

Supplementary Information

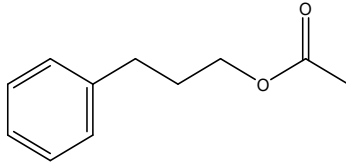
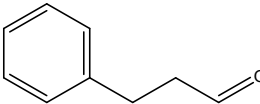
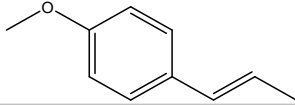
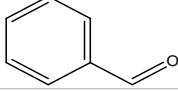
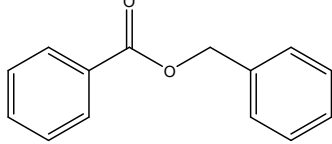
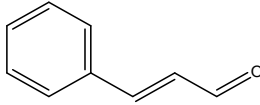
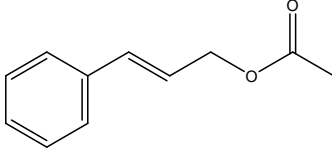
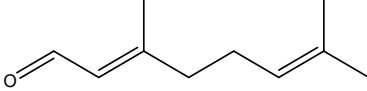
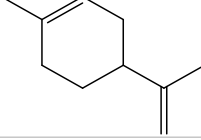
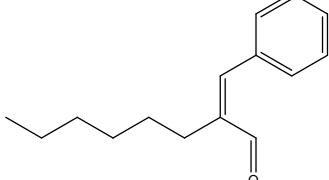
Towards a Sustainable and Green Extraction of Curcuminoids Using the Essential Oil of *Cinnamomum Cassia*

Verena Huber ^{*a†}, Michael Schmidt ^{a†}, Didier Touraud ^a, and Werner Kunz ^a

^a Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany.

[†] Both authors contributed equally to the work and are primary authors of this manuscript.

Table S 1: Important chemical structures.

Name	Structure
3-Phenylpropyl Acetate	
3-Phenylpropional Hydro-cinnamaldehyde	
Anethole	
Benzaldehyde	
Benzyl Benzoate	
Cinnamaldehyde	
Cinnamyl Acetate	
Citral	
Limonene	
α -Hexyl cinnamaldehyde	

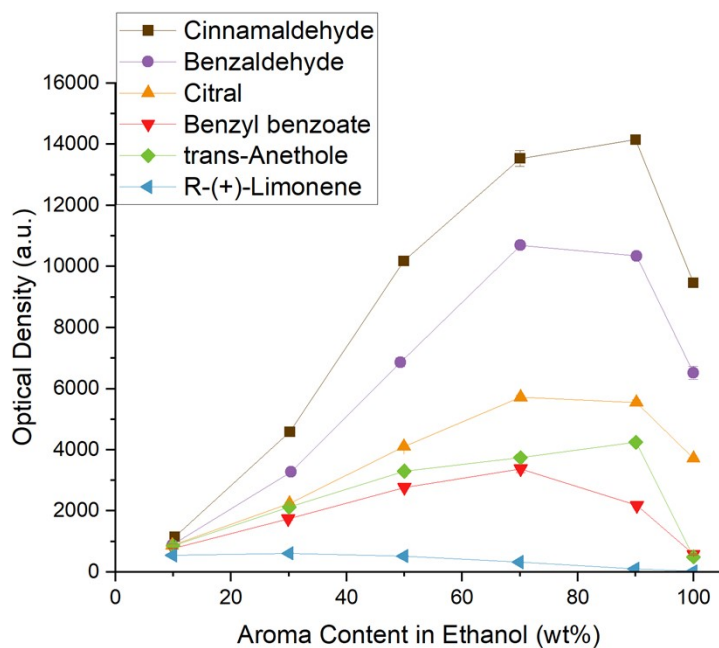


Figure S 1: UV/Vis examination of the solubility of curcumin in ethanolic solutions of natural flavors (w/w). Cinnamaldehyde is presented by brown squares, benzaldehyde by purple circles, citral by orange triangles, trans-anethole by red down-facing triangles, benzyl benzoate by green diamonds, and limonene by blue left-facing triangles.

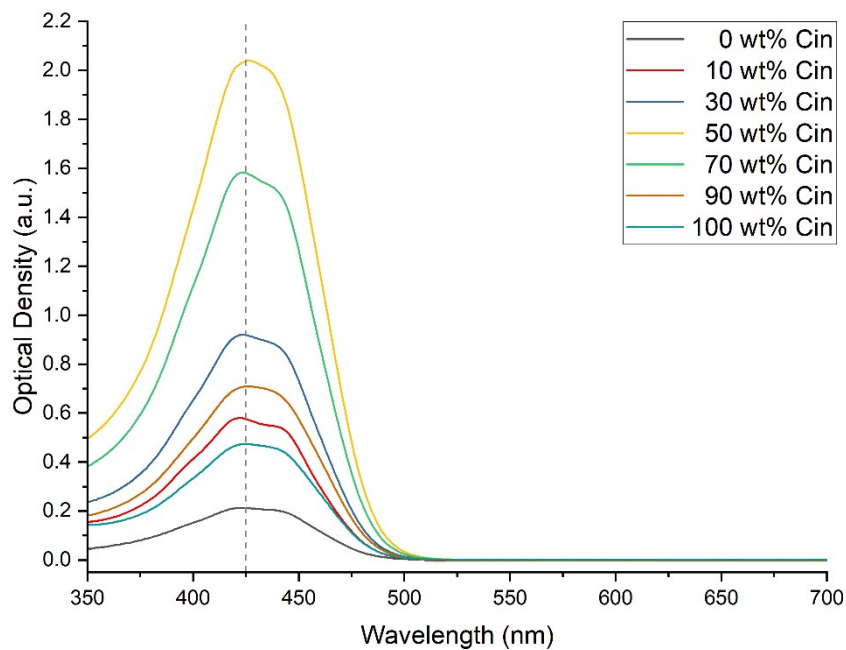


Figure S 2: UV/Vis spectra of curcumin in binary mixtures of EtOH/Cin (w/w) over a spectral range of 350-700 nm. The presented spectra are the mean curves of three measurements each. The dashed line shows the wavelength of 425 nm which was used to examine all measured samples.

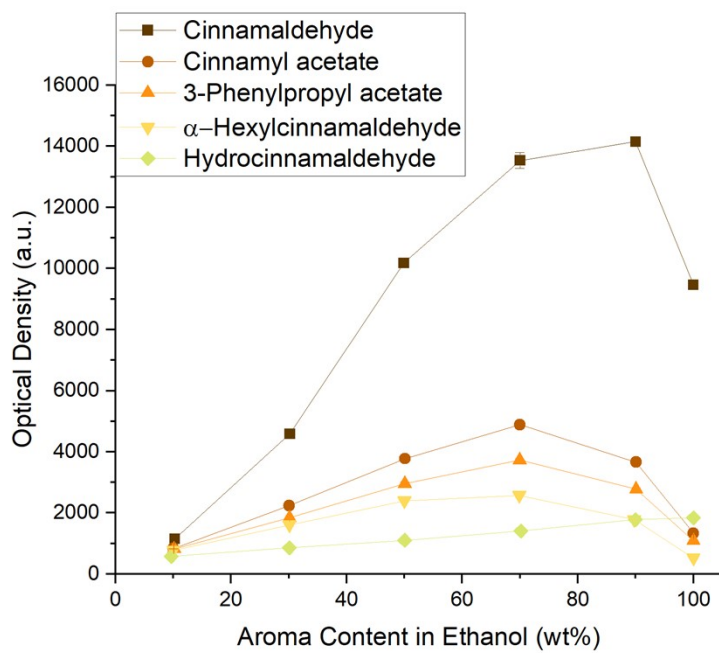


Figure S 3: UV/Vis examination of curcumin in ethanolic solutions of natural flavors (w/w). Cinnamaldehyde is presented by brown squares, cinnamyl acetate by marron circles, 3-phenylpropyl acetate by orange triangles, α-hexyl cinnamaldehyde by golden down-facing triangles, and hydrocinnamaldehyde by yellow diamonds.

Schmidt, MS101, MeOD, 1H
 rau_sPROTON_16 MeOD (C:\Bruker\TopSpin3.5pl7) AK_Kunz 29

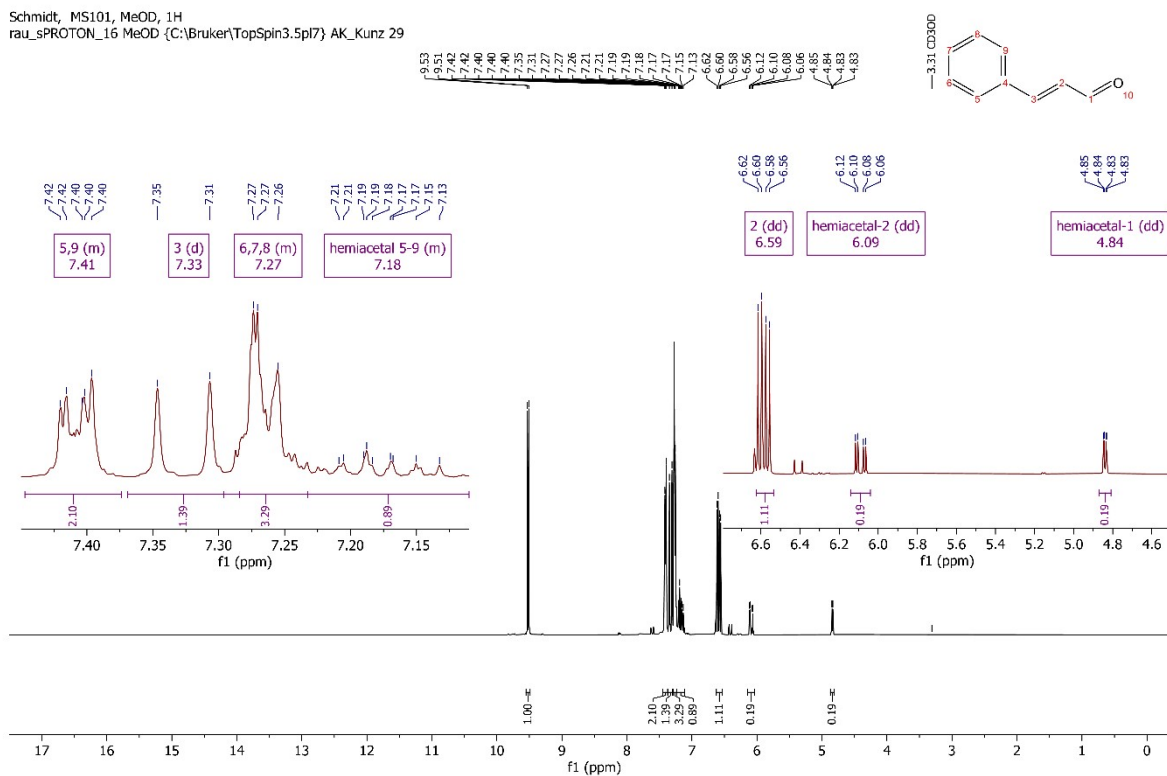


Figure 4 ¹H-NMR spectrum of trans-cinnamaldehyde in methanol-d₄.

Signals of trans-cinnamaldehyde: δ_H (400 MHz, MeOD) 4.84 (0 H, dd, J 5.1, 1.2), 6.09 (0 H, dd, J 16.2, 5.1), 6.59 (1 H, dd, J 15.9, 7.8), 7.11 – 7.23 (1 H, m), 7.23 – 7.30 (3 H, m), 7.33 (1 H, d, J 15.9), 7.37 – 7.45 (2 H, m), 9.52 (1 H, d, J 7.7).

