Appendix - Identification of Bioactive Plant Volatiles in the Carob Moth by means of GC-EAD and GC-Orbitrap MS

1 TIC Chromatograms

TIC chromatogram in EI mode of Pomegranate extract is depicted in figure 1.

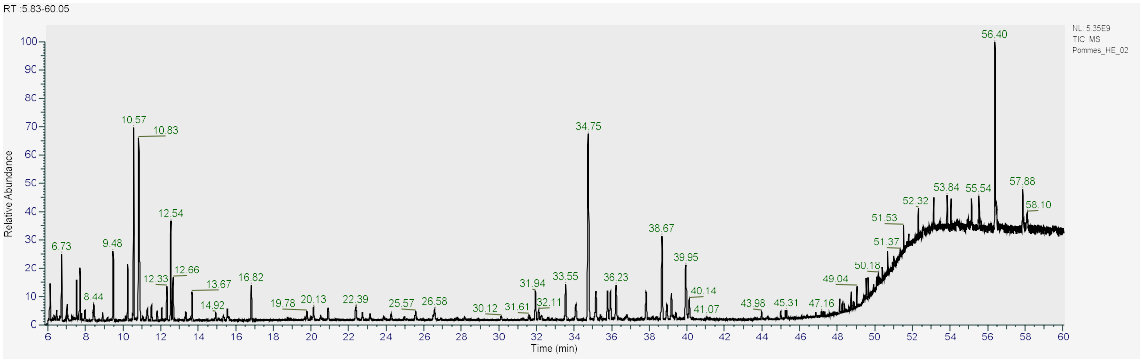

Figure 1. TIC EI of Pomegranate extract.

TIC chromatogram in PCI (CH4) mode of Pomegranate extract is depicted in figure 2.

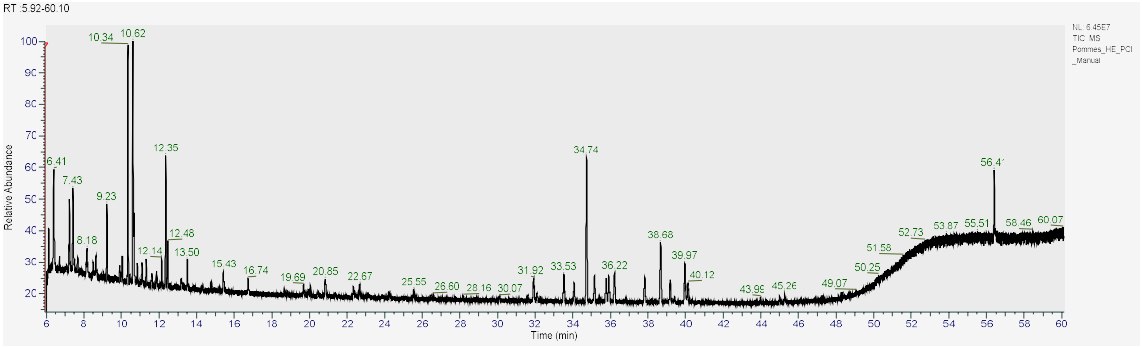

Figure 2. TIC PCI (CH4) of Pomegranate extract.

TIC chromatogram in EI mode of beta caryophyllene extract is depicted in figure 3.

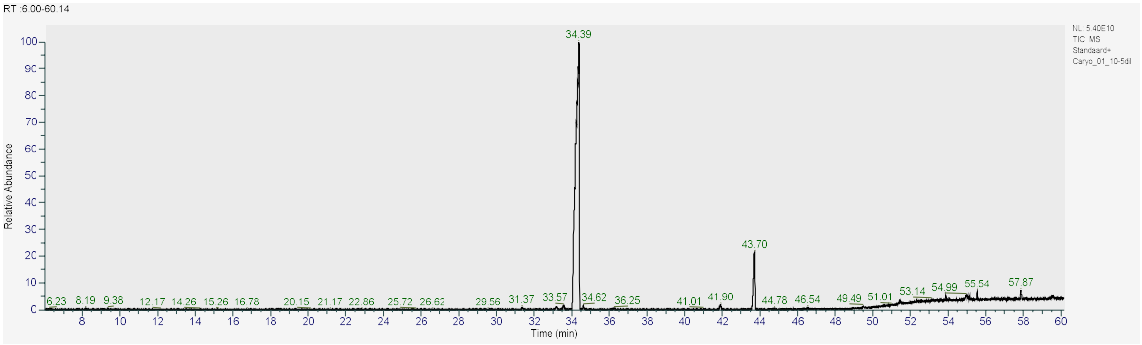

Figure 3. TIC EI of beta caryophyllene extract.

TIC chromatogram in PCI (CH4) mode of beta caryophyllene extract is depicted in figure 4.

