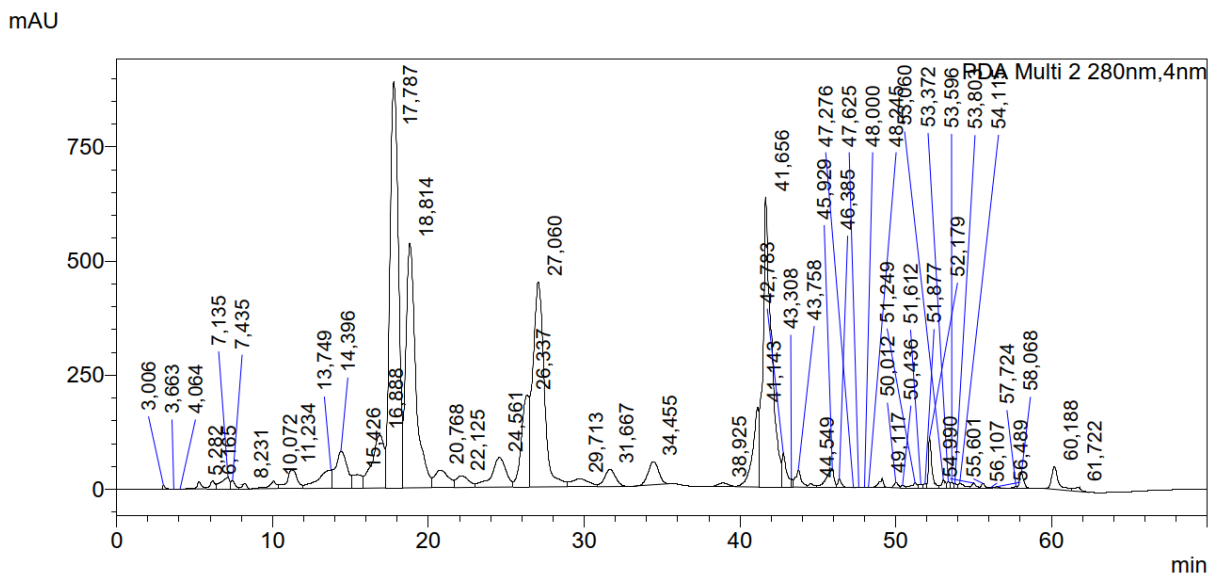


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Figure S7: Percolation extract-Fraction 0-50 ml



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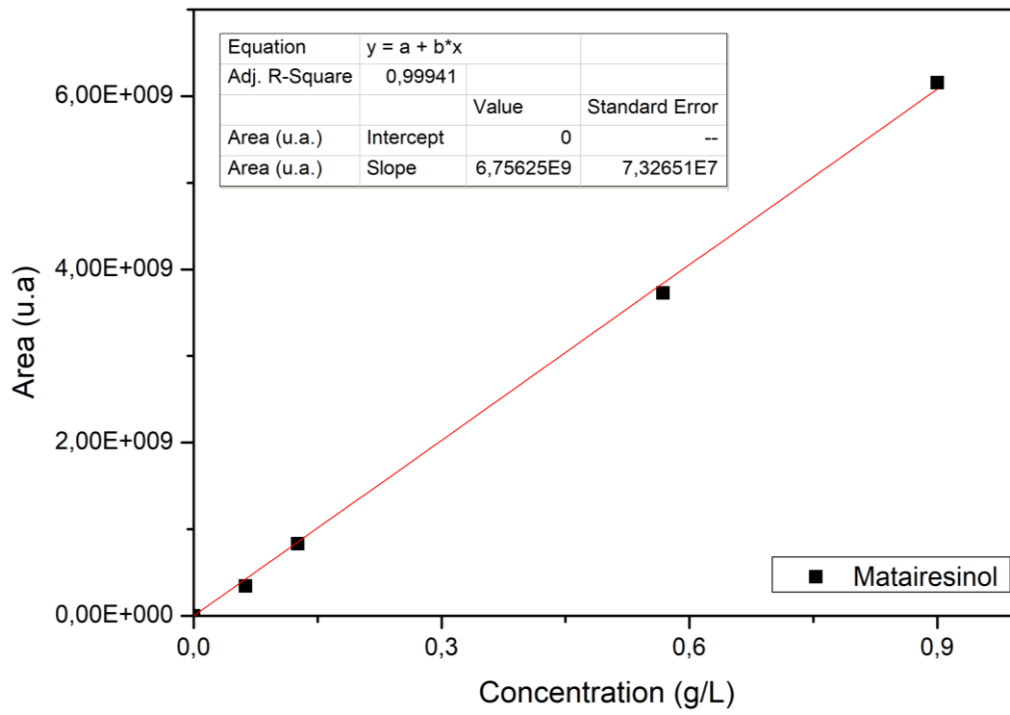
Figure S8: Supercritical extraction

(220 bar, dynamic time 120 min, static time 30 min, 40 °C, 40 mL of ethanol)

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GC-FID/MS Standards

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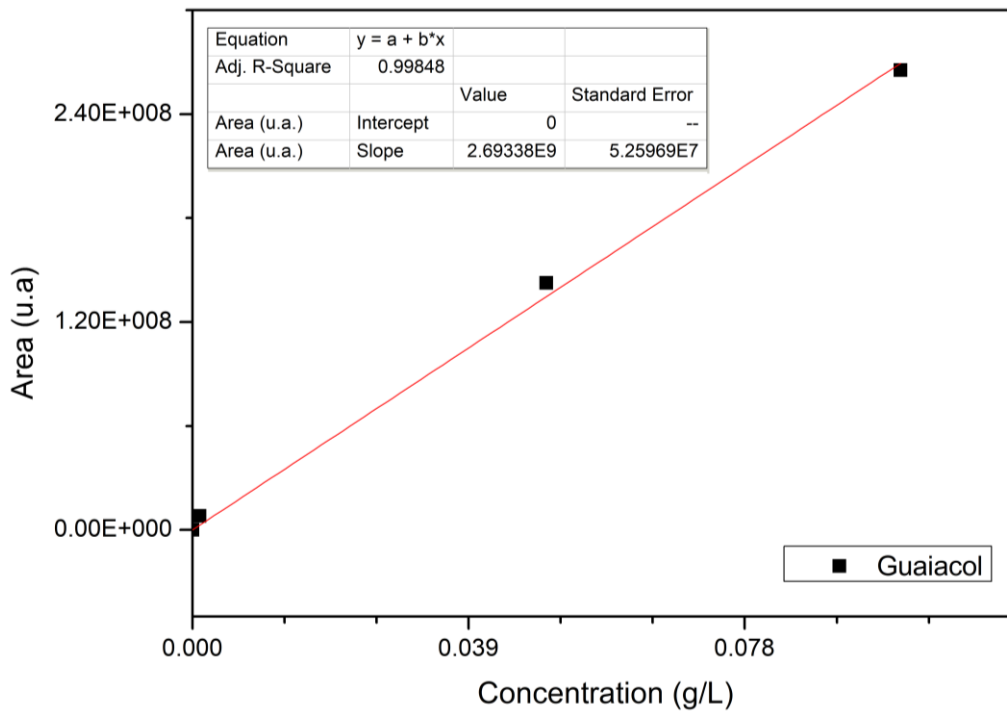


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Figure S9: Calibration curve **Matairesinol (split 1:15)**