Schmidt, MS102, MeOD, 1H
 rau_sPROTON_16 MeOD (C:\Bruker\TopSpin3.5pl7) AK_Kunz 30

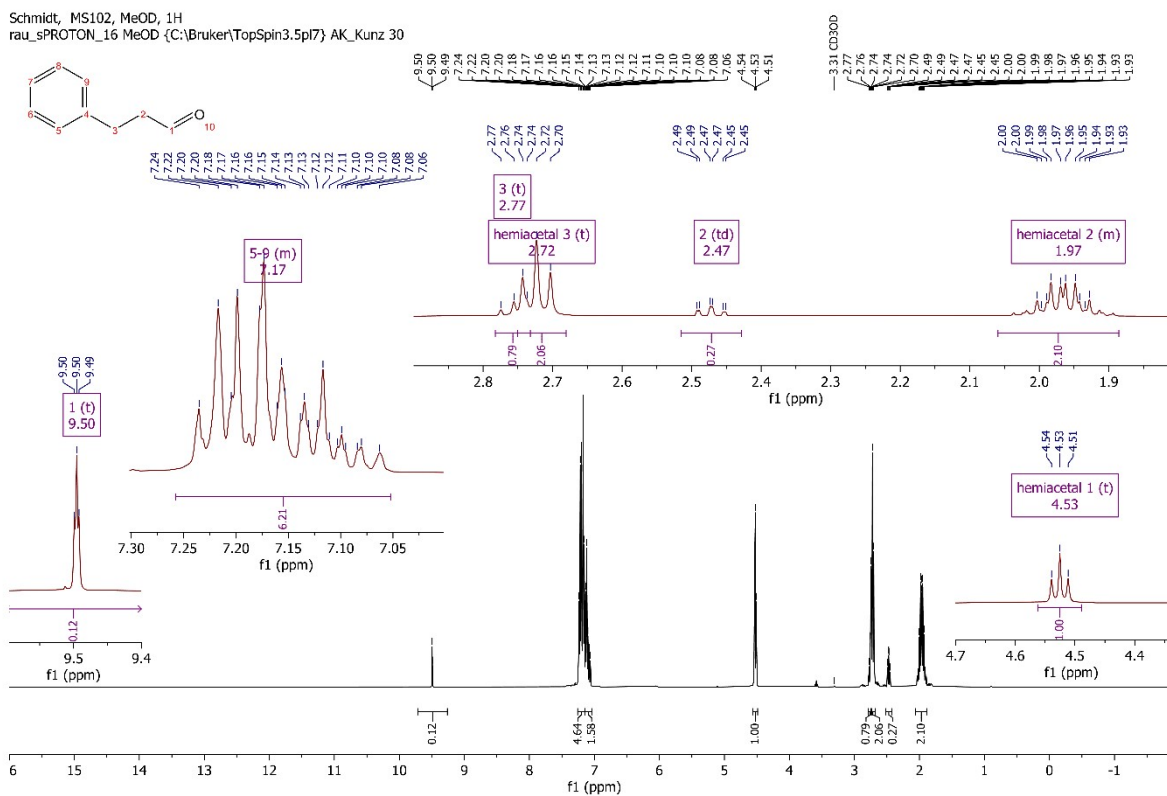


Figure 5 ¹H-NMR spectrum of hydrocinnamaldehyde in methanol-d₄.

Signals of hydrocinnamaldehyde: δ_H (400 MHz, MeOD) 1.89 – 2.06 (2 H, m), 2.47 (0 H, td, J 7.5, 1.4), 2.72 (2 H, t, J 8.0), 2.77 (1 H, t, J 7.5), 4.53 (1 H, t, J 5.5), 7.04 – 7.14 (2 H, m), 7.14 – 7.26 (5 H, m), 9.50 (0 H, t, J 1.4).

Schmidt, Curcumin5, MeOD, 1H
 rau_sPROTON_16 MeOD {C:\Bruker\TopSpin3.0} AK_Kunz 2

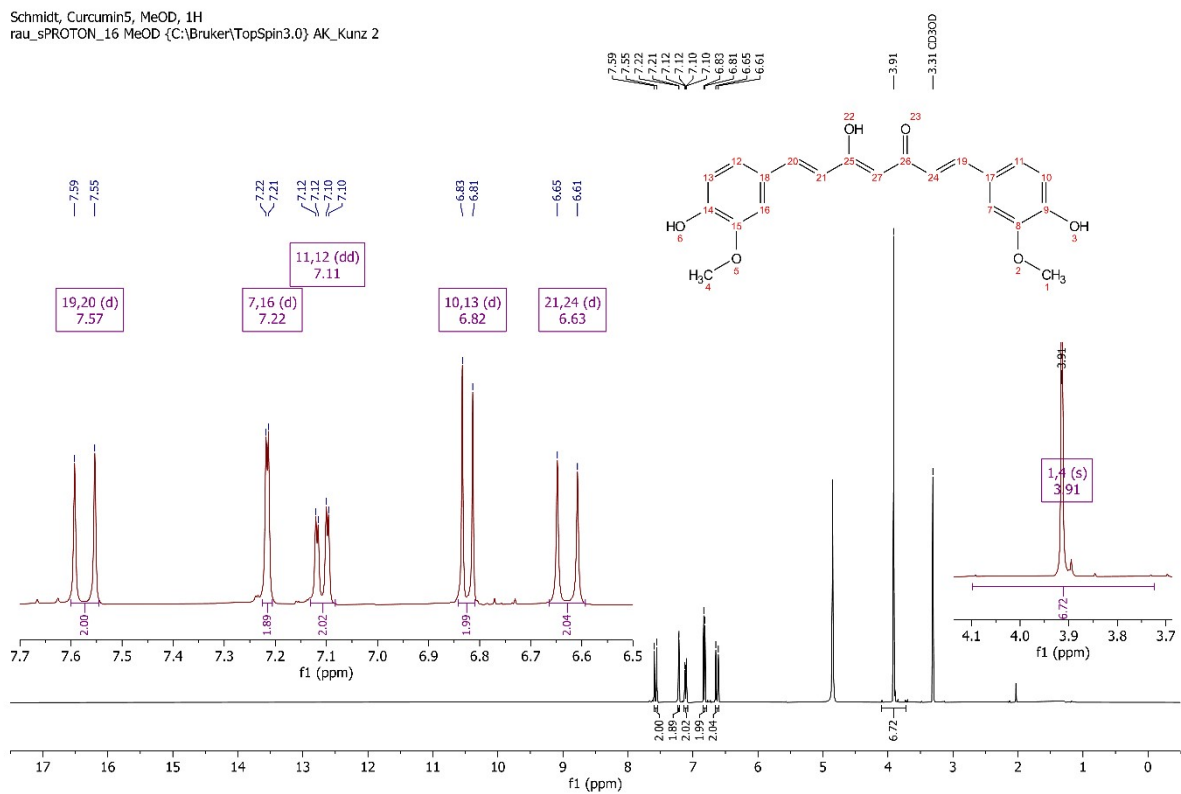


Figure S 6 $^1\text{H-NMR}$ spectrum of curcumin in methanol- d_4 .

Signals of curcumin: δ_{H} (400 MHz, MeOD) 3.91 (7 H, s), 6.63 (2 H, d, J 15.8), 6.82 (2 H, d, J 8.2), 7.11 (2 H, dd, J 8.2, 1.9), 7.22 (2 H, d, J 1.9), 7.57 (2 H, d, J 15.8).

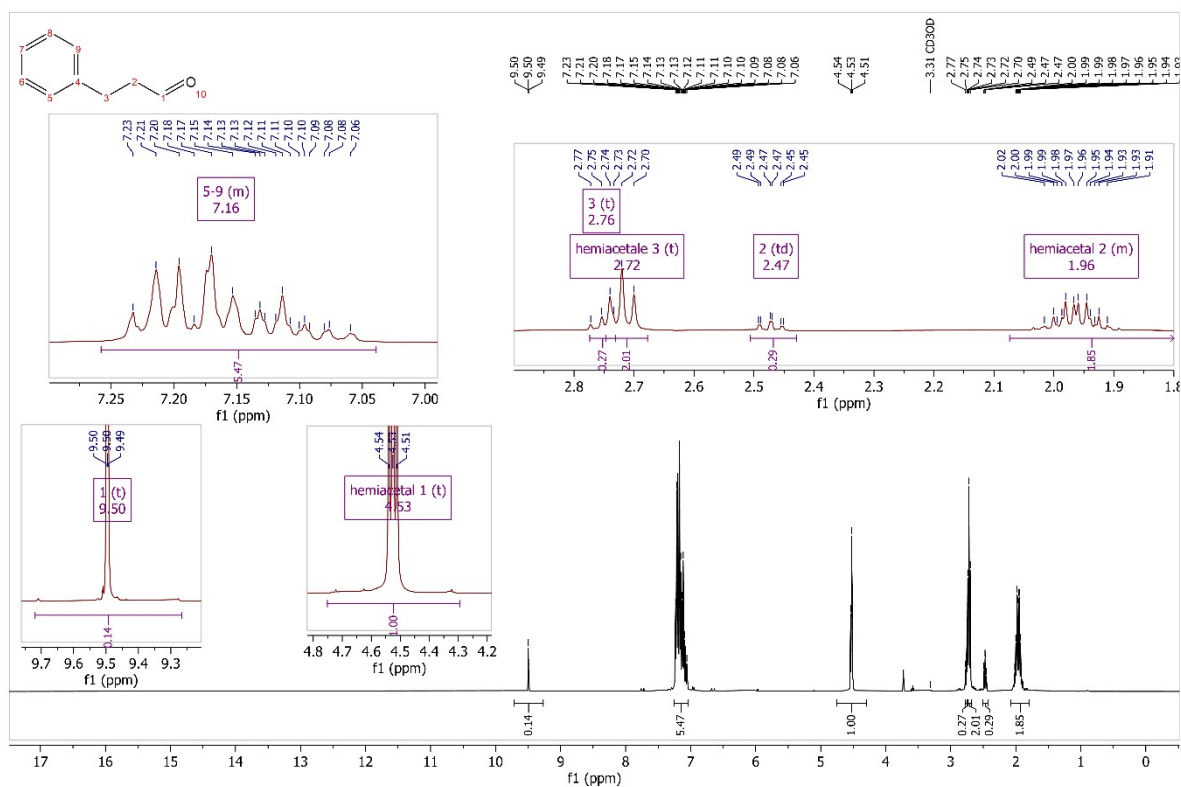


Figure S 8 $^1\text{H-NMR}$ spectrum of curcumin in hydrocinnamaldehyde/methanol- d_4 (30/70) (n/n) with assigned signals of trans-cinnamaldehyde (top) and of curcumin (bottom).

Signals of hydrocinnamaldehyde: δ_{H} (400 MHz, MeOD) 1.79 – 2.07 (2 H, m), 2.47 (0 H, td, J 7.6, 1.4), 2.72 (2 H, t, J 8.0), 2.76 (0 H, t, J 7.5), 4.53 (1 H, t, J 5.6), 7.04 – 7.26 (5 H, m), 9.50 (0 H, t, J 1.4).

Signals of curcumin: δ_{H} (400 MHz, MeOD) 3.73 (6 H, s), 5.97 (1 H, s), 6.66 (2 H, d, J 15.7), 6.96 (2 H, d, J 8.6), 7.74 (2 H, d, J 15.7).