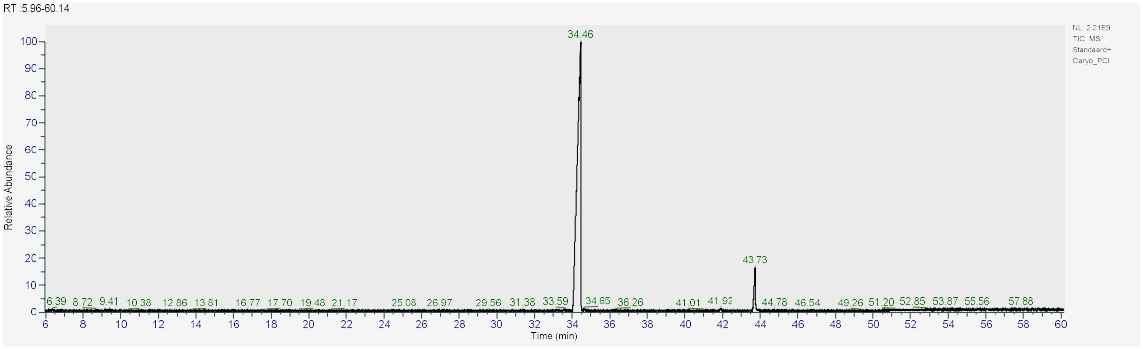

Figure 4. TIC PCI (CH4) of beta caryophyllene extract.

2 Identified compounds

Components identified using a GC-Orbitrap MS standardized workflow are presented in table 1.

Table 1. Component identification by means of GC-Orbitrap MS standardized workflow.

Peak	RT (min)	EAD	Candidate	TIC area	MF [1]	HRF [2]	RI [3]	ΔRI [4]	PCI [5]	A_{ppm} [6]	FISh [7]
1	6.26	N	Hexanal	9788062	C6H12O	98.8	n/a*	n/a	+	0.45	+
2	7.06	N	*trans*-3-Hexen-1-ol	5693447	C6H12O	99.3	834	18	-	n/a	+
3	7.53	N	*cis*-3-Hexen-1-ol	495934241	C6H12O	99.8	861	4	-	n/a	+
4	9.48	Y	α-Pinene	969038547	C10H16	98.3	945	3	+	-0.67	+
5	**34.08**	**Y**	**β-Caryophyllene**	**244444607**	C15H24	99.9	**1424**	**5**	**+**	**0.78**	**+**
6	34.75	Y	*cis*-α-Bergamotene	3107441600	C15H24	99.7	1435	20	+	0.65	+
7	35.16	Y	β-Cedrene	455112611	C15H24	99.7	1442	21	+	0.57	+
8	35.78	Y	*cis*-β-Farnesene	467888846	C15H24	99.8	1452	12	+	0.48	+
9	35.92	Y	Isogermacrene D	468220393	C15H24	99.7	1455	7	+	0.09	+
10	36.23	Y	α-Humulene	573861939	C15H24	99.8	1460	6	+	0.49	+
11	37.83	Y	9-epi-(E)-Caryophyllene	477749145	C15H24	99.8	1486	8	+	0.21	+
12	38.67	Y	Pentadecane	1383693628	C15H32	n/a	1500	0	-	n/a	+
13	39.18	Y	Valencene	438004037	C15H24	99.5	1509	9	+	-0.03	+
14	39.95	Y	Ethyl-4-ethoxy benzoate	916220747	C11H14O3	98.0	1523	1	+	-0.28	+

2.1 Peak 1 - Hexanal

EI spectrum of hexanal in the Pomegranate extract is presented in figure 5.

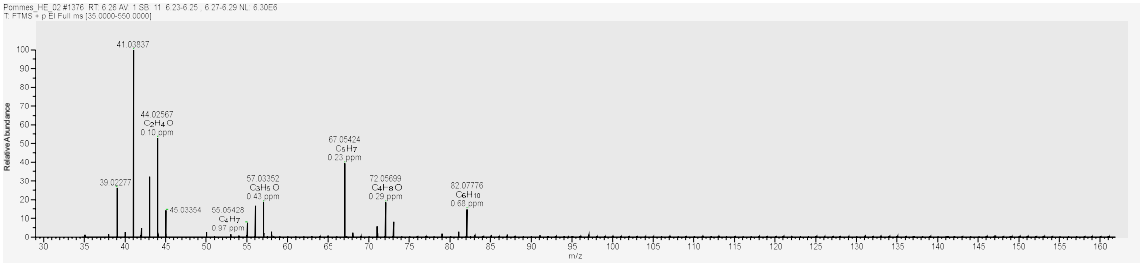

Figure 5. EI m/z spectrum of hexanal in the Pomegranate extract.

PCI (CH4) spectrum of hexanal in the Pomegranate extract is presented in figure 6. The adducts of methane are depicted above the corresponding m/z.

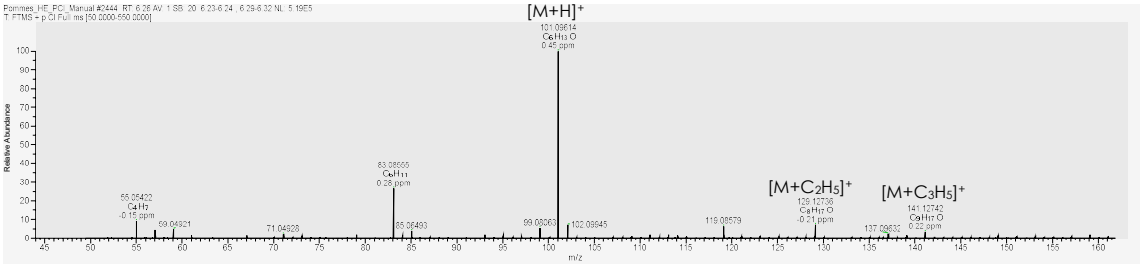

Figure 6. PCI (CH4) m/z spectrum of hexanal in the Pomegranate extract.