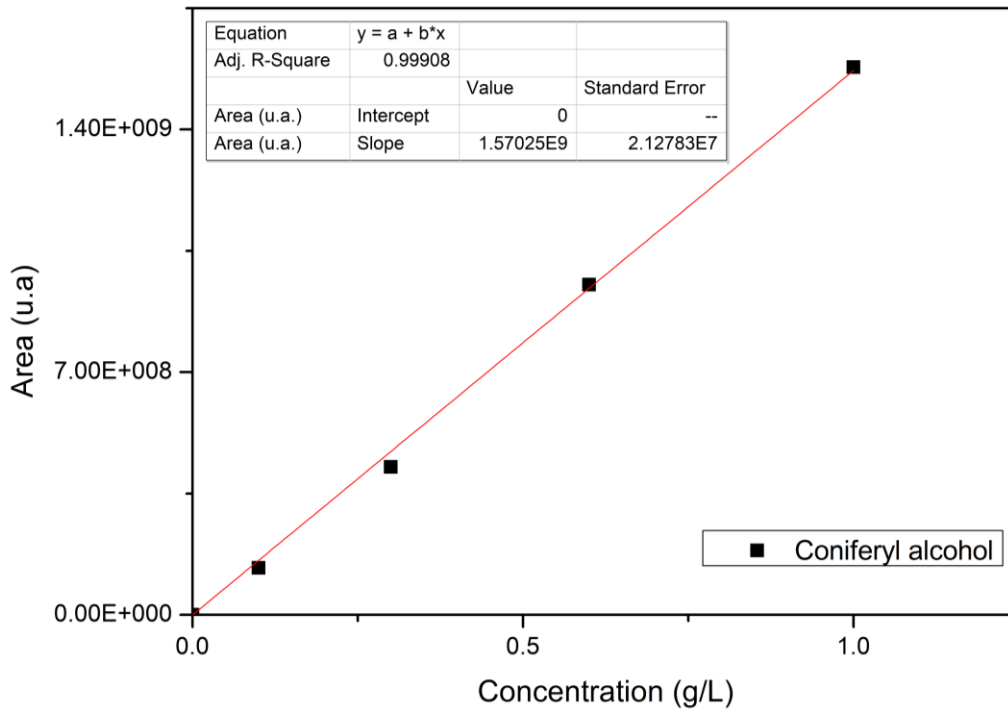


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Figure S10: Calibration curve **o-Guaiacol (split 1:15)**

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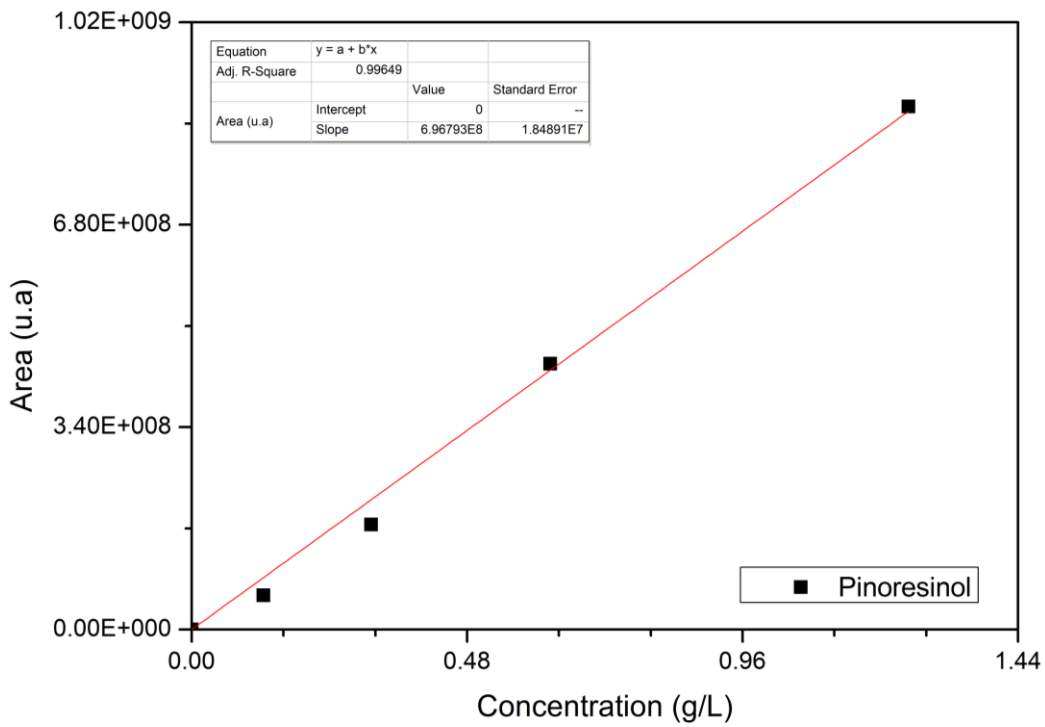
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Figure S11: Calibration curve **Coniferyl alcohol (split 1:15)**

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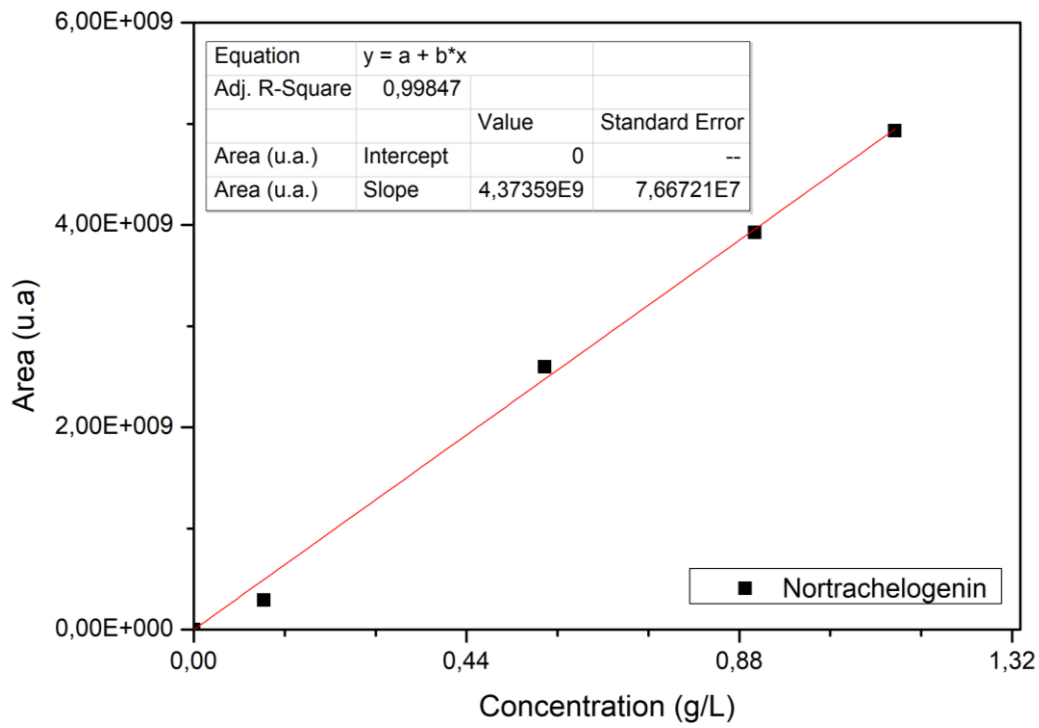
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Figure S12: Calibration curve **Pinoresinol (split 1:100)**