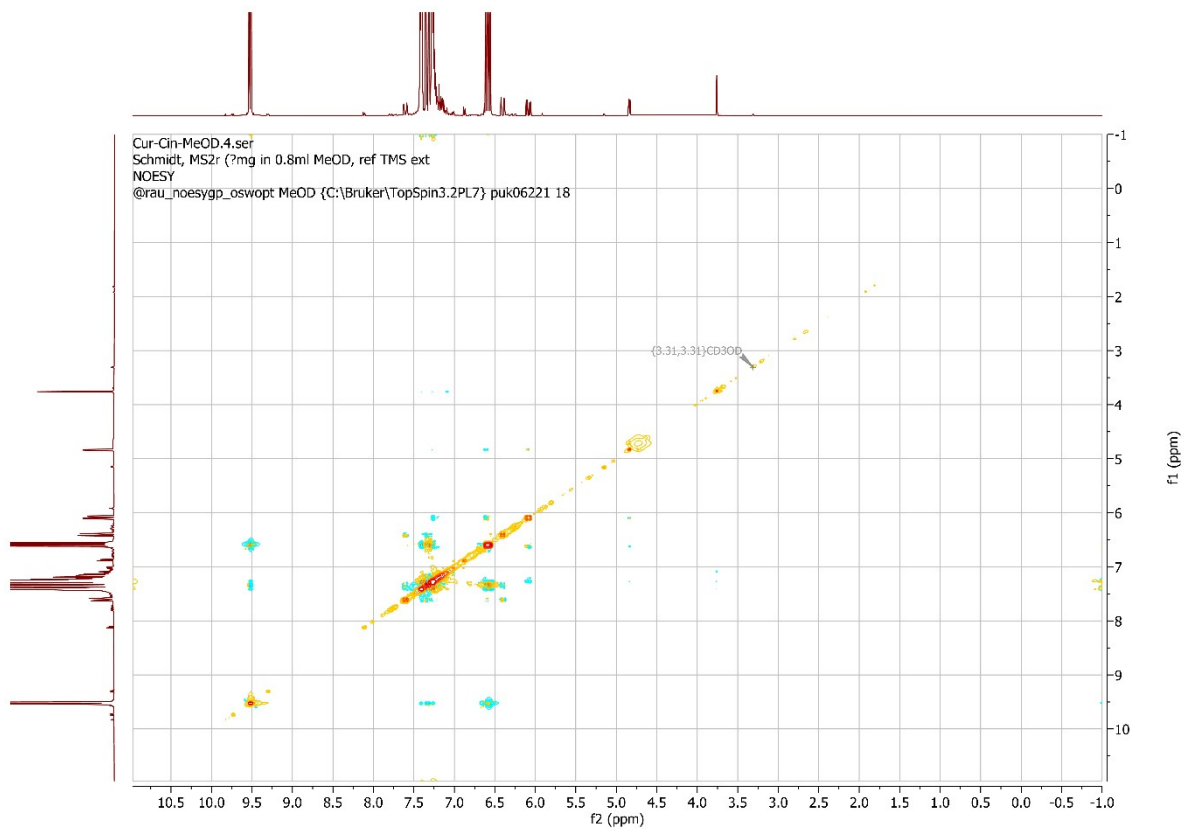


Figure S 9 ^1H - ^1H -NOESY spectrum of curcumin in *trans*-cinnamaldehyde/methanol- d_4 (30/70) (n/n).

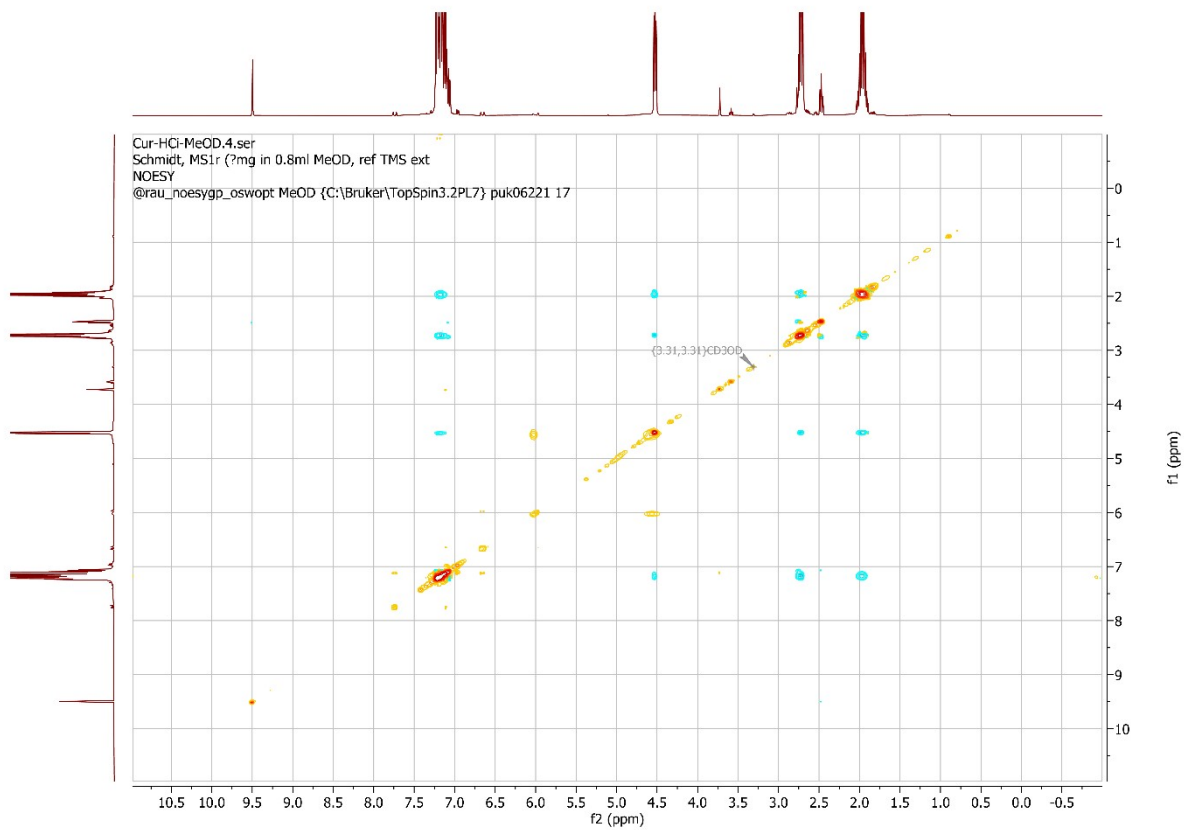


Figure S 10 ^1H - ^1H -NOESY spectrum of curcumin in hydrocinnamaldehyde/methanol- d_4 (30/70) (n/n).

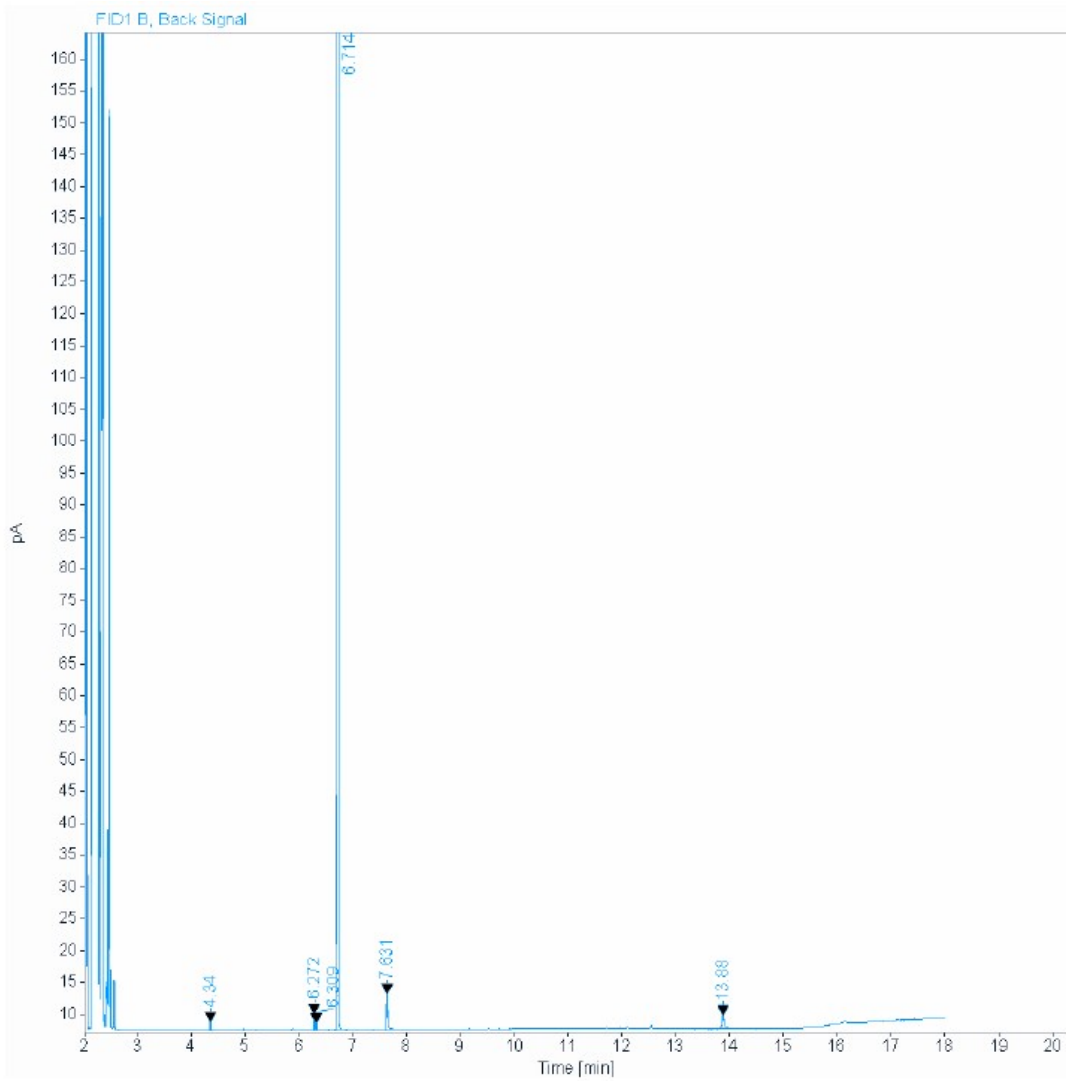


Figure S 11: Chromatogram of the pure, synthetic cinnamaldehyde as obtained via GC-FID.

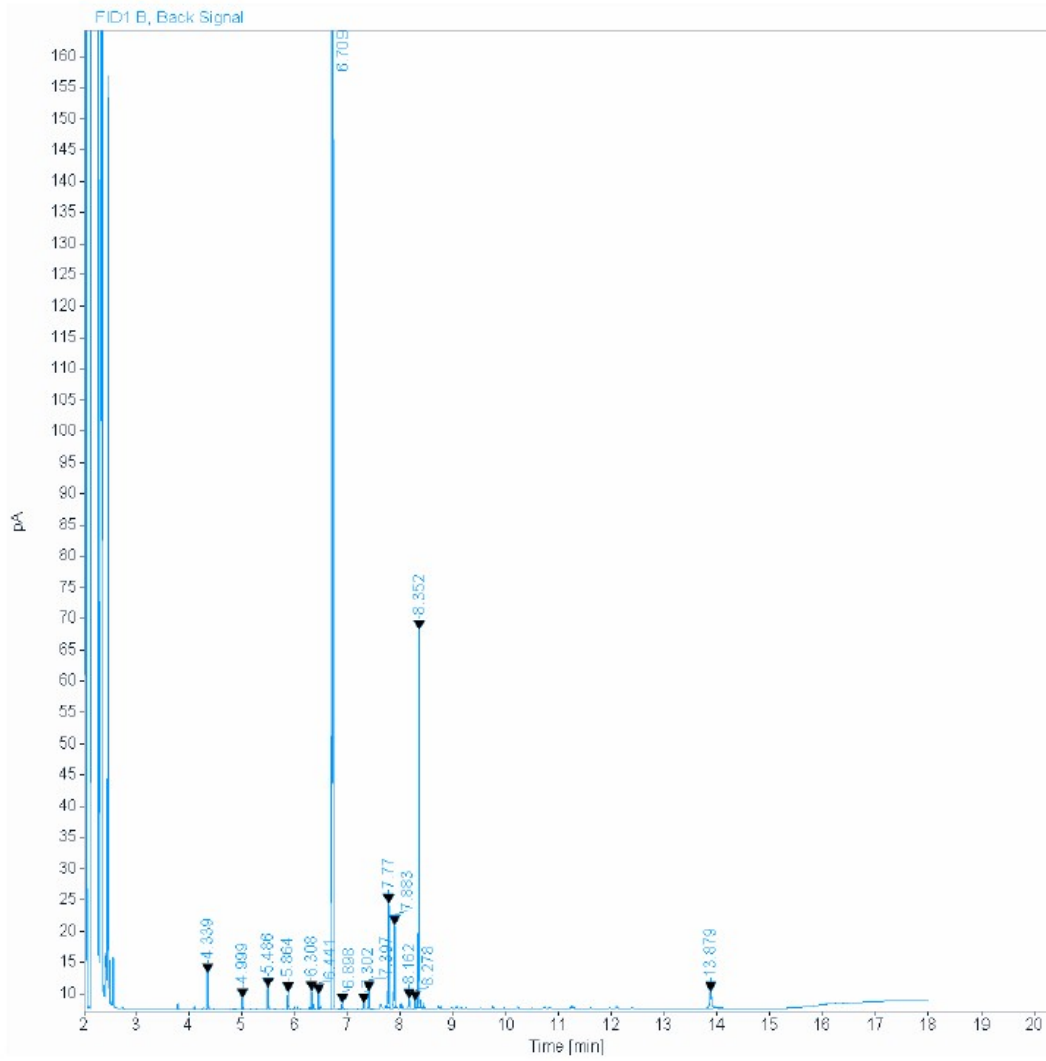


Figure S 12: Chromatogram of Cinnamomum Cassia oil by PCW as obtained via GC-FID.