The theoretical fragmentation pattern of hexanal (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 7. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

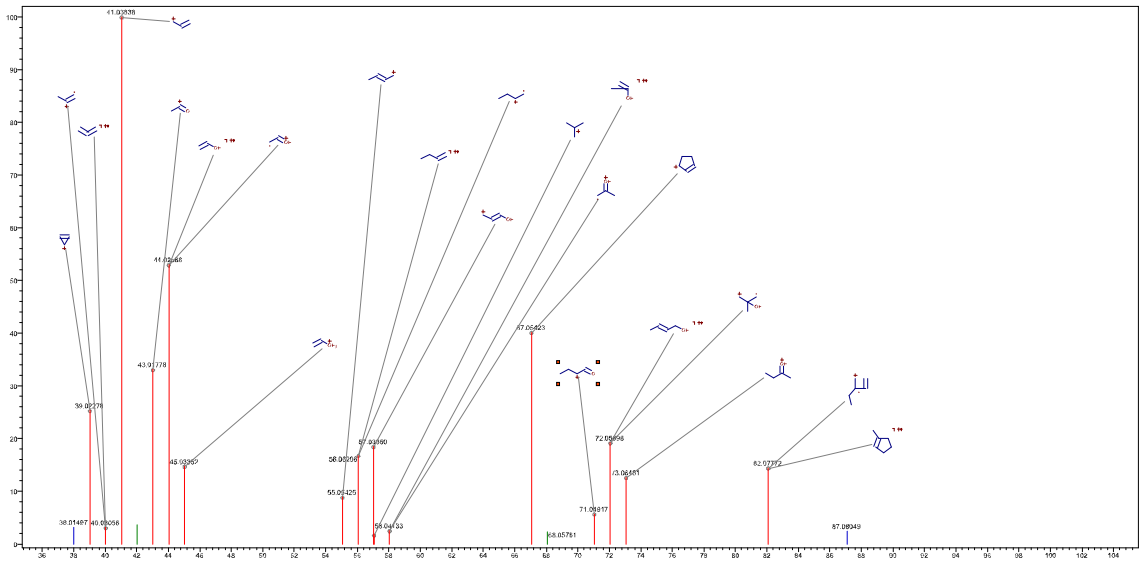

Figure 7. EI m/z spectrum with assigned fragments of hexanal in the Pomegranate extract.

2.2 Peak 2 - *trans*-3-Hexen-1-ol

EI spectrum of *trans*-3-Hexen-1-ol in the Pomegranate extract is presented in figure 8.

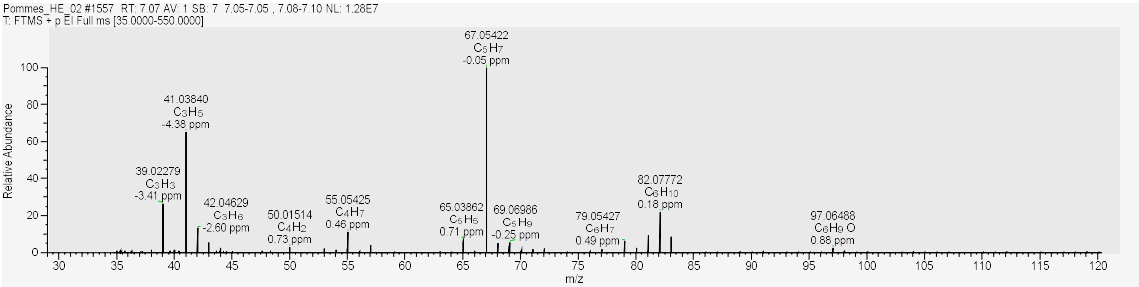

Figure 8. EI m/z spectrum of *trans*-3-Hexen-1-ol in the Pomegranate extract.

The molecular ion and corresponding adducts in the PCI (CH4) spectrum are not visible for *trans*-3-Hexen-1-ol.

The theoretical fragmentation pattern of *trans*-3-Hexen-1-ol (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 9. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

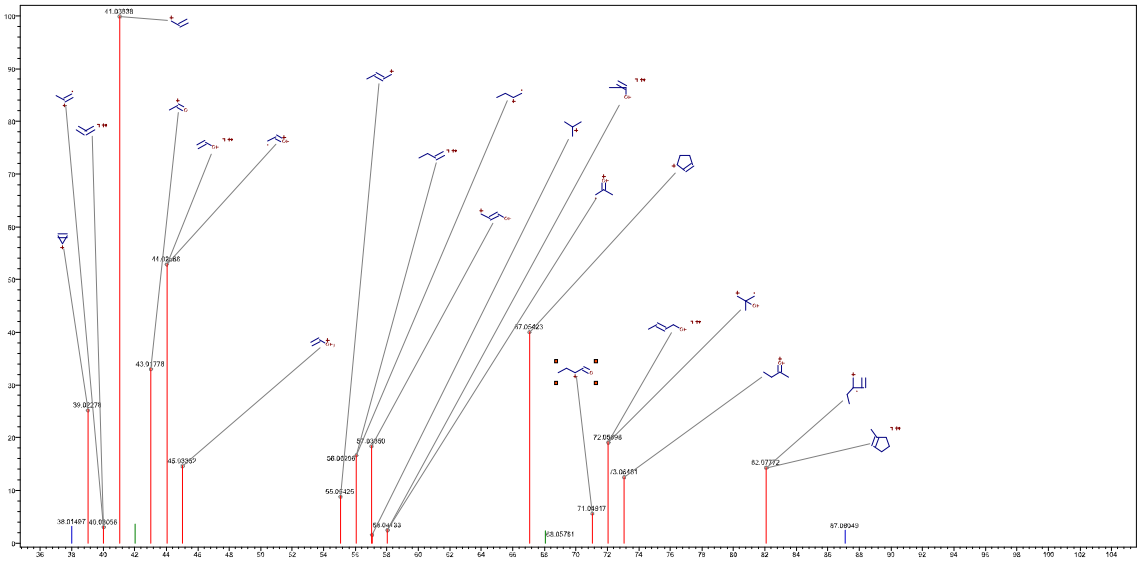

Figure 9. EI m/z spectrum with assigned fragments of *trans*-3-Hexen-1-ol in the Pomegranate extract.