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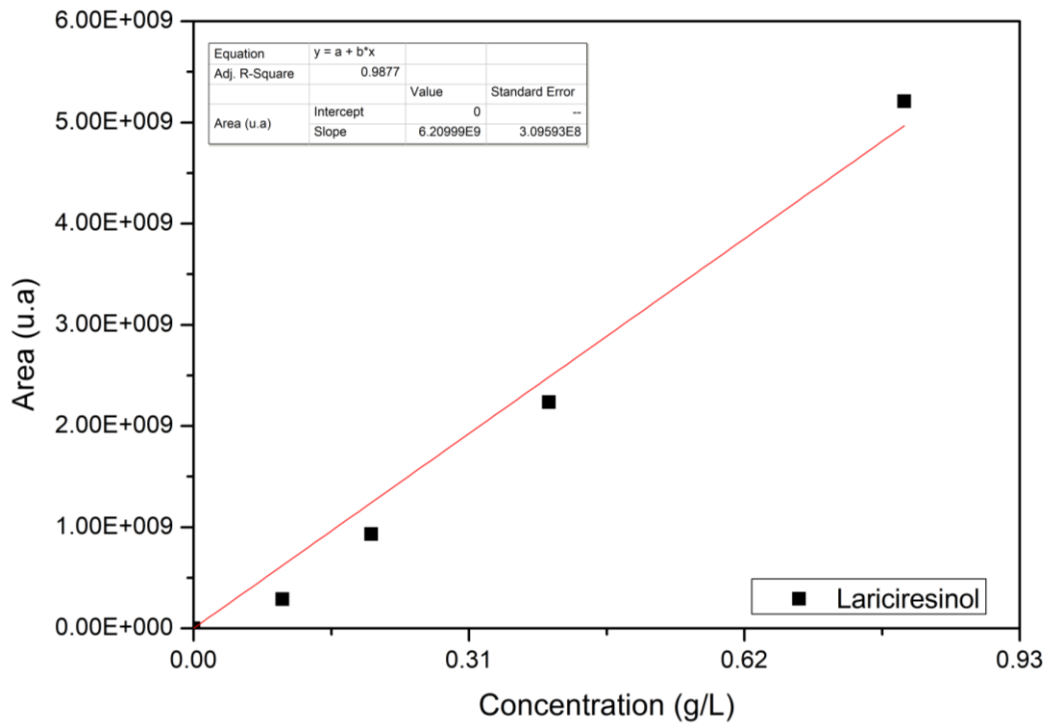


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Figure S13: Calibration curve **Notrachelogenin(split 1:15)**

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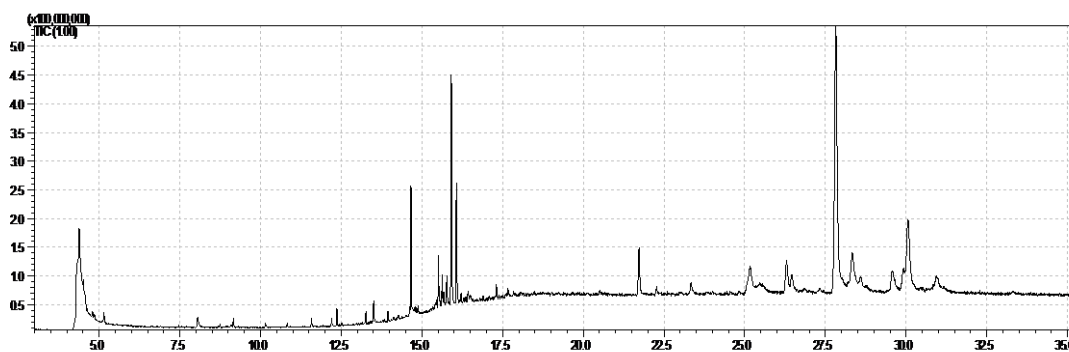
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Figure S14: Calibration curve **Lariciresinol (split 1:15)**

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GC-FID/MS



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Figure S15: CO₂-SC extract (40 °C, 220 bar, EtOH:30 mL)

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Table S2: Identified chemicals by GC-MS

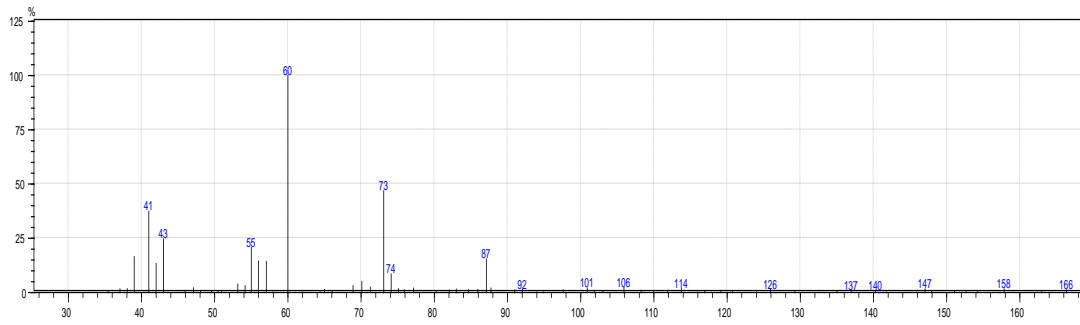
Retention time (min)	Chemical compounds
6.885	Hexanoic acid
7.644	Eucalyptol
8.174	o-Guaiacol
9.235	Alpha-terpineol
10.221	Terpin-hydrate
10.900	Vanillin
12.265	Benzene butanoic acid,2,5-dimethyl
12.420	Nerolidyl acetate
13.564	Coniferyl Alcohol
14.718	Tumerone
15.558	Juvabione
15.974	DehydroJuvabione
16.131	Manool
17.271	4'-methoxy-2-hydroxystilbene
21.795	Lignane1
22.307	Lignane 2
23.427	Lignane 3
25.244	Lignane4
26.400	Matairesinol
26.568	Hydroxymatairesinol
27.295	Nortrachelogenin
27.986	Hydroxymatairesinol
28.484	Secoisolariciresinol
28.715	Dehydro-Coniferyl alcohol
29.728	Lariciresinol
30.070	Isolariciresinol
30.238	Alpha-Conidendrin
31.123	HMR derivative
33.459	Gamma-Sitosterol

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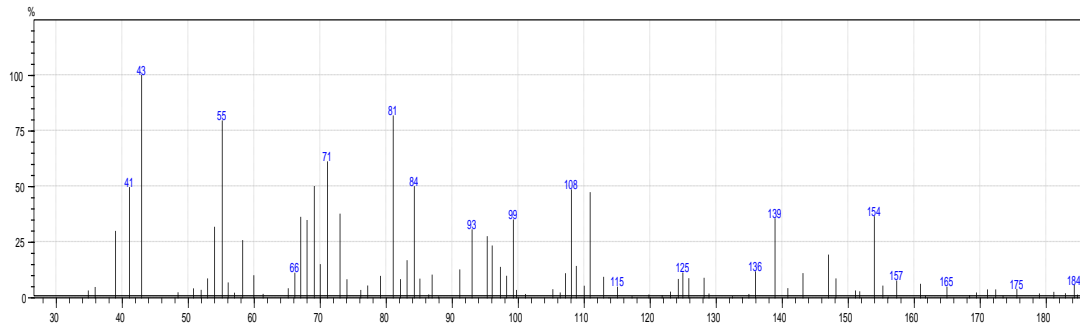
Identified mass spectra compounds