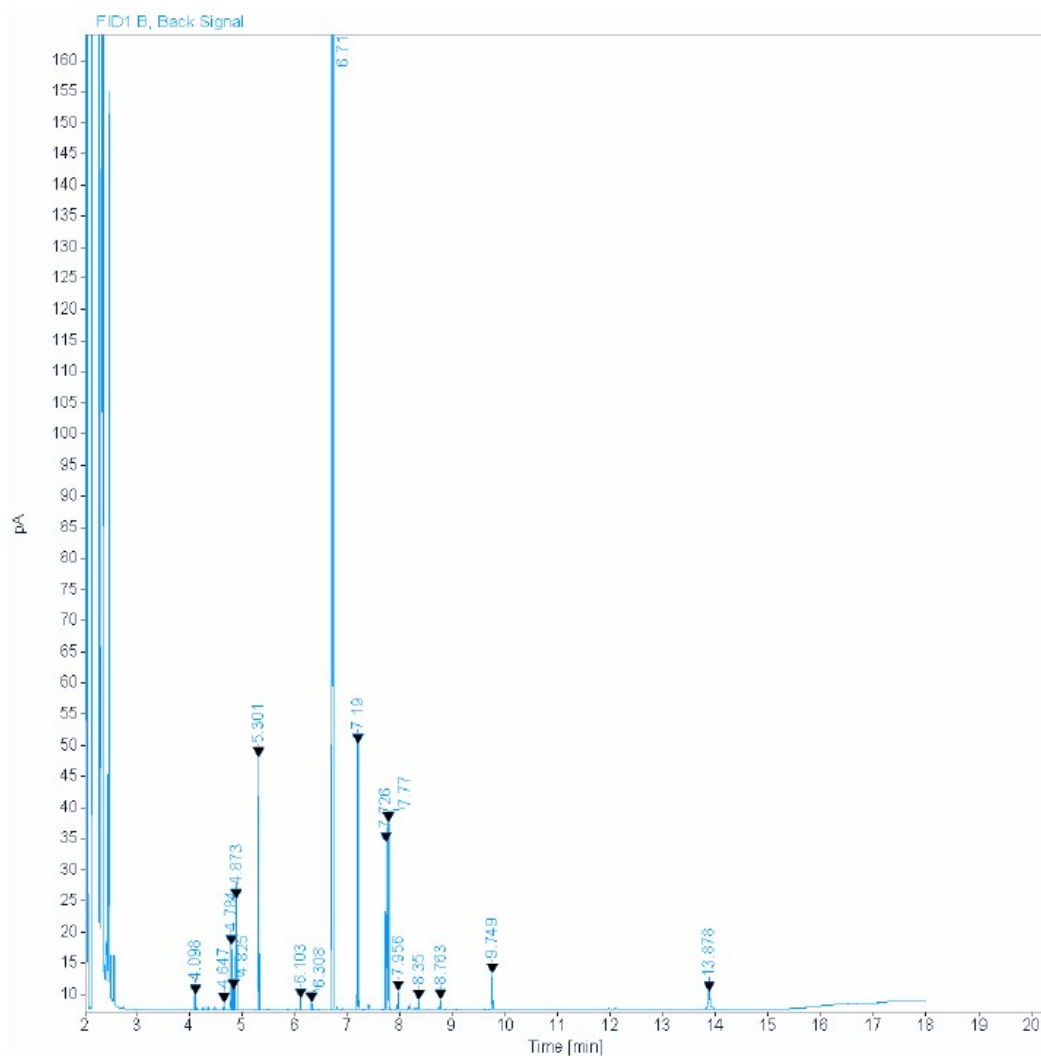


Figure S 13: Chromatogram of Cinnamomum Cassia oil by Jean Pütz as obtained via GC-FID.

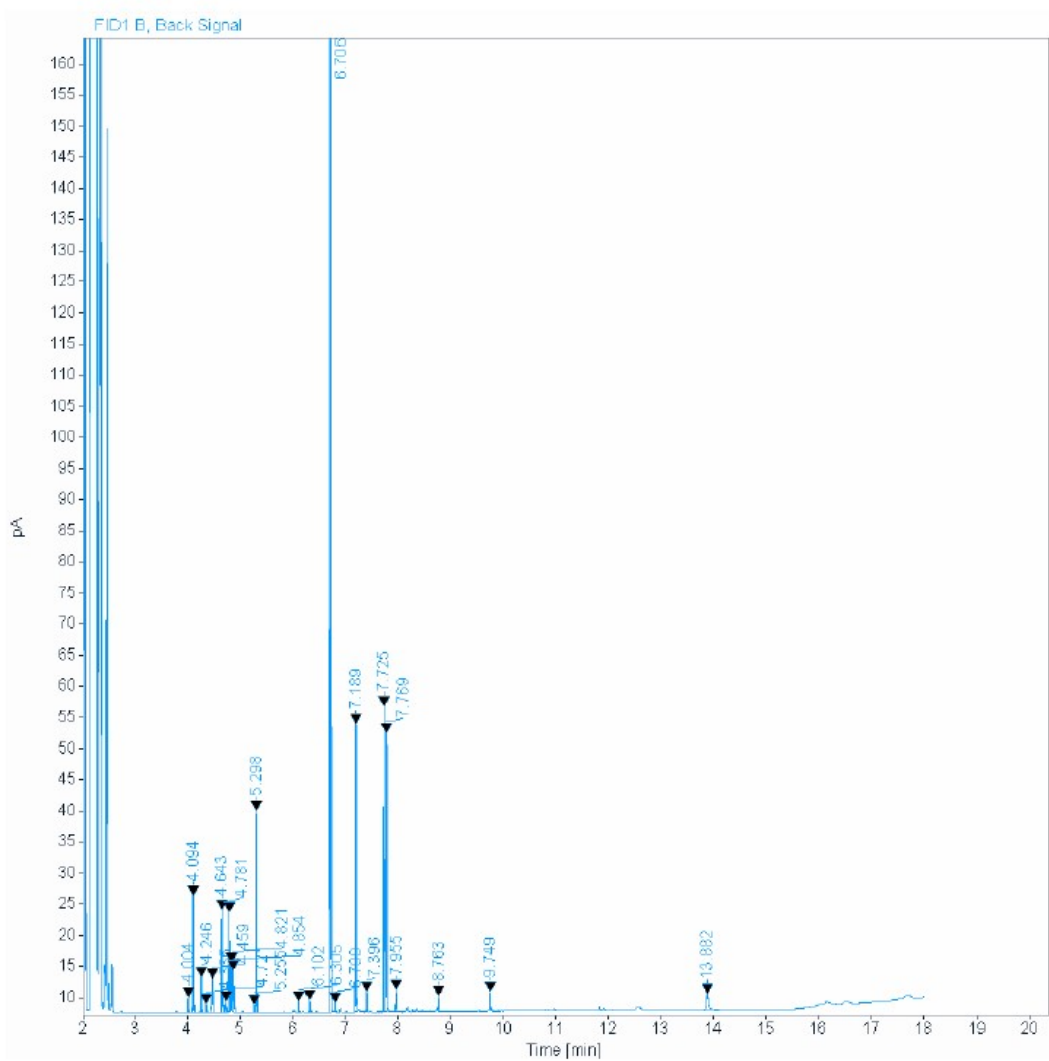


Figure S 14: Chromatogram of Cinnamomum Verum oil by PCW as obtained via GC-FID.

Table S 2: Retention time of Cinnamaldehyde and purity as determined by GC-FID.

Retention Time (min)	Reference Cinnamaldehyde	Cassia	Zeylanicum	Verum
6.71	97%	79%	74%	62%

Table S 3: Retention time of all analyzable ingredients of the different cinnamon oils as assessed via GC-MS.

Retention Time (min)	Cassia	Zeylanicum	Verum
3.38	-	-	α -Pinene
3.52	-	-	Camphene
3.59	Benzaldehyde	-	-
3.75	-	-	β -Myrcene
3.94	-	-	α -Phellandrene
4.07	-	o-Cymene	o-Cymene
4.12	-	Limonene	Limonene
4.15	-	-	β -Phellandrene
4.16	-	Eucalyptol	-
4.62	-	Linalool	Linalool
5.98	Cinnamaldehyde	Cinnamaldehyde	Cinnamaldehyde
6.51	-	Eugenol	Eugenol
7.05	-	Caryophyllene	Caryophyllene
7.11	Cinnamyl acetate	Cinnamyl acetate	Cinnamyl acetate
7.15	Coumarin	-	-
7.67	2-Methoxy-cinnamaldehyde	-	-
9.1	-	Benzyl benzoate	-

Cinnamaldehyde Reference

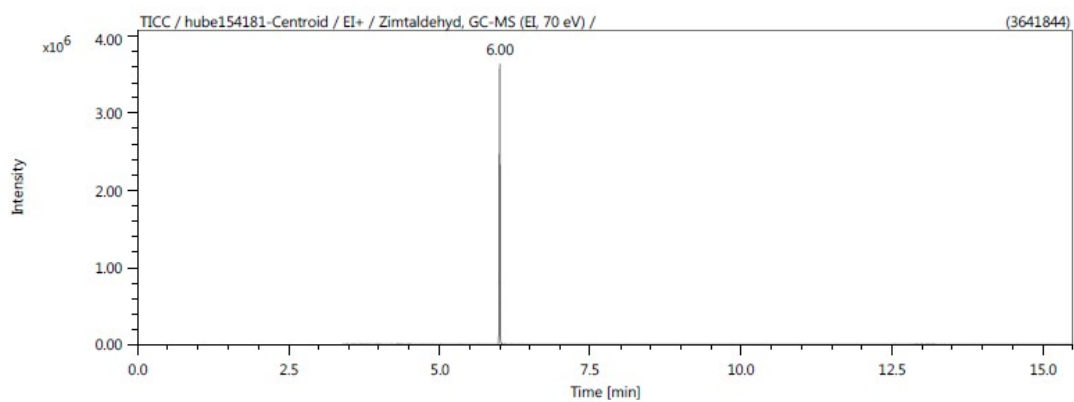


Figure S 15: Chromatogram of cinnamaldehyde as obtained by GC-MS.

Hit 2 : Cinnamaldehyde, (E)-
C₉H₈O; MF: 958; RMF: 958; Prob 32.3%; CAS: 14371-10-9; Lib: replib; ID: 20946.