2.3 Peak 3 - *cis*-3-Hexen-1-ol

EI spectrum of *cis*-3-Hexen-1-ol in the Pomegranate extract is presented in figure 10.

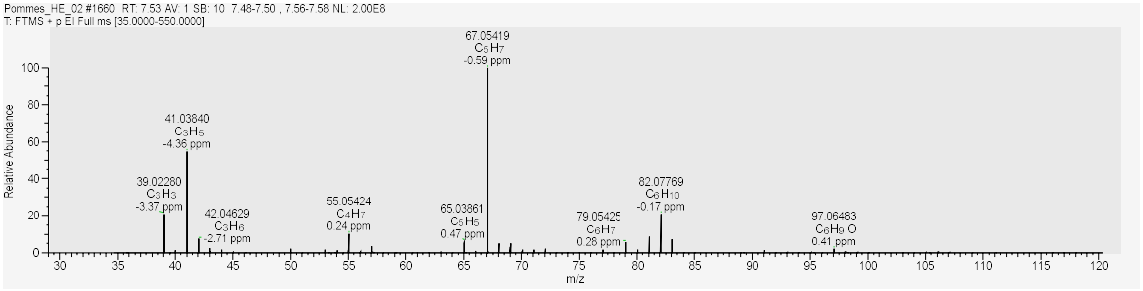

Figure 10. EI m/z spectrum of *cis*-3-Hexen-1-ol in the Pomegranate extract.

The molecular ion and corresponding adducts in the PCI (CH4) spectrum are not visible for *cis*-3-Hexen-1-ol.

The theoretical fragmentation pattern of *cis*-3-Hexen-1-ol (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 9. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

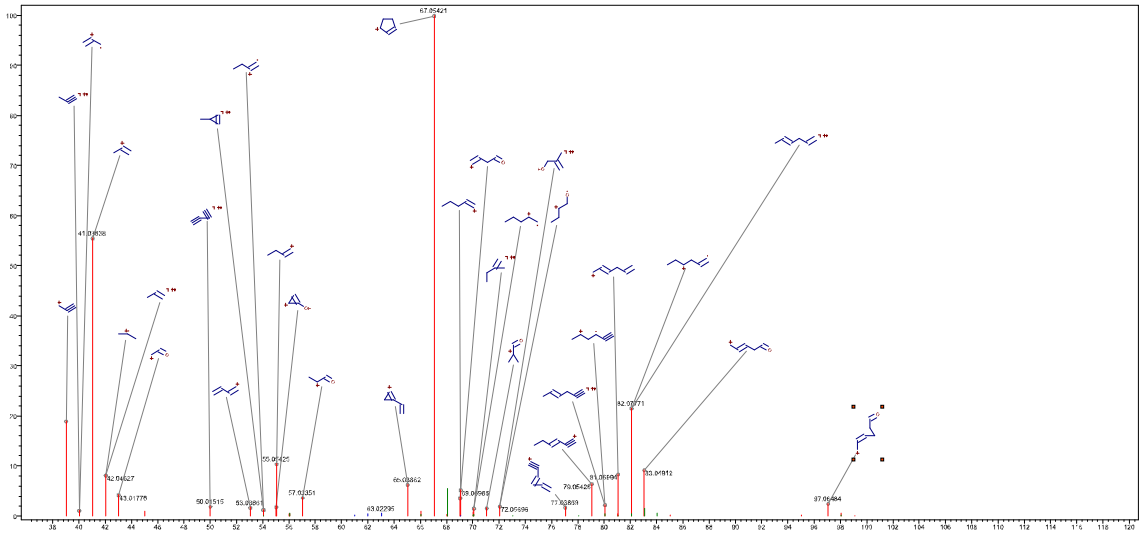

Figure 11. EI m/z spectrum with assigned fragments of *cis*-3-Hexen-1-ol in the Pomegranate extract.

2.4 Peak 4 - α-Pinene

EI spectrum of α-Pinene in the Pomegranate extract is presented in figure 12.

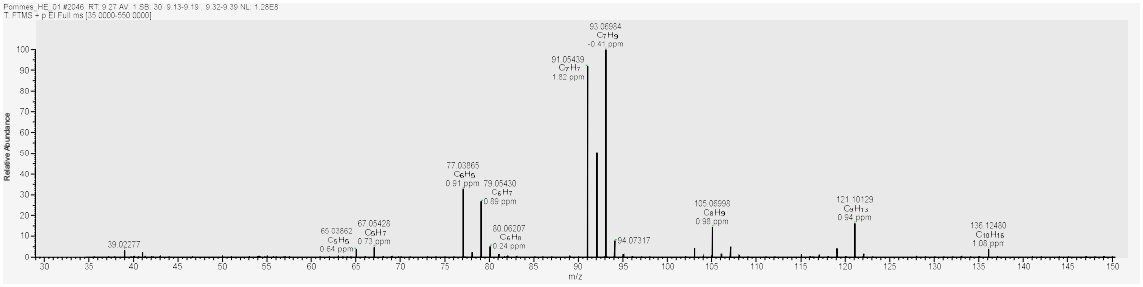

Figure 12. EI m/z spectrum of α-Pinene in the Pomegranate extract.