78 **Hexanoic acid**



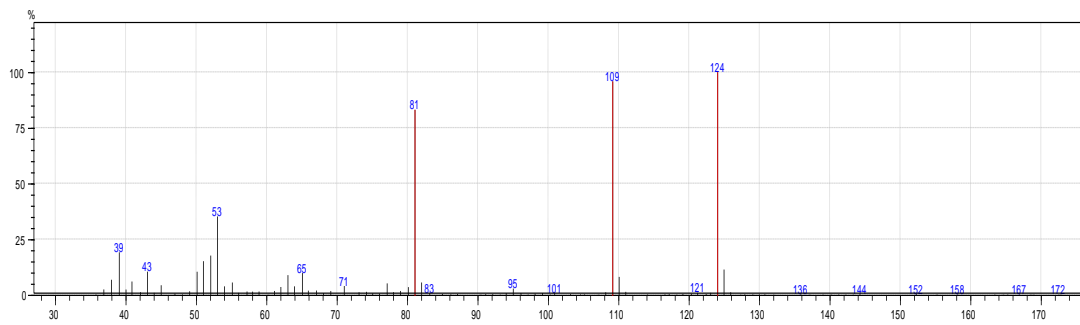
79

80 **Eucalyptol**



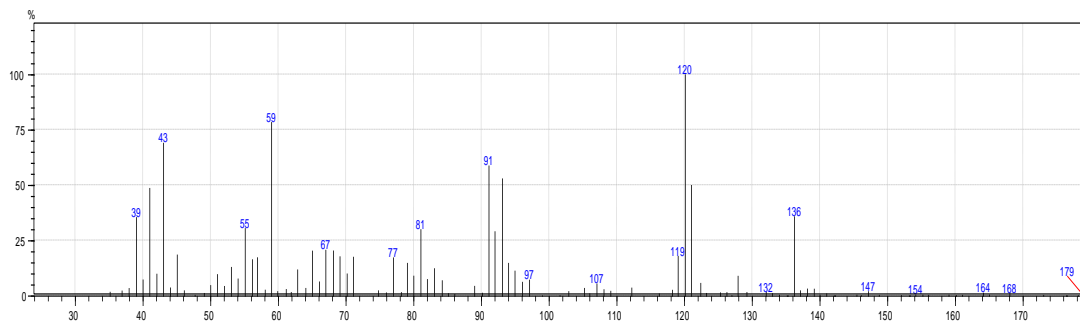
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82 **o-Guaiacol**



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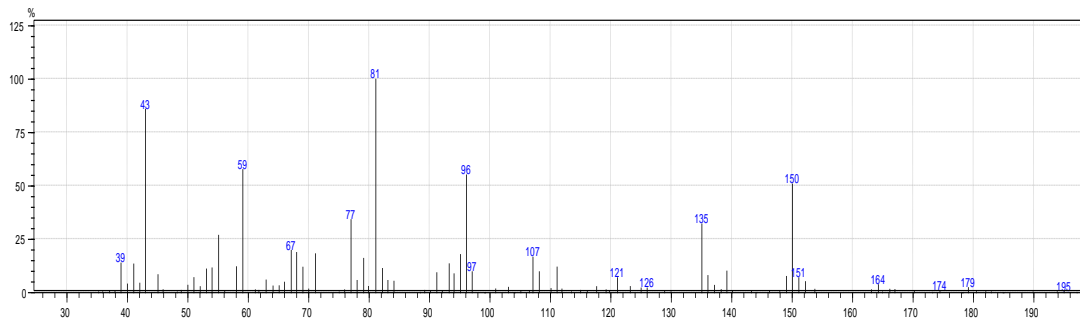
84 **Alpha-Terpineol**



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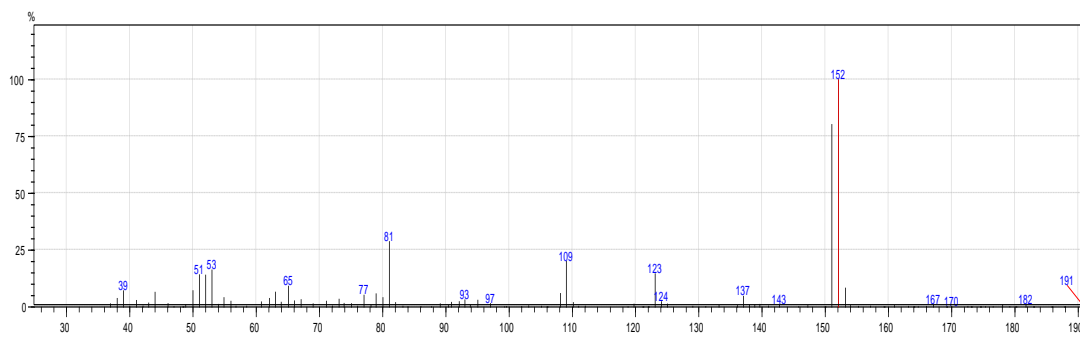
86

87 **Terpin-Hydrate**



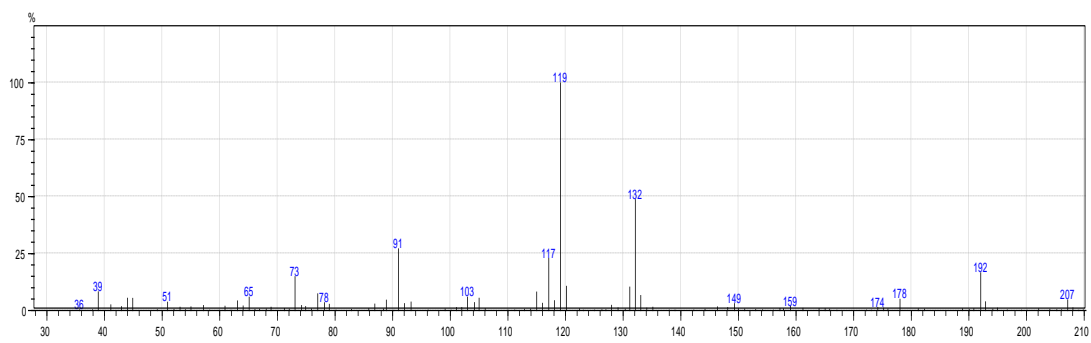
88

89 **Vanillin**



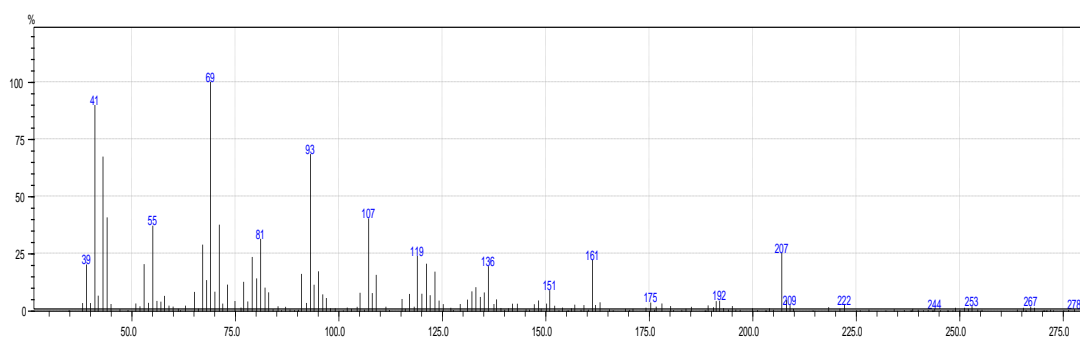
90

91 **Benzene butanoic acid 2,5-dimethyl**



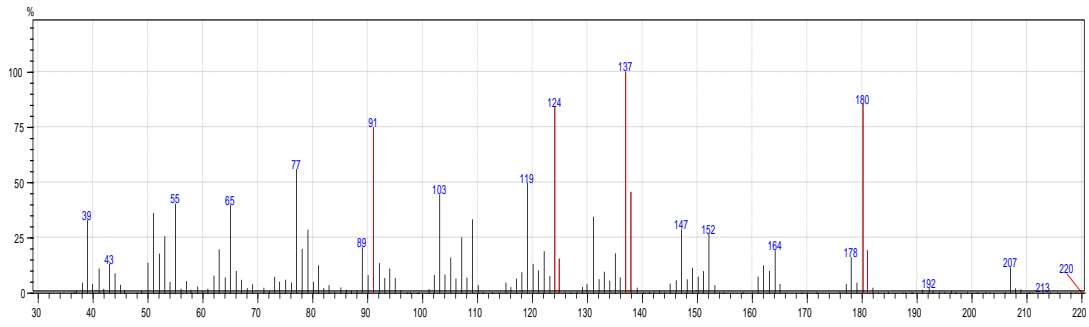
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93 **Nerolidyl acetate**