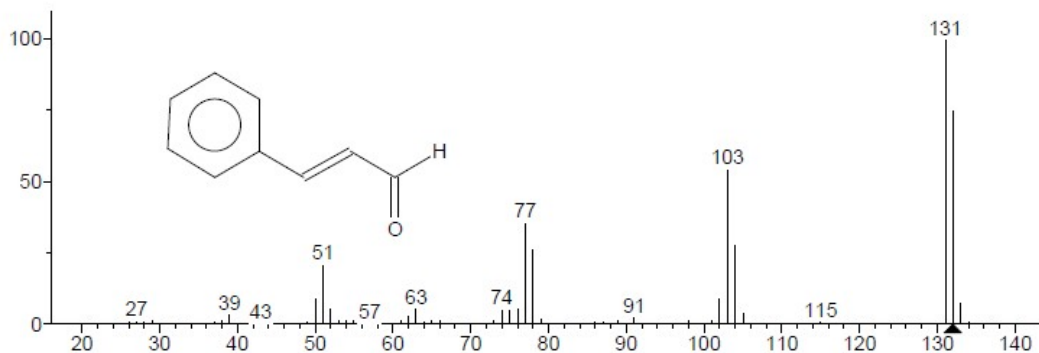


Figure S 16: Mass spectrum of cinnamaldehyde corresponding to the peak at a retention time of 5.98 min of the chromatogram of pure, synthetic cinnamaldehyde.

Cinnamomum Cassia Oil by PCW

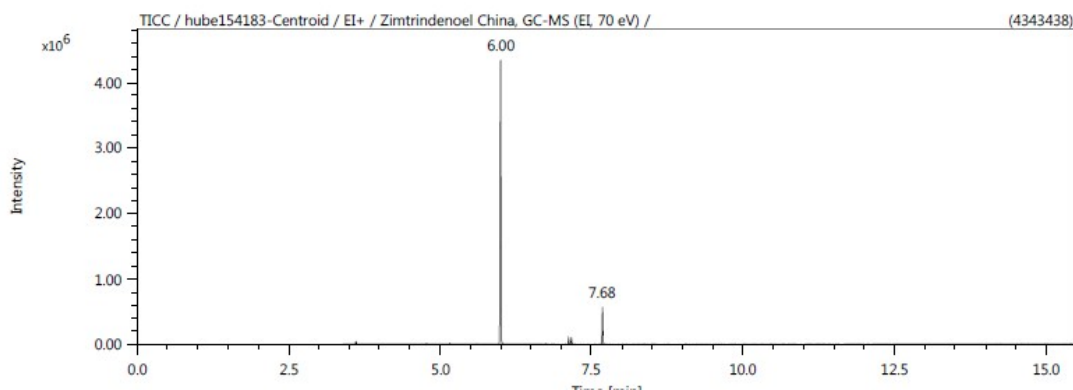


Figure S 17: Chromatogram of the Cinnamomum cassia oil by PCW as obtained by GC-MS.

Hit 1 : Benzaldehyde
C₇H₆O; MF: 899; RMF: 916; Prob 73.5%; CAS: 100-52-7; Lib: replib; ID: 10911.

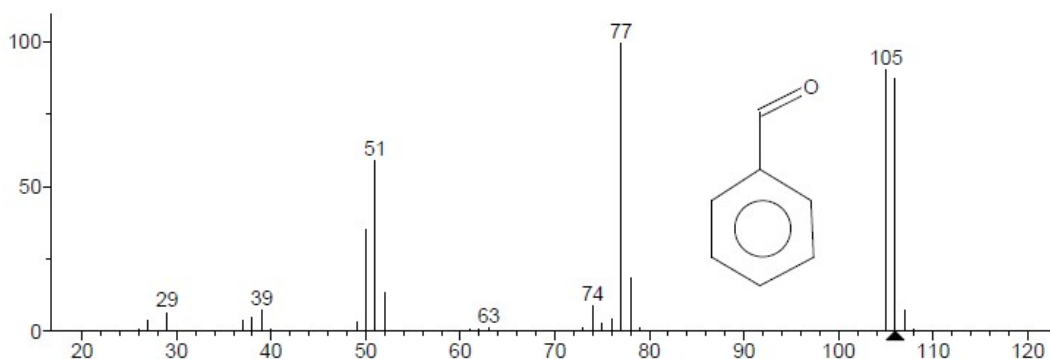


Figure S 18: Mass spectrum of benzaldehyde corresponding to the peak at a retention time of 3.59 min of the chromatogram of Cinnamomum Cassia by PCW.

Hit 2 : Cinnamaldehyde, (E)-
C₉H₈O; MF: 959; RMF: 959; Prob 31.9%; CAS: 14371-10-9; Lib: replib; ID: 20946.

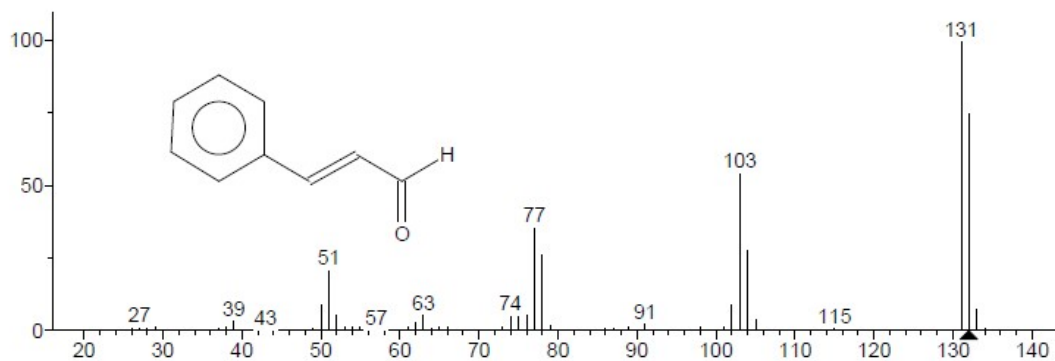


Figure S 19: Mass spectrum of cinnamaldehyde corresponding to the peak at a retention time of 5.98 min of the chromatogram of Cinnamomum Cassia by PCW.

Hit 1 : Acetic acid, cinnamyl ester
C₁₁H₁₂O₂; MF: 888; RMF: 889; Prob 64.6%; CAS: 103-54-8; Lib: mainlib; ID: 11373.

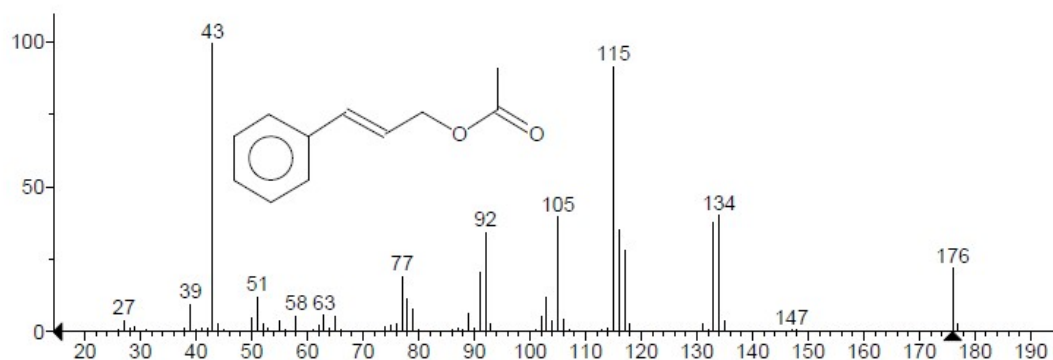


Figure S 20: Mass spectrum of cinnamyl acetate corresponding to the peak at a retention time of 7.11 min of the chromatogram of Cinnamomum Cassia by PCW.

Hit 1 : Coumarin
C₉H₆O₂; MF: 937; RMF: 951; Prob 48.7%; CAS: 91-64-5; Lib: replib; ID: 18483.

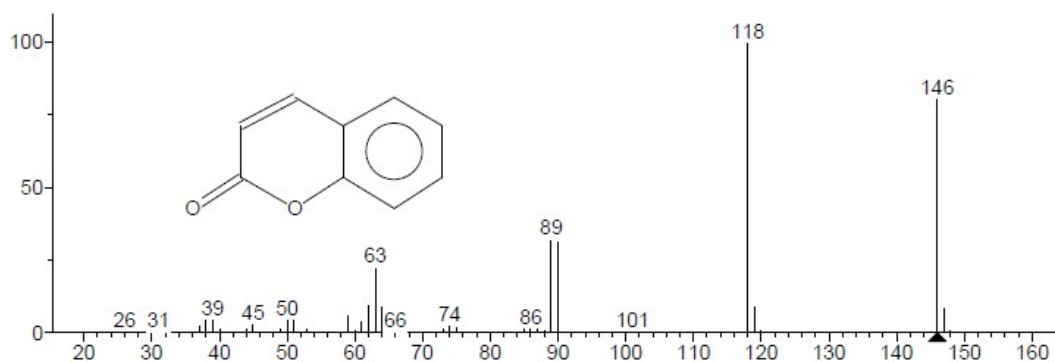


Figure S 21 Mass spectrum of coumarin corresponding to the peak at a retention time of 7.1 min of the chromatogram of Cinnamomum Cassia by PCW.

Hit 2 : (Z)-2-Methoxycinnamaldehyde
 C₁₀H₁₀O₂; MF: 929; RMF: 941; Prob 37.5%; CAS: 76760-43-5; Lib: mainlib; ID: 115636.

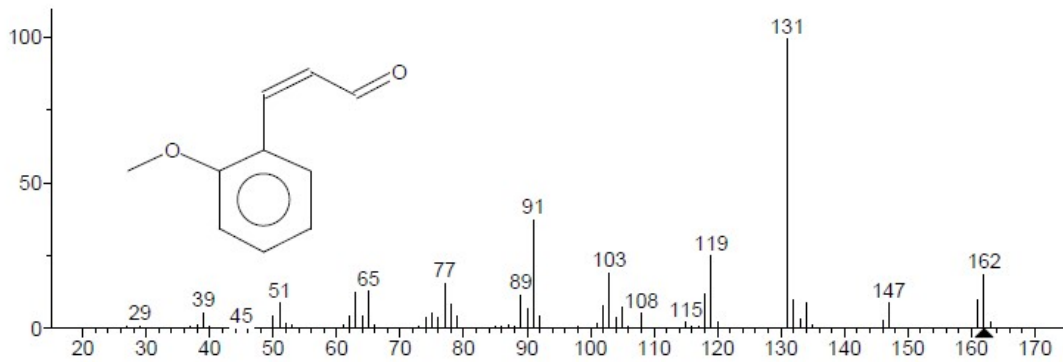


Figure S 22: Mass spectrum of 2-methylcinnamaldehyde corresponding to the peak at a retention time of 7.67 min of the chromatogram of *Cinnamomum Cassia* by PCW.

Cinnamon Oil by Jean Pütz

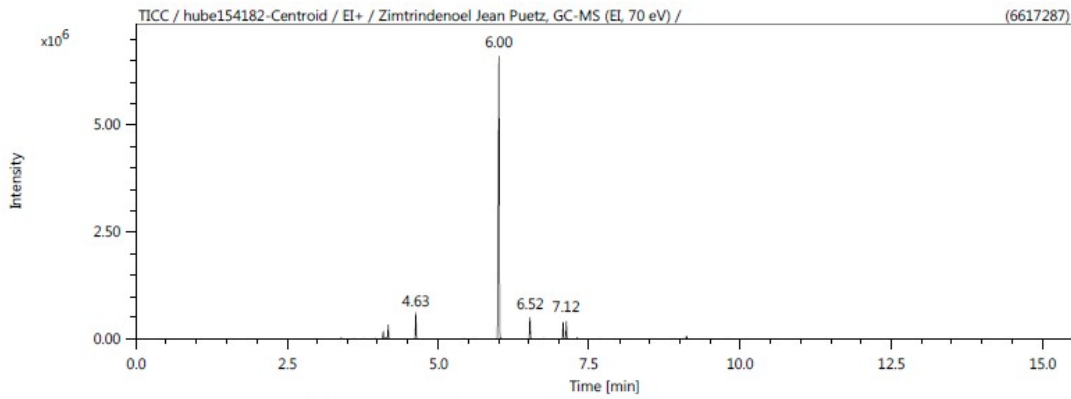


Figure S 23: Chromatogram of the *Cinnamomum verum* – *zeylanicum* oil by Jean Pütz as obtained by GC-MS.

Hit 2 : o-Cymene
 C₁₀H₁₄; MF: 909; RMF: 910; Prob 21.6%; CAS: 527-84-4; Lib: replib; ID: 18731.