PCI (CH4) spectrum of α-Pinene in the Pomegranate extract is presented in figure 13. The adducts of methane are depicted above the corresponding m/z.

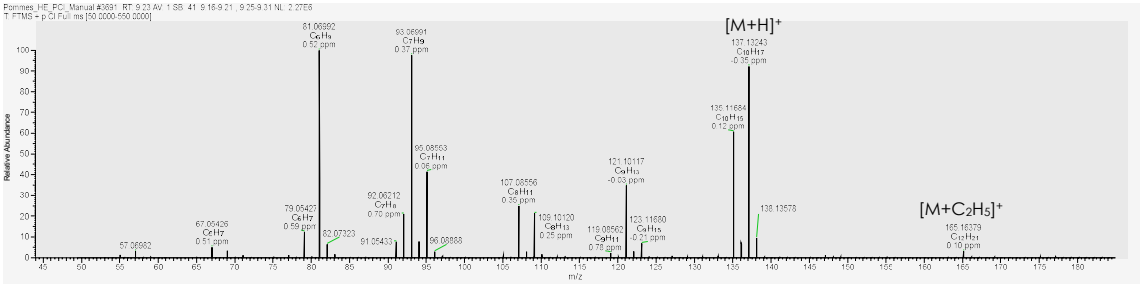

Figure 13. PCI (CH4) m/z spectrum of α-Pinene in the Pomegranate extract.

The theoretical fragmentation pattern of α-Pinene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 14. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

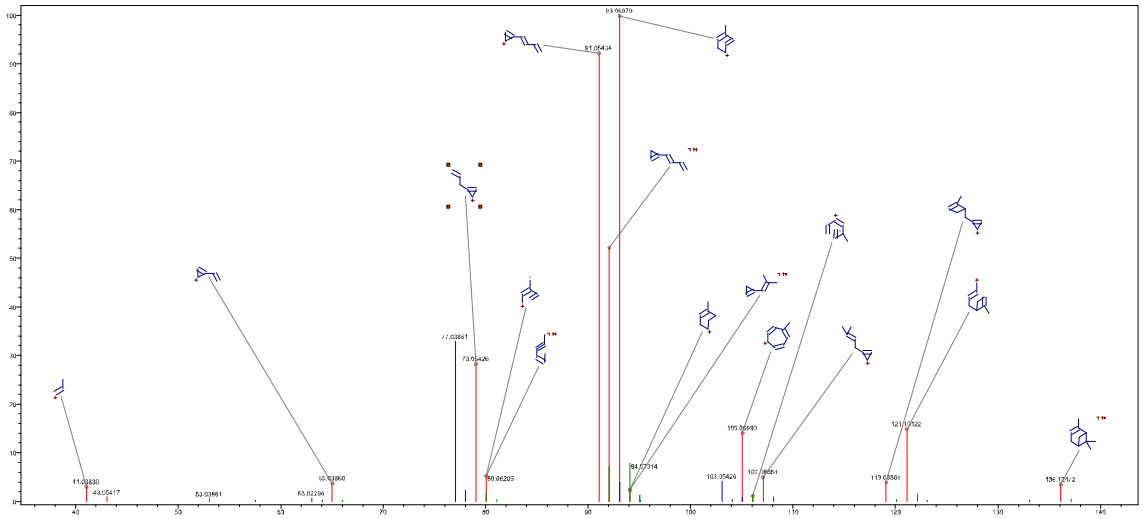

Figure 14. EI m/z spectrum with assigned fragments of α-Pinene in the Pomegranate extract.

2.5 Peak 5 - β-Caryophyllene

EI spectrum of β-Caryophyllene in the Pomegranate extract is presented in figure 15.

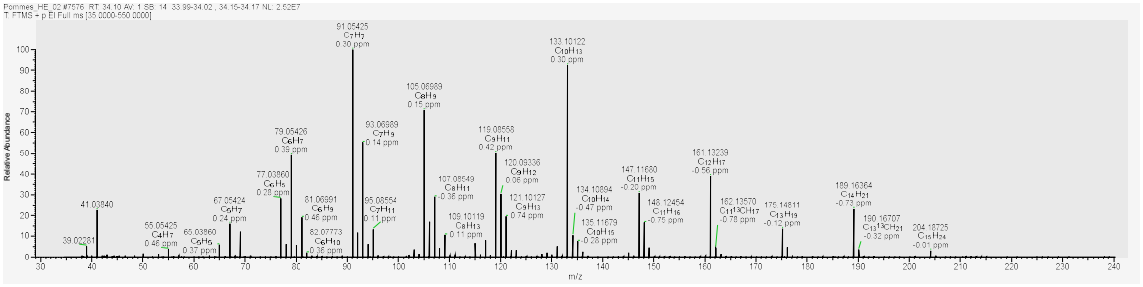

Figure 15. EI m/z spectrum of β-Caryophyllene in the Pomegranate extract.