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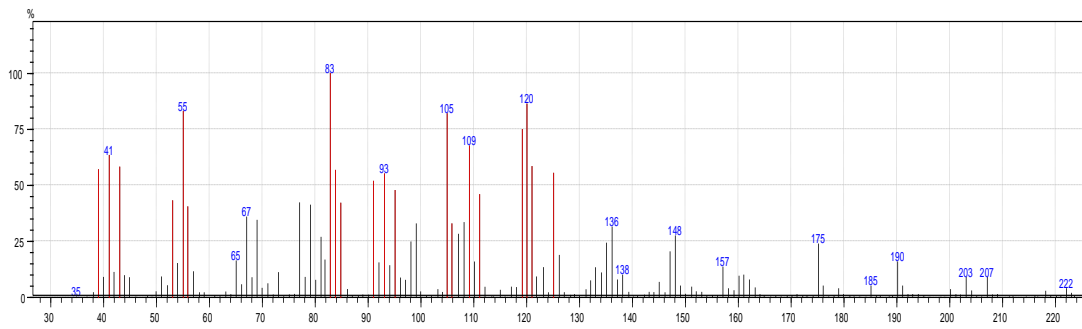
95 **Coniferyl alcohol**



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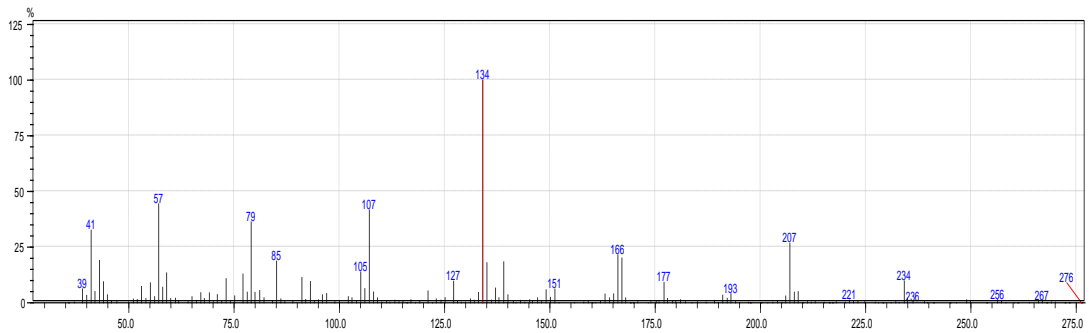
98 **Tumerone**



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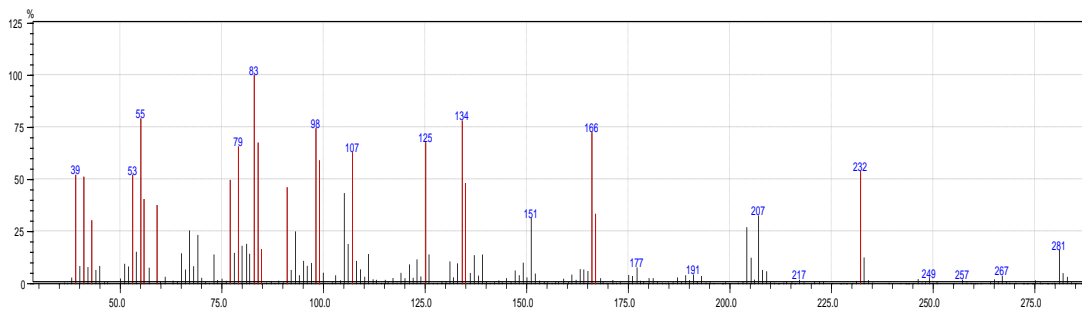
101 **Juvabione**



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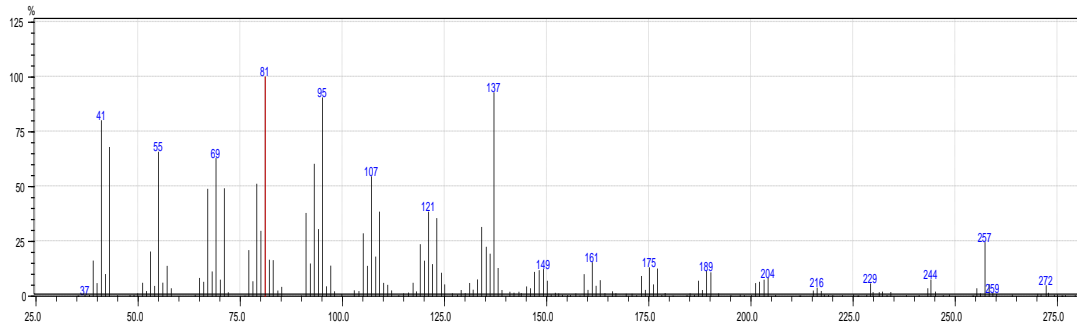
103

104 **DehydroJuvabione**



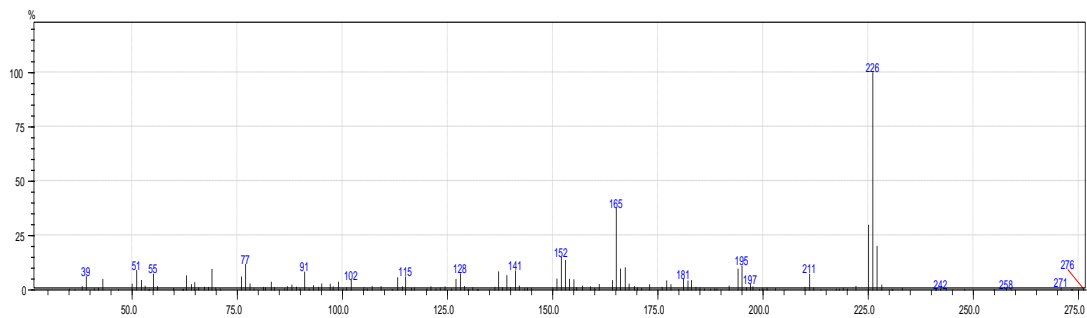
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106 **Manool**



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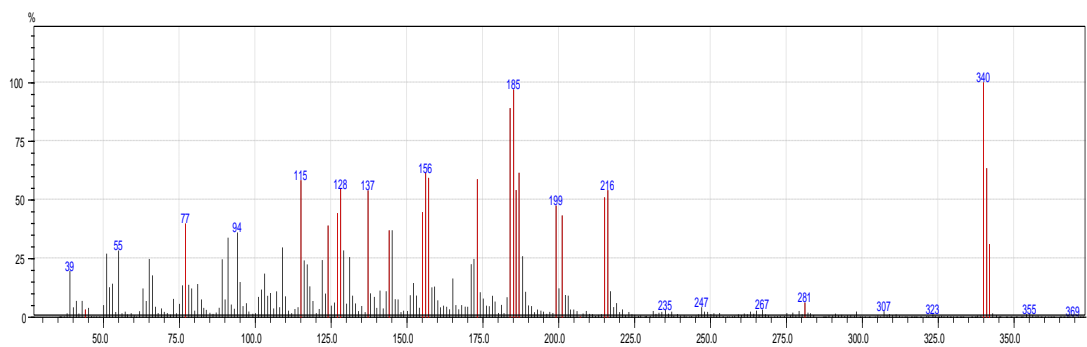
108 **4'-methoxy-2-hydroxystilbene**