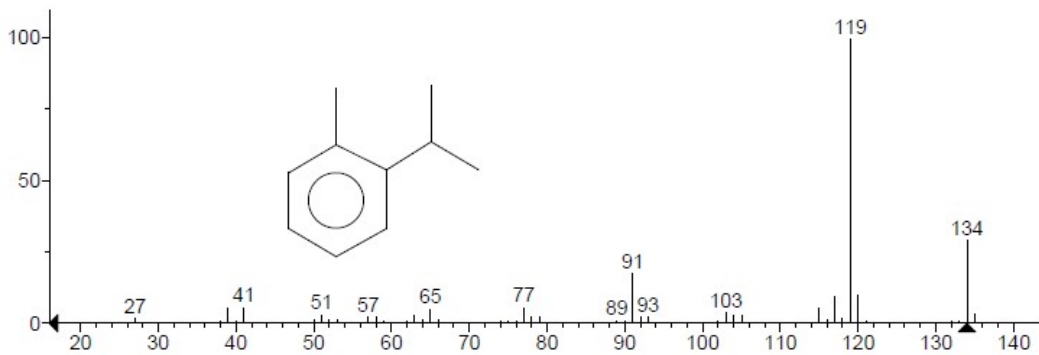


Figure S 24: Mass spectrum of o-cymene corresponding to the peak at a retention time of 4.0 min of the chromatogram of *Cinnamomum Cassia* by Jean Pütz.

Hit 1 : D-Limonene
C₁₀H₁₆; MF: 868; RMF: 868; Prob 61.1%; CAS: 5989-27-5; Lib: replib; ID: 8354.

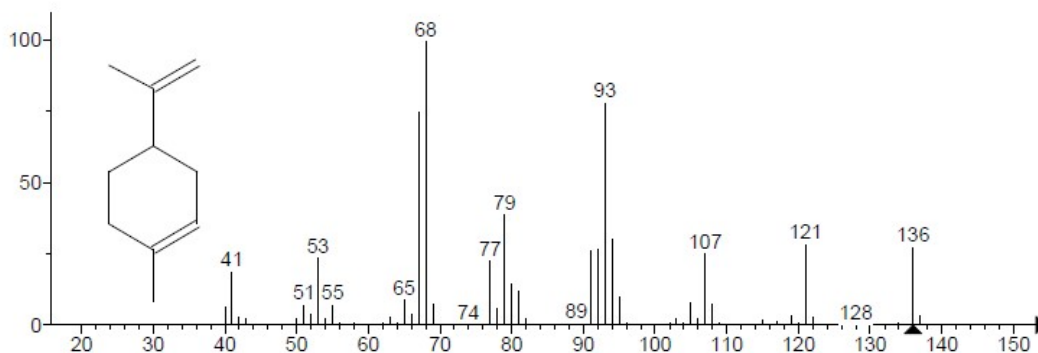


Figure S 25: Mass spectrum of limonene corresponding to the peak at a retention time of 4.12 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Eucalyptol
C₁₀H₁₈O; MF: 938; RMF: 941; Prob 91.0%; CAS: 470-82-6; Lib: mainlib; ID: 9537.

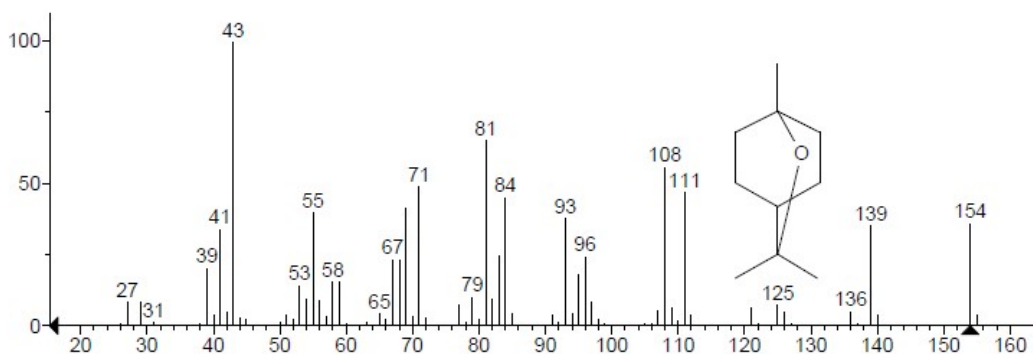


Figure S 26: Mass spectrum of eucalyptol corresponding to the peak at a retention time of 4.16 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Linalool
C₁₀H₁₈O; MF: 924; RMF: 925; Prob 72.3%; CAS: 78-70-6; Lib: mainlib; ID: 39161.

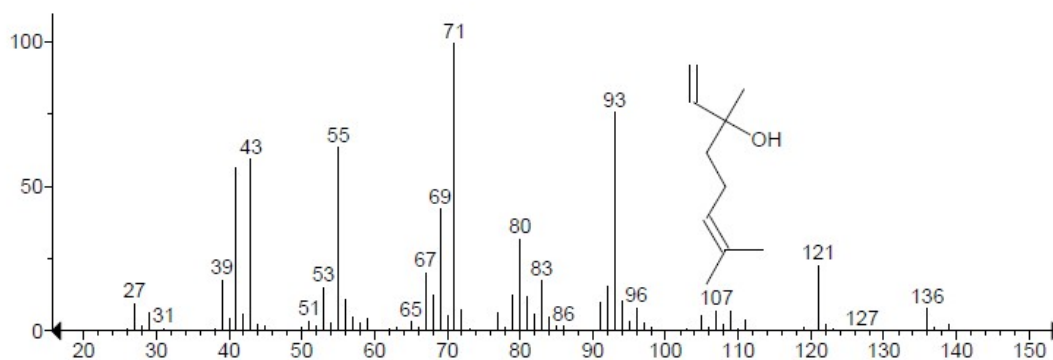


Figure S 27: Mass spectrum of linalool corresponding to the peak at a retention time of 4.62 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 2 : Cinnamaldehyde, (E)-
C₉H₈O; MF: 952; RMF: 952; Prob 29.2%; CAS: 14371-10-9; Lib: replib; ID: 20946.

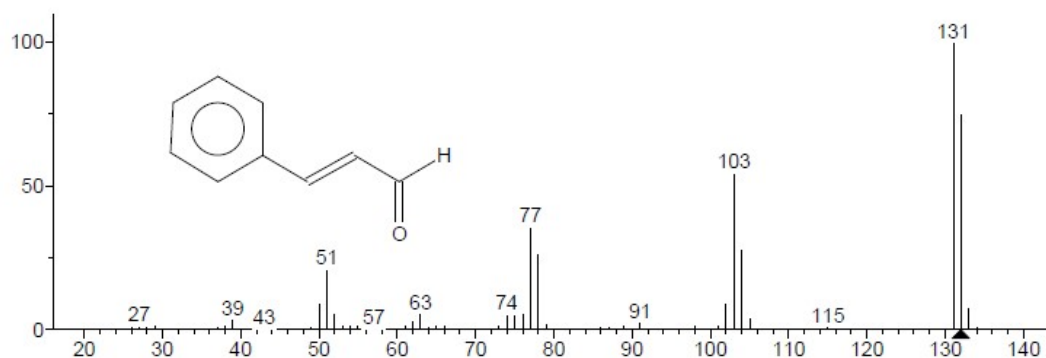


Figure S 28: Mass spectrum of cinnamaldehyde corresponding to the peak at a retention time of 5.98 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Eugenol
C₁₀H₁₂O₂; MF: 934; RMF: 934; Prob 31.1%; CAS: 97-53-0; Lib: mainlib; ID: 153183.

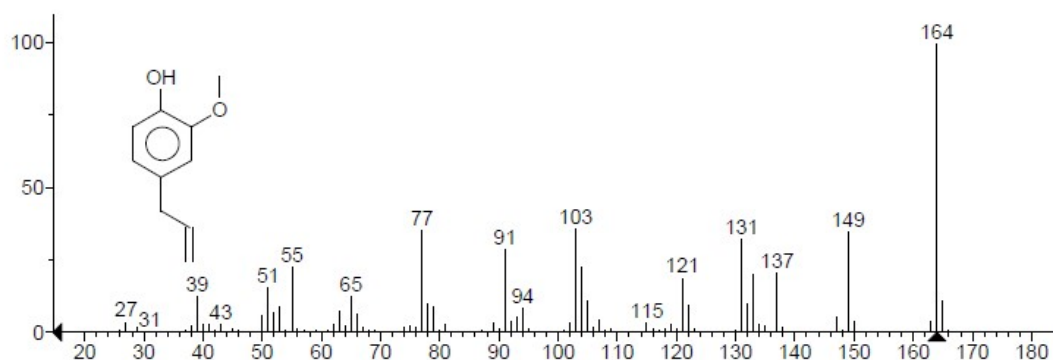


Figure S 29: Mass spectrum of eugenol corresponding to the peak at a retention time of 6.51 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Caryophyllene
C₁₅H₂₄; MF: 953; RMF: 954; Prob 36.1%; CAS: 87-44-5; Lib: mainlib; ID: 66572.

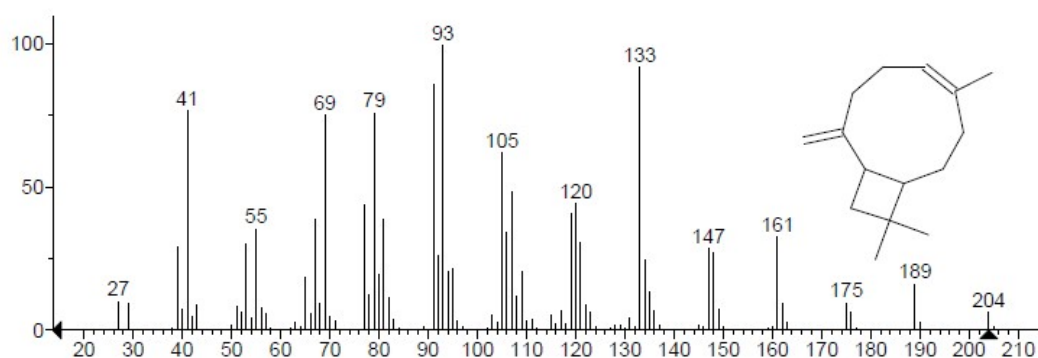


Figure S 30: Mass spectrum of caryophyllene corresponding to the peak at a retention time of 7.05 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Acetic acid, cinnamyl ester
C11H12O2; MF: 933; RMF: 933; Prob 67.7%; CAS: 103-54-8; Lib: mainlib; ID: 11373.

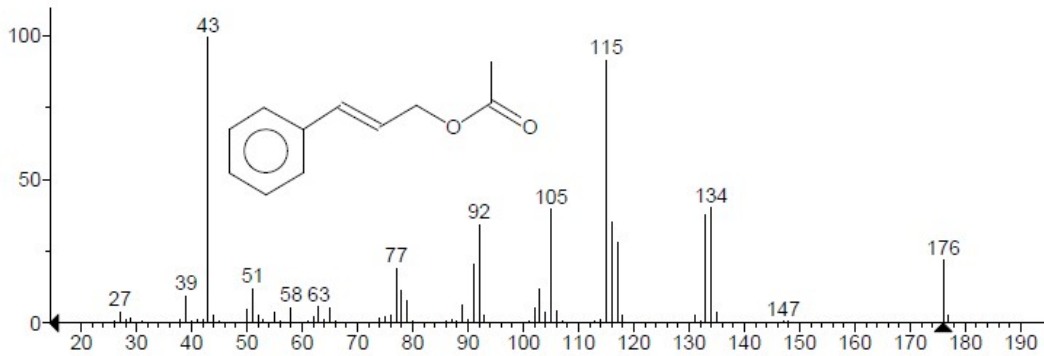


Figure S 31: Mass spectrum of cinnamyl acetate corresponding to the peak at a retention time of 7.11 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Hit 1 : Benzyl Benzoate
C14H12O2; MF: 929; RMF: 929; Prob 96.2%; CAS: 120-51-4; Lib: replib; ID: 16232.