PCI (CH4) spectrum of β-Caryophyllene in the Pomegranate extract is presented in figure 16. The adducts of methane are depicted above the corresponding m/z.

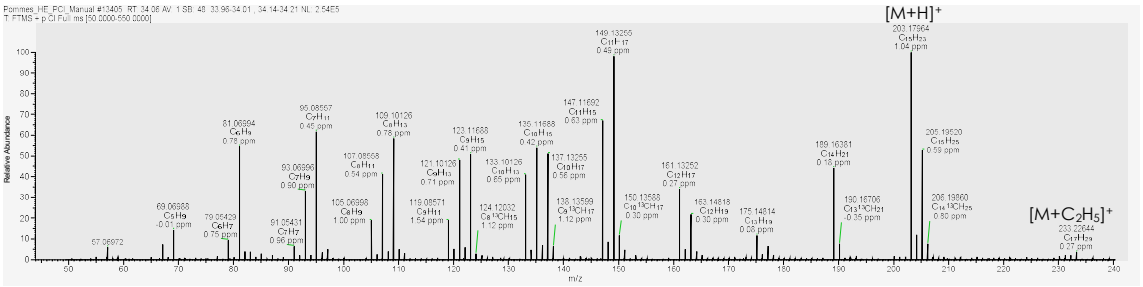

Figure 16. PCI (CH4) m/z spectrum of β-Caryophyllene in the Pomegranate extract.

The theoretical fragmentation pattern of β-Caryophyllene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 17. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

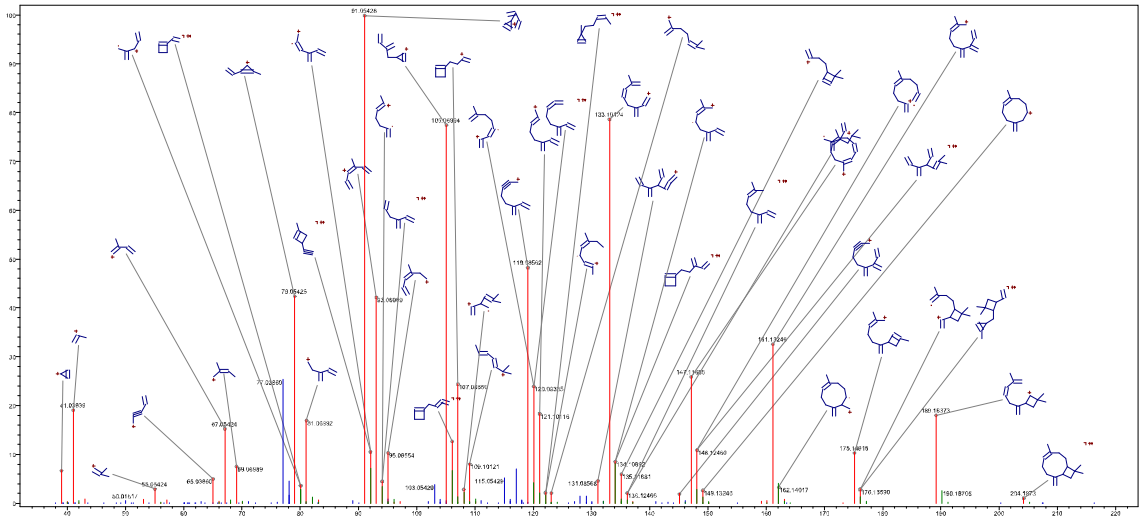

Figure 17. EI m/z spectrum with assigned fragments of β-Caryophyllene in the Pomegranate extract.

2.6 Peak 6 - cis-α-Bergamotene

EI spectrum of cis-α-Bergamotene in the Pomegranate extract is presented in figure 18.

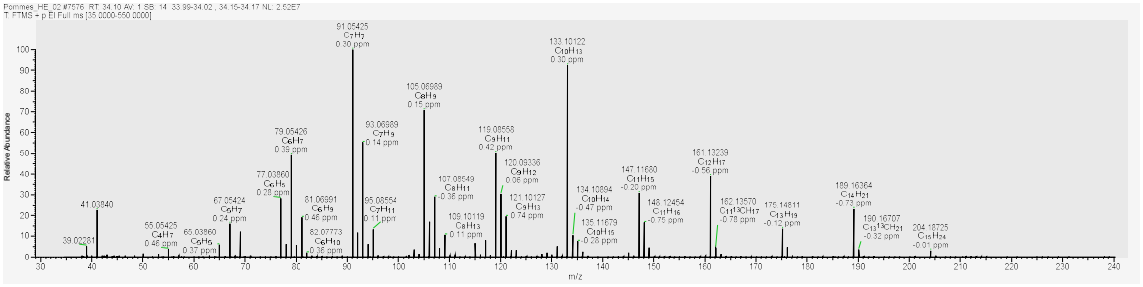

Figure 18. EI m/z spectrum of cis-α-Bergamotene in the Pomegranate extract.

PCI (CH4) spectrum of cis-α-Bergamotene in the Pomegranate extract is presented in figure 19. The adducts of methane are depicted above the corresponding m/z.