109

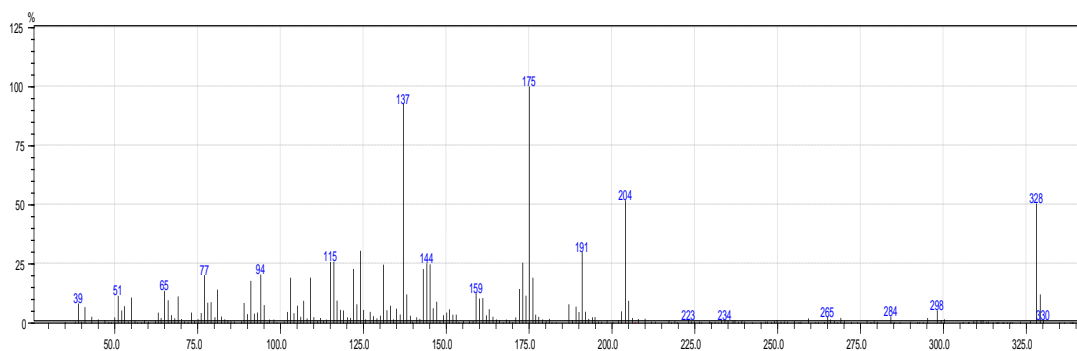
110

111 **Lignan 1**



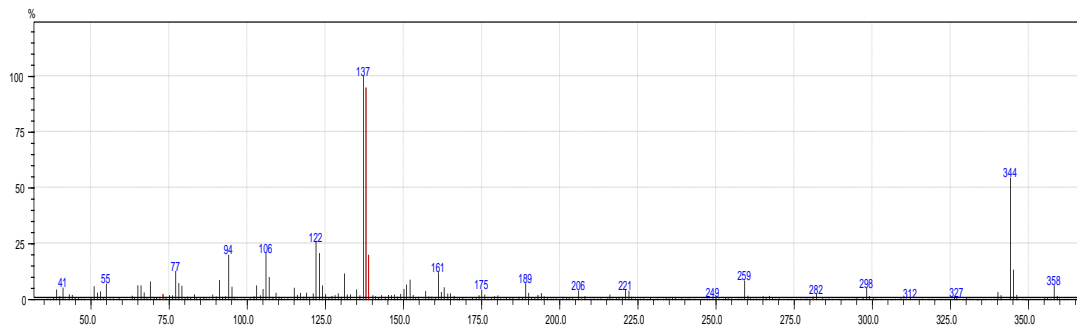
112

113 **Lignan 2**



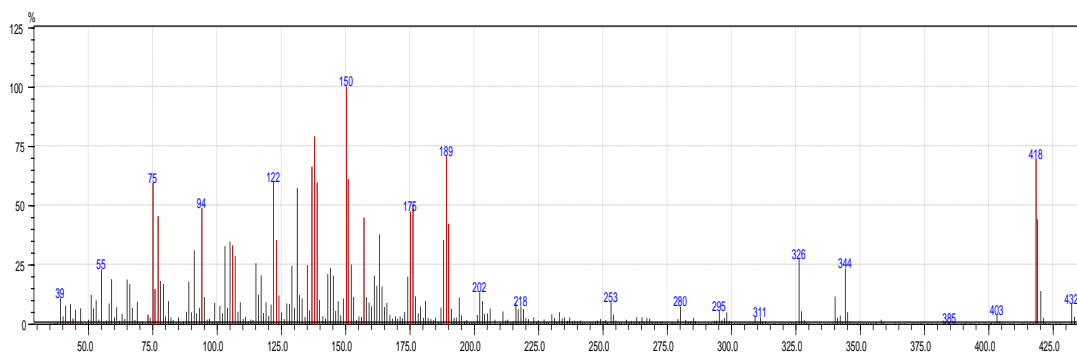
114

115 **Lignan 3**



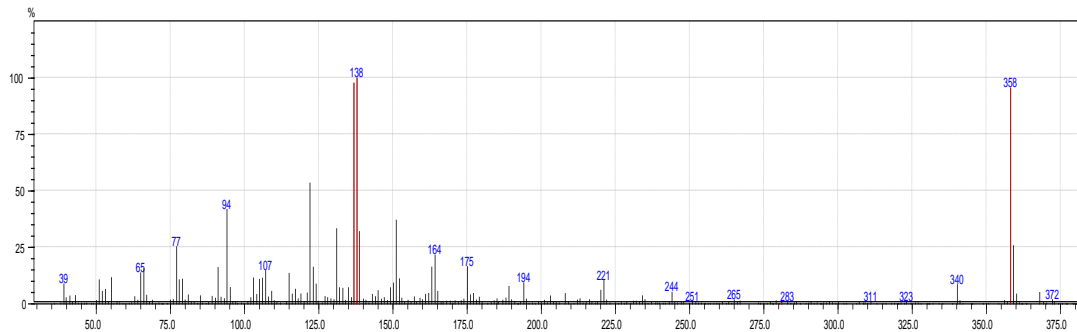
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117 **Lignan 4**



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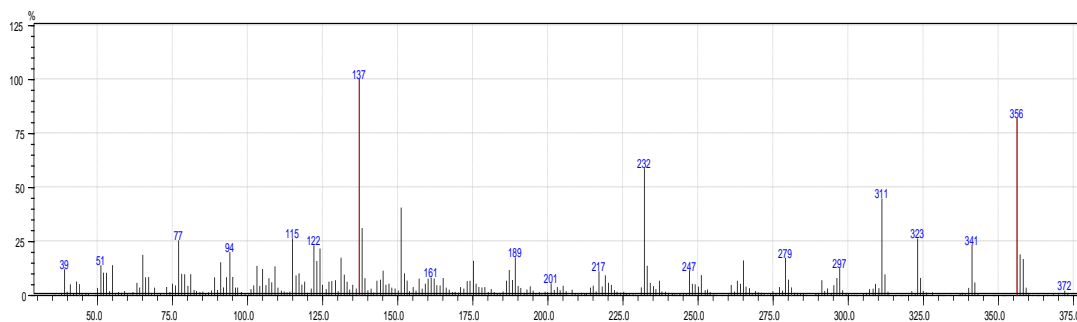
119 **Matairesinol**



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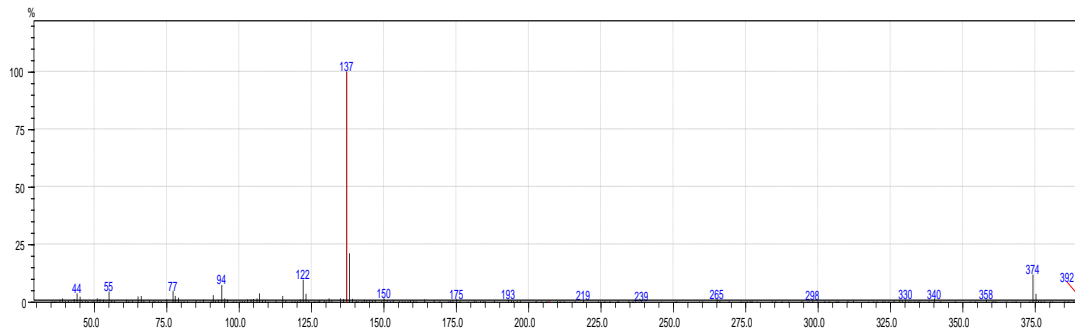
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122 **Hydroxymatairesinol 1**



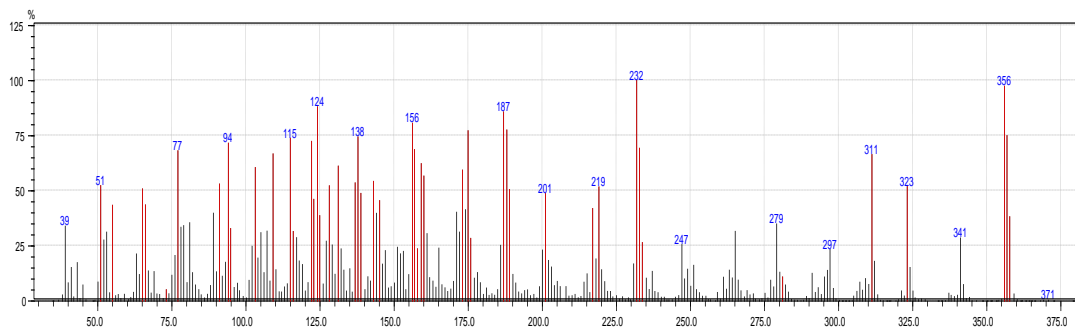
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124 **Nortrachelogenin**