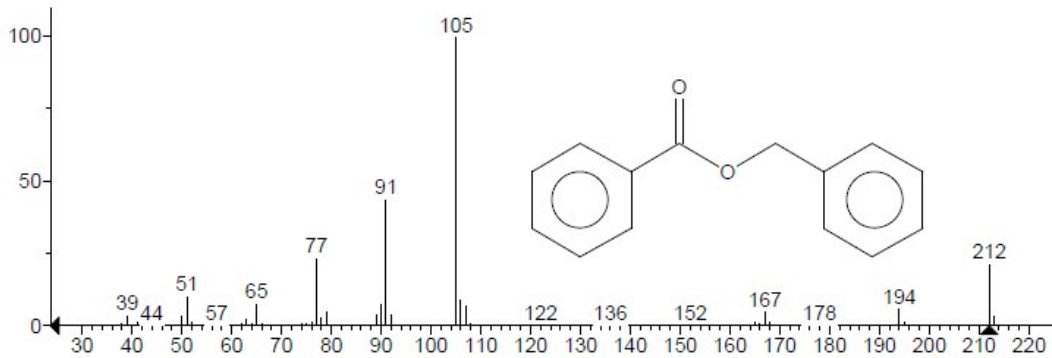


Figure S 32: Mass spectrum of benzyl benzoate corresponding to the peak at a retention time of 9.10 min of the chromatogram of Cinnamomum Cassia by Jean Pütz.

Cinnamomum Verum – Ceylon Oil by PCW

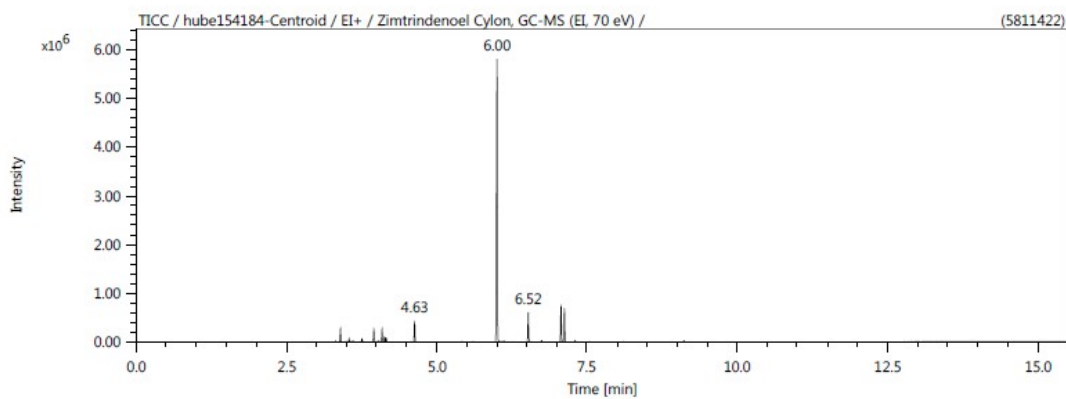


Figure S 33: Chromatogram of the Cinnamomum verum oil by PCW.

Hit 1 : (1R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene
C₁₀H₁₆; MF: 917; RMF: 917; Prob 15.3%; CAS: 7785-70-8; Lib: mainlib; ID: 66241.

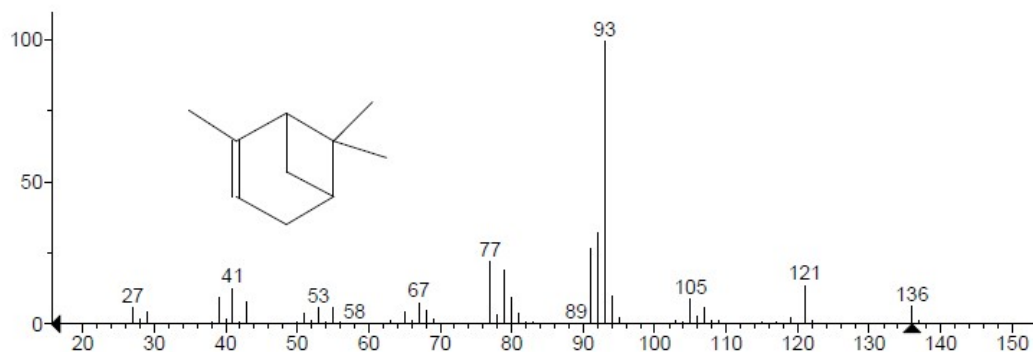


Figure S 34: Mass spectrum of α -pinene corresponding to the peak at a retention time of 3.38 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : Camphene
C₁₀H₁₆; MF: 894; RMF: 895; Prob 28.0%; CAS: 79-92-5; Lib: mainlib; ID: 66500.

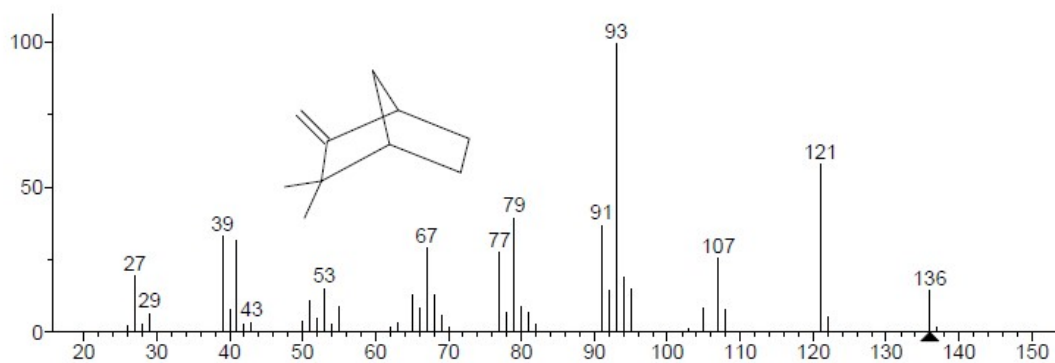


Figure S 35: Mass spectrum of camphene corresponding to the peak at a retention time of 3.52 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : β -Myrcene
C₁₀H₁₆; MF: 879; RMF: 886; Prob 28.5%; CAS: 123-35-3; Lib: replib; ID: 14068.

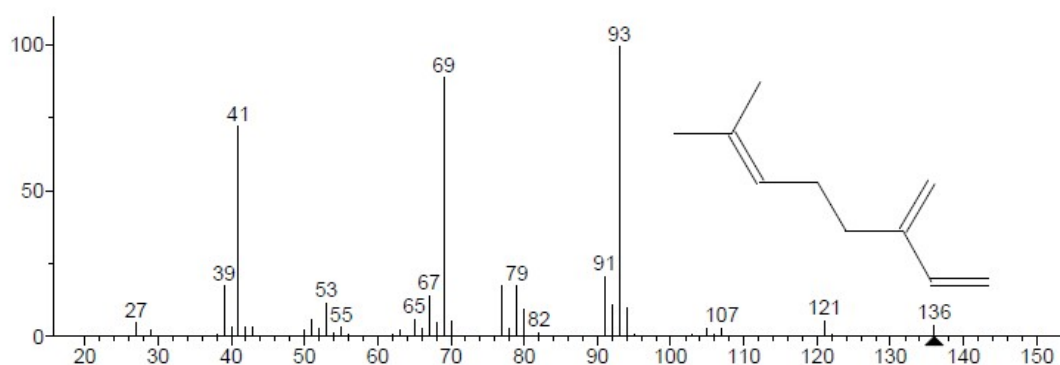


Figure S 36: Mass spectrum of β -myrcene corresponding to the peak at a retention time of 3.75 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : α -Phellandrene
C₁₀H₁₆; MF: 911; RMF: 914; Prob 50.2%; CAS: 99-83-2; Lib: replib; ID: 14115.

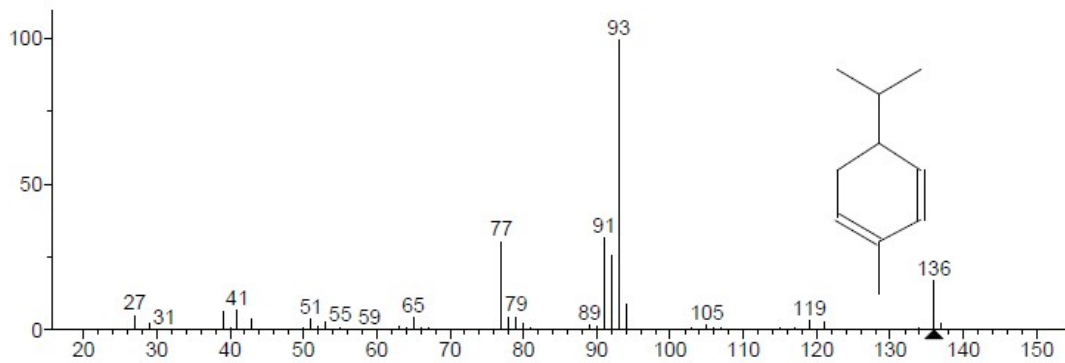


Figure S 37: Mass spectrum of α -phellandrene corresponding to the peak at a retention time of 3.94 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : o-Cymene
C₁₀H₁₄; MF: 935; RMF: 935; Prob 27.1%; CAS: 527-84-4; Lib: replib; ID: 18731.

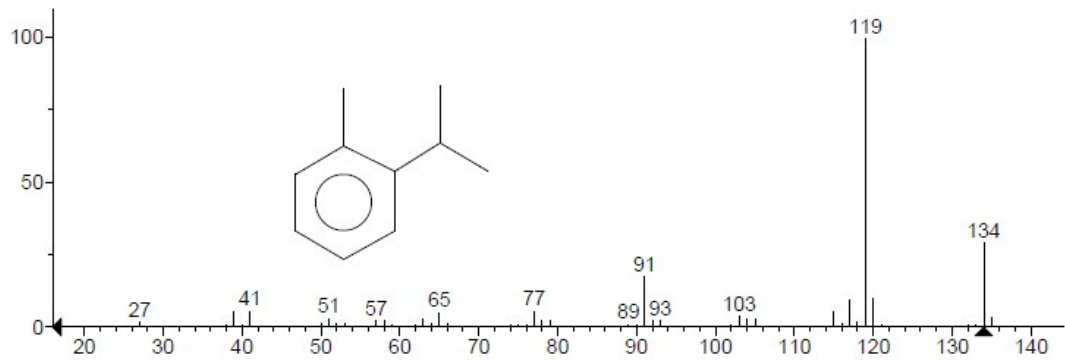


Figure S 38: Mass spectrum of o-cymene corresponding to the peak at a retention time of 4.07 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : D-Limonene
C₁₀H₁₆; MF: 923; RMF: 923; Prob 49.8%; CAS: 5989-27-5; Lib: replib; ID: 8354.

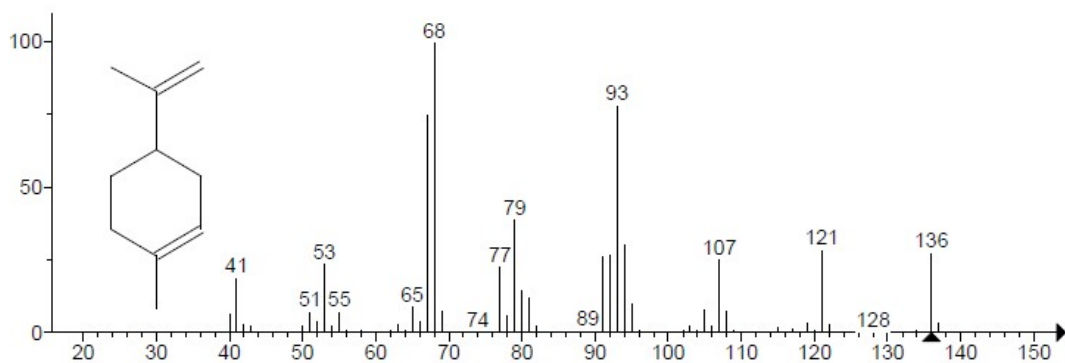


Figure S 39: Mass spectrum of limonene corresponding to the peak at a retention time of 4.12 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 2 : β -Phellandrene
C₁₀H₁₆; MF: 925; RMF: 926; Prob 37.3%; CAS: 555-10-2; Lib: mainlib; ID: 66050.