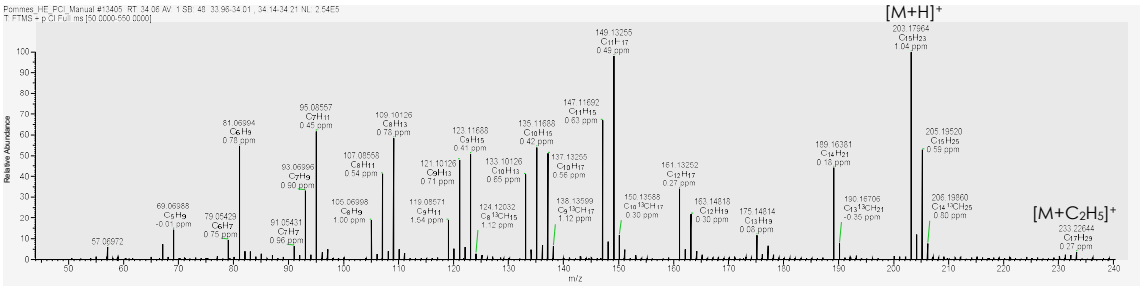

Figure 19. PCI (CH4) m/z spectrum of cis-α-Bergamotene in the Pomegranate extract.

The theoretical fragmentation pattern of cis-α-Bergamotene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 20. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

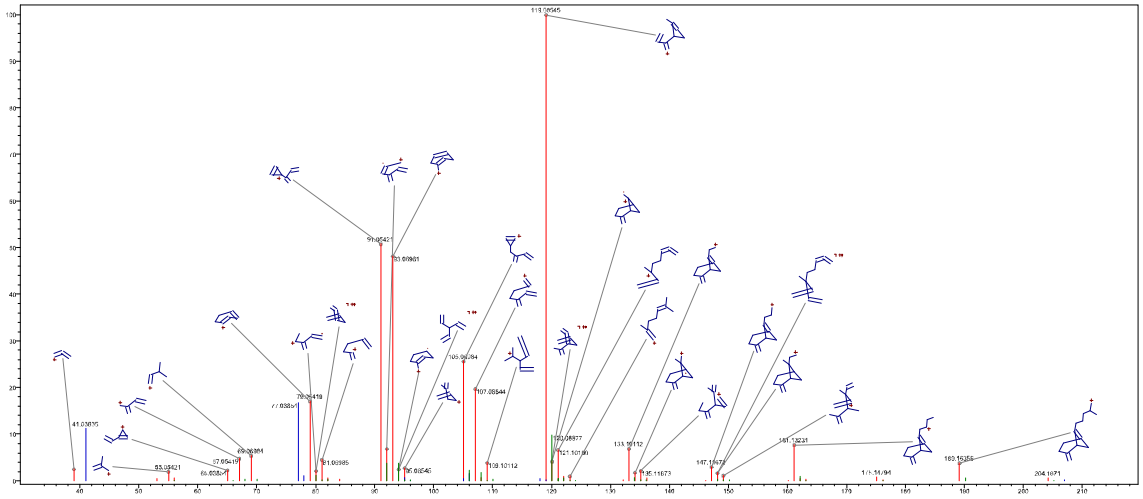

Figure 20. EI m/z spectrum with assigned fragments of cis-α-Bergamotene in the Pomegranate extract.

2.7 Peak 7 - β-Cedrene

EI spectrum of β-Cedrene in the Pomegranate extract is presented in figure 21.

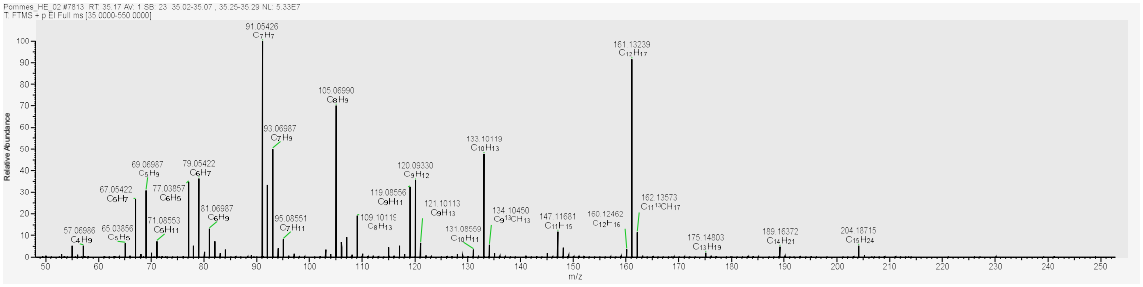

Figure 21. EI m/z spectrum of β-Cedrene in the Pomegranate extract.

PCI (CH4) spectrum of β-Cedrene in the Pomegranate extract is presented in figure 22. The adducts of methane are depicted above the corresponding m/z.

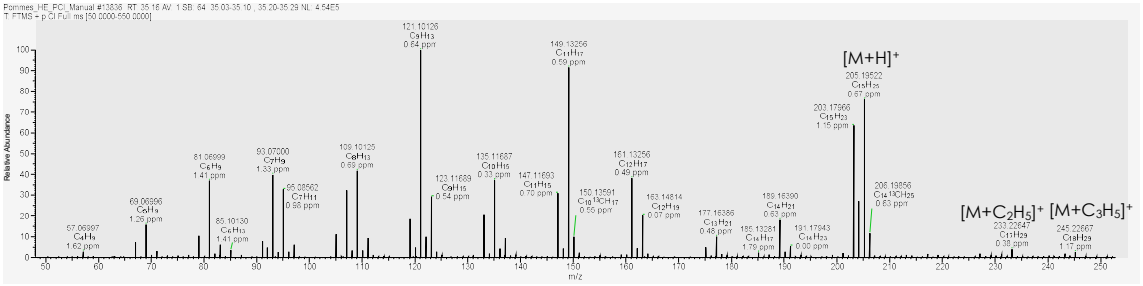

Figure 22. PCI (CH4) m/z spectrum of β-Cedrene in the Pomegranate extract.