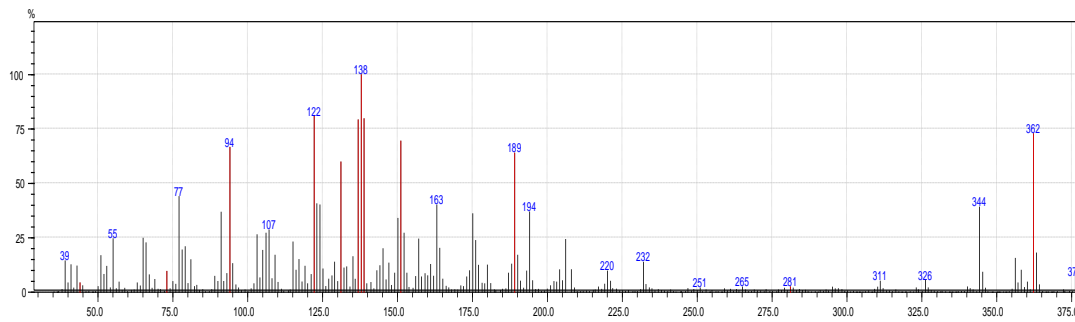
125

126 **Hydroxymatairesinol 2**



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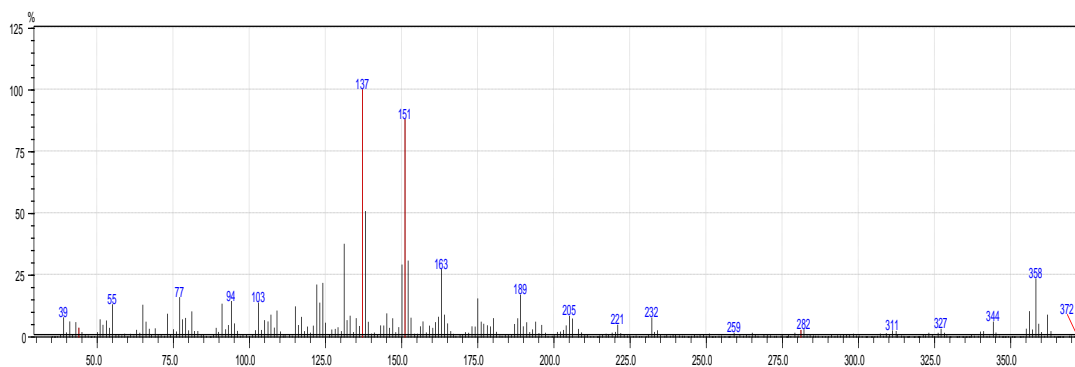
128 **Secoisolariciresinol**



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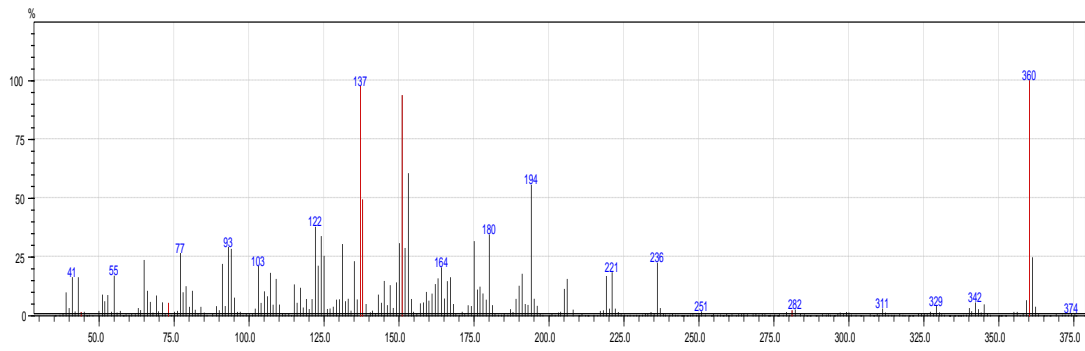
130 **Pinoresinol**

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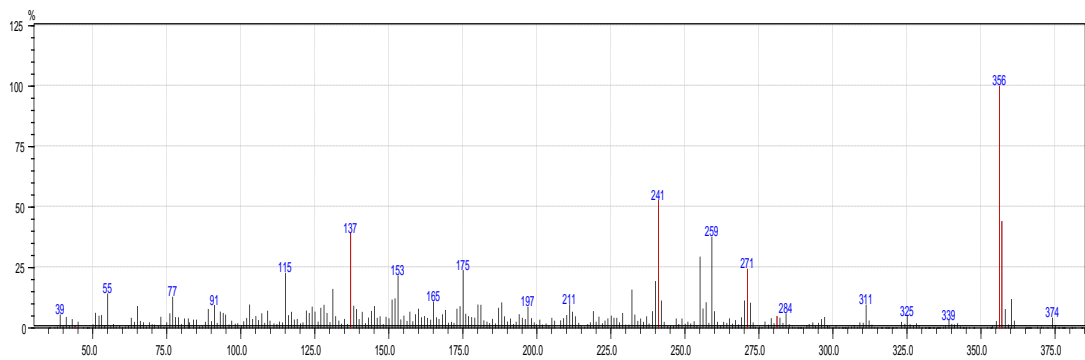
133 **Lariciresinol**



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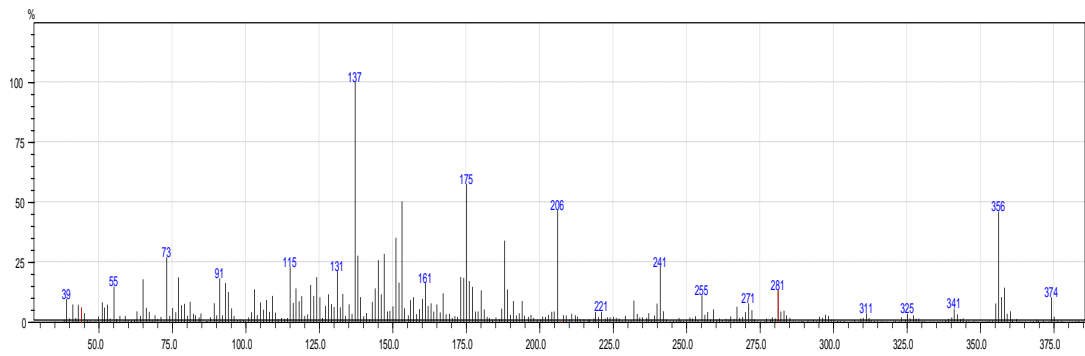
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136 **Alpha-Conidendrin**



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138 **Hydroxymatairesinol derivative**



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Quantitative analysis of Soxhlet ethanol extract