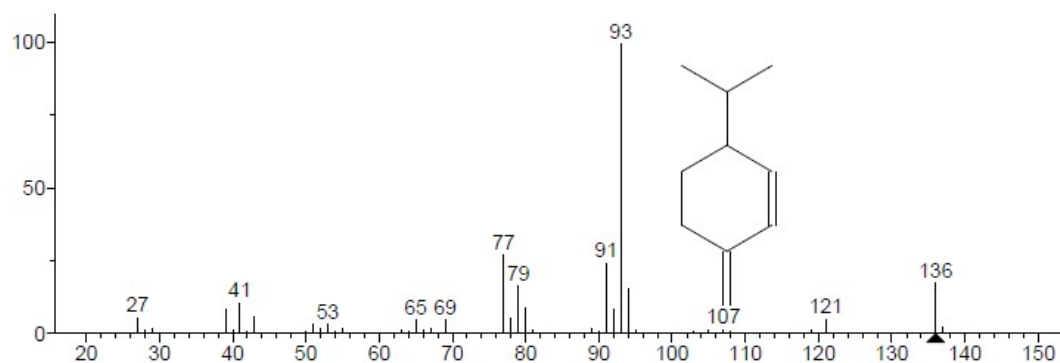


Figure S 40: Mass spectrum of β -phellandrene corresponding to the peak at a retention time of 4.15 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : Linalool
C₁₀H₁₈O; MF: 928; RMF: 928; Prob 75.3%; CAS: 78-70-6; Lib: mainlib; ID: 39161.

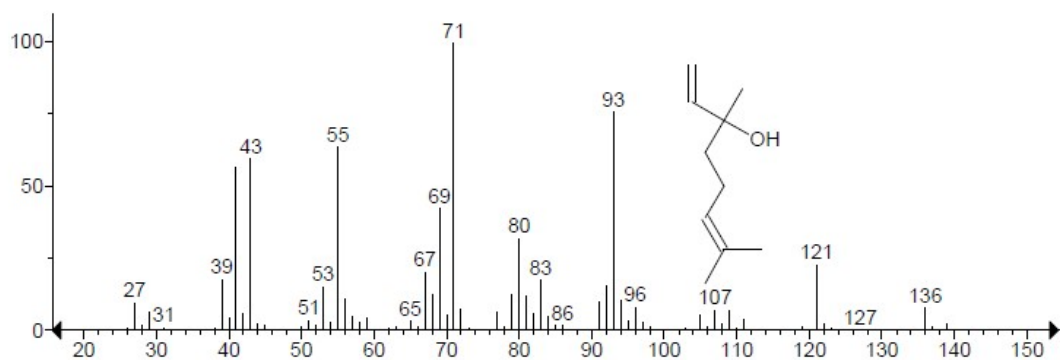


Figure S 41: Mass spectrum of linalool corresponding to the peak at a retention time of 4.62 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : 2-Propenal, 3-phenyl-
C₉H₈O; MF: 960; RMF: 960; Prob 35.8%; CAS: 104-55-2; Lib: mainlib; ID: 115882.

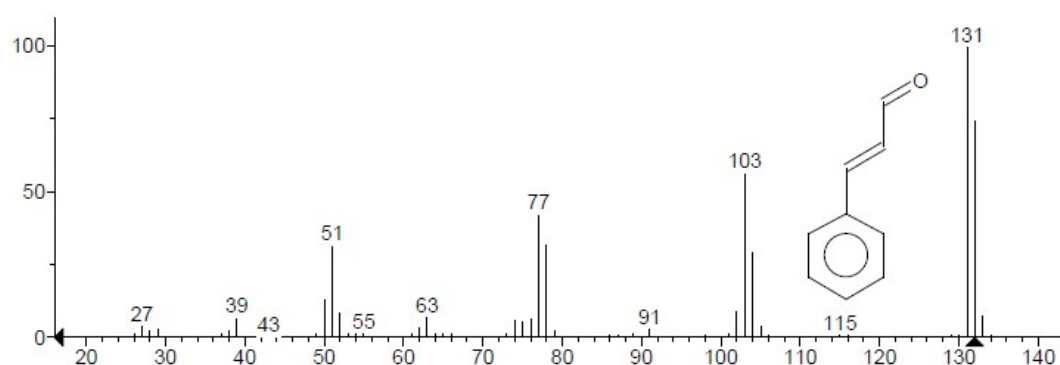


Figure S 42: Mass spectrum of cinnamaldehyde corresponding to the peak at a retention time of 5.98 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : Eugenol
C10H12O2; MF: 929; RMF: 929; Prob 26.4%; CAS: 97-53-0; Lib: replib; ID: 25335.

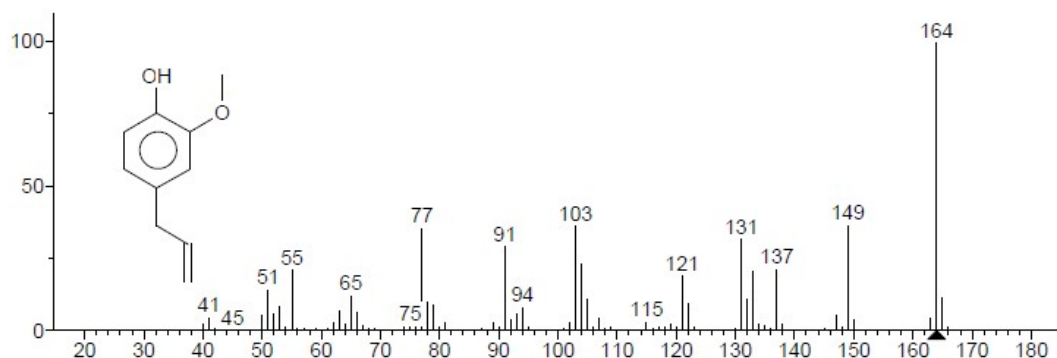


Figure S 43: Mass spectrum of eugenol corresponding to the peak at a retention time of 6.51 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : Caryophyllene
C15H24; MF: 963; RMF: 964; Prob 42.2%; CAS: 87-44-5; Lib: mainlib; ID: 66572.

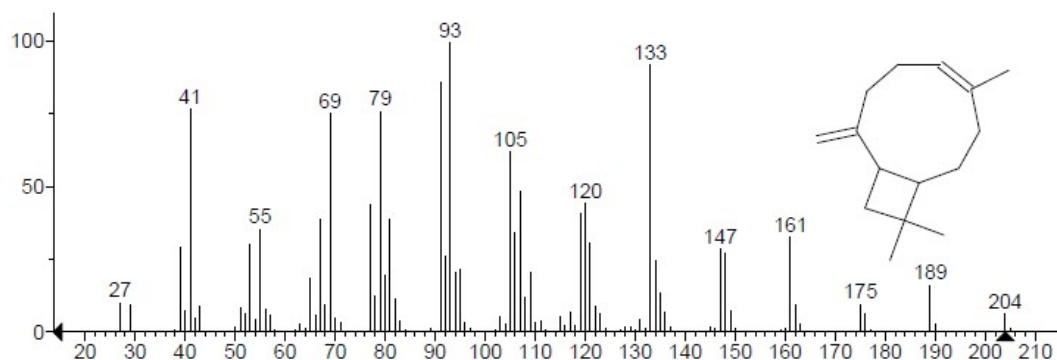


Figure S 44: Mass spectrum of caryophyllene corresponding to the peak at a retention time of 7.05 min of the chromatogram of *Cinnamomum Verum* by PCW.

Hit 1 : Acetic acid, cinnamyl ester
C11H12O2; MF: 928; RMF: 928; Prob 80.7%; CAS: 103-54-8; Lib: mainlib; ID: 11373.

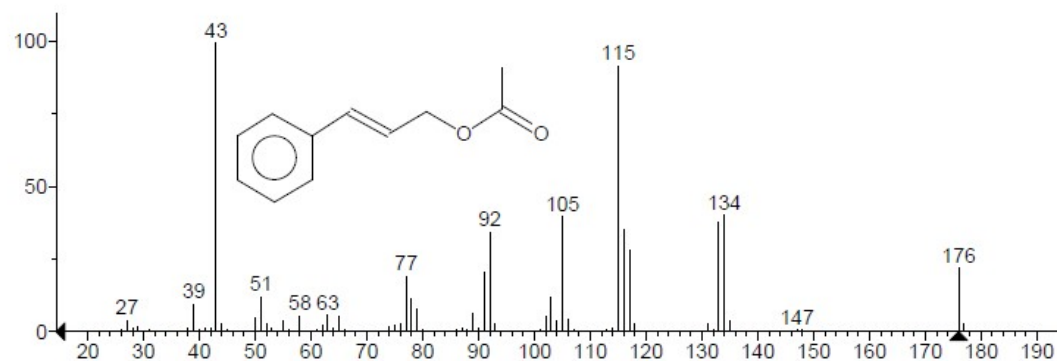


Figure S 45: Mass spectrum of cinnamyl acetate corresponding to the peak at a retention time of 7.11 min of the chromatogram of *Cinnamomum Verum* by PCW.

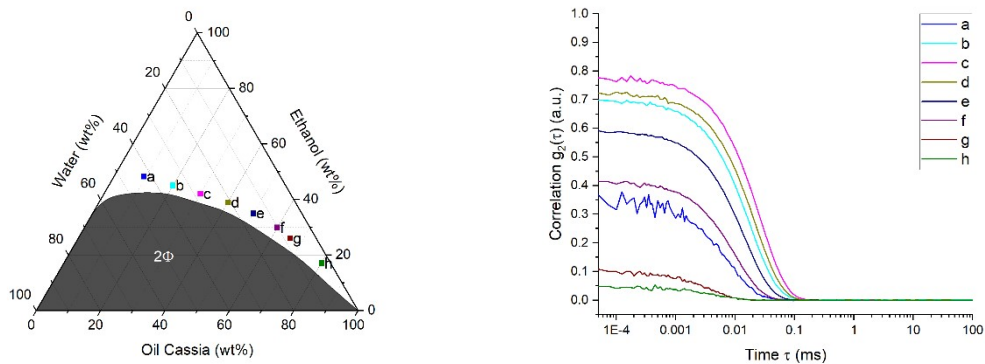


Figure S 46: Ternary phase diagram of water/ethanol/oil cassia with corresponding correlation curves.

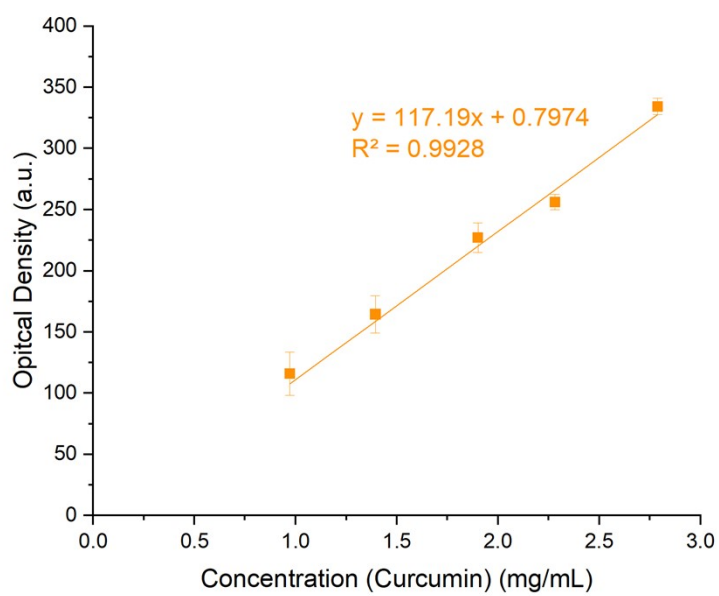


Figure S 47: Calibration curve of curcumin in EtOH at $\lambda=425$ nm.