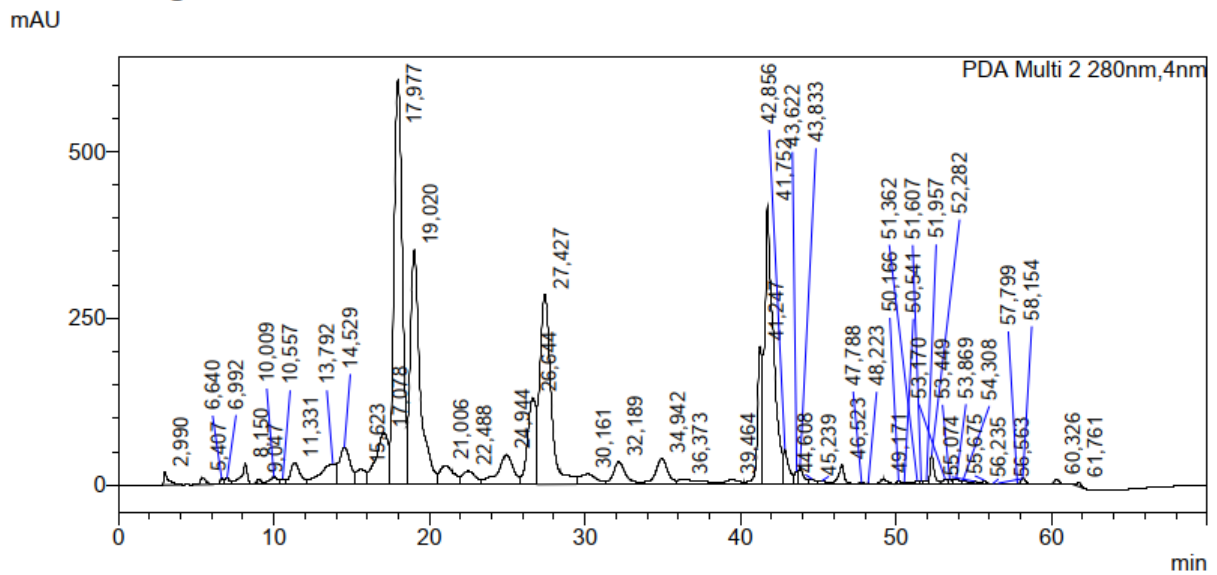
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Table S3. Experimental conditions of Soxhlet ethanol extraction

Ethanol volume	600 mL
Wood mass	50.2768 g
duration	8 h
Extract volume	555 mL

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Figure S16: HPLC-PDA chromatogram of Soxhlet ethanol extract

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162 Table S4. HPLC-PDA external quantitative analysis of Soxhlet ethanol extract

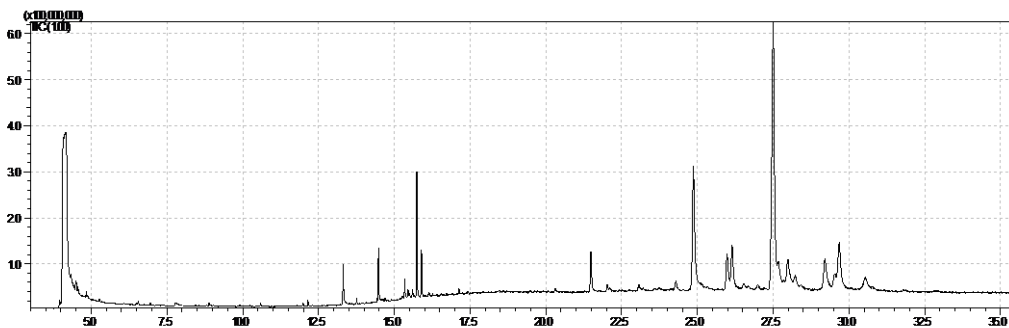
Retention time (min.)	Chemical compounds	Surface area	Calibration curve slope	C (g/L)	m (mg)
17.98	Hydroxymatairesinol-S	22 263 477	25 195 682	1.767	
19.02	Hydroxymatairesinol-R	15 825 854	15 488 497	2.044	
	Hydroxymatairesinol-S+R			3.811	2115
34.94	α -conidendrin	2 149 517	23 138 204	0.186	103.2

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164 $C = (\text{surface area/slope}) \times 2$

165 $m=C \times V(\text{extract})$; m: extract chemical compound mass

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168 Figure S17: GC-FID/MS chromatogram of Soxhlet ethanol extract

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177 Table S5: GC-FID/MS external quantitative analysis of Soxhlet ethanol extract

Retention time (min.)	Chemical compounds	Surface area	Calibration curve slope	C (g/L)	m (mg)
29.728	lariresinol	423 108 442	6 209 990 002	0.273	151.3
26.400	matairesinol	441 276 326	6 756 250 096	0.261	145.0
28.715	pinoresinol	136 379 843	5 422 497 344	0.101	55.8
27.295	nortrachelogenin	49 353 972	4 373 591 181	0.041	25.1
8.174	o-guaiacol	42 068 376	9 600 753 944	0.018	9.7
13.564	Coniferyl alcohol	186 308 465	5 828 329 038	0.128	70.9

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179 $C = (\text{surface area/slope}) \times 4$

180 $M = C \times V(\text{extract}); m: \text{extract chemical compound mass}$

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Supercritical carbon dioxide extraction

Table S6. Supercritical extraction – P = 110 bar, $t_{dynamic} = 120$ minutes

Temperature (°C)	20	40	60	40	40	40
t_{Static} (min)	30	30	30	30	30	30
V_{EtOH} (mL)	30	30	30	5	10	20
m feed wood (g)	8.88	8.70	8.77	8.52	12.44	8.85
Feed wood water (wt %)	11.00	11.00	11.00	11.47	11.47	11.31
m raffinate wood (g)	9.40	7.73	7.71	7.90	11.58	7.95
raffinate wood water (wt%)	4.48	2.71	2.51	5.44	4.74	3.38
m CO₂ (g)	627.7	684.0	666.6	573.9	725.5	662.4
m S1(g)	11.71	12.81	13.48	1.42	3.30	6.34
m S2(g)	10.66	10.53	9.18	1.77	3.98	8.57
m_{s1} dry (mg)	185.3	198.7	244.8	39.2	68.6	121.5
m_{s2} dry (mg)	140.5	104.7	76.7	37.3	88.7	104.3
m extractives (mg)	325.8	303.4	321.5	76.5	157.3	225.8
m CO₂(kg)/m extractives(g)	1.9	2.2	2.0	7.5	4.6	2.9
Mass balance(%)	97.5	95.9	93.5	89.2	92.7	92.8

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$$\text{Mass balance (\%)} = ((\text{raffinate} + m_{S1} + m_{S2}) / (m_{\text{feed}} + m_{\text{EtOH}})) \times 100$$

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Table S7. Supercritical extraction – P = 220 bar, $t_{\text{dynamic}} = 120$ minutes

Temperature (°C)	20	40	60	40	40	40	40	40	40	40	40	40
t_{Static} (min)	30	30	30	30	30	30	30	30	30	0	120	240
V_{EtOH} (mL)	30	30	30	0	5	10	20	25	40	30	30	30
m feed wood (g)	8.75	9.07	8.71	8.75	8.39	8.86	8.96	8.81	8.85	8.59	8.81	8.80
Feed wood water (wt%)	11.00	11.31	11.00	11.00	11.31	11.31	11.31	11.00	11.31	11.00	11.00	11.00
m raffinate wood (g)	8.02	7.96	7.61	8.00	7.62	8.05	8.00	7.91	7.54	7.50	7.92	7.68
raffinate wood water (wt%)	4.44	2.80	2.61	2.52	2.64	2.53	3.24	3.10	2.47	2.63	3.47	2.39
m CO ₂ (g)	689.4	633.6	670.2	646.8	648.6	678.1	663.0	687.6	631.2	629.4	613.8	652.8
m S1(g)	9.04	11.52	10.34	0.14	2.13	3.63	9.08	12.77	9.82	11.78	12.34	11.89
m S2(g)	13.42	10.60	12.29	0.48	1.66	3.68	6.05	4.74	18.20	11.02	10.55	11.32
m _{S1} dry (mg)	160.3	204.6	179.4		55.4	71.3	149.7	240.7	170.1	195.8	198.1	227.0
m _{S2} dry (mg)	205.0	151.3	150.5		41.6	67.0	101.1	67.4	280.9	165.0	133.5	149.3
m extractives (mg)	365.3	355.9	329.9	5.0	97.0	138.3	250.8	308.1	451.0	360.8	331.6	376.3
m CO ₂ (kg)/m extractives(g)	1.9	1.8	2.0	129.9	6.7	2.7	2.6	2.2	1.4	1.7	1.8	1.7
Mass balance (%)	93.9	91.8	93.3	102	92.8	91.5	93.5	89.1	87.9	91.6	94.8	95.0

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