The theoretical fragmentation pattern of β-Cedrene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 23. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

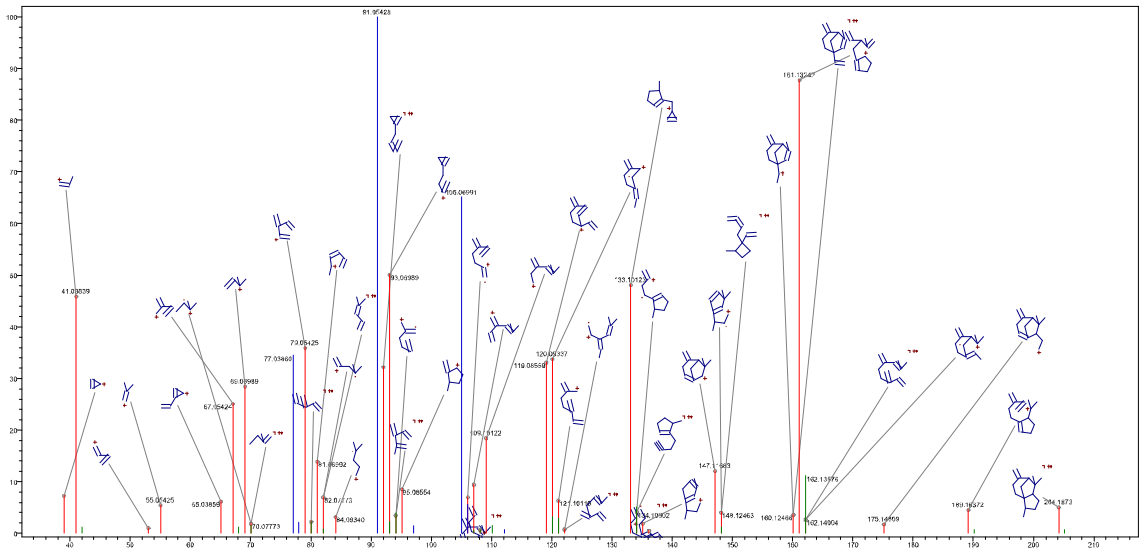

Figure 23. EI m/z spectrum with assigned fragments of β-Cedrene in the Pomegranate extract.

2.8 Peak 8 - cis-β-Farnesene

EI spectrum of cis-β-Farnesene in the Pomegranate extract is presented in figure 24.

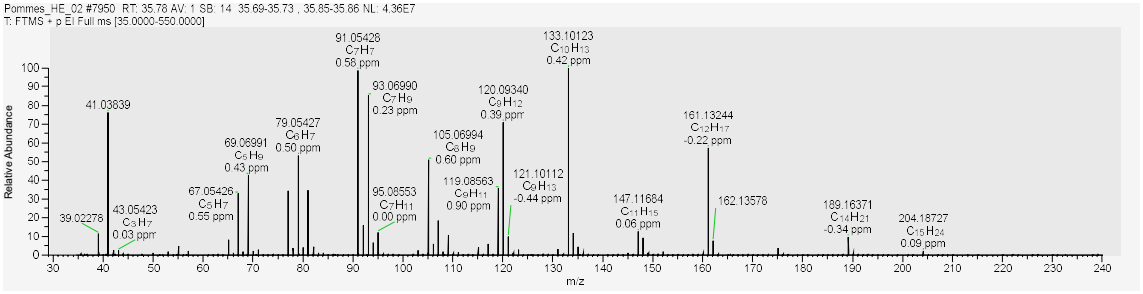

Figure 24. EI m/z spectrum of cis-β-Farnesene in the Pomegranate extract.

PCI (CH4) spectrum of cis-β-Farnesene in the Pomegranate extract is presented in figure 25. The adducts of methane are depicted above the corresponding m/z.

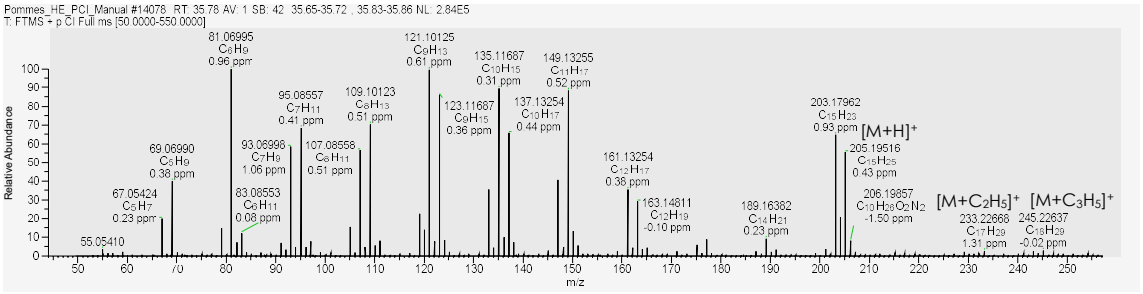

Figure 25. PCI (CH4) m/z spectrum of cis-β-Farnesene in the Pomegranate extract.

The theoretical fragmentation pattern of cis-β-Farnesene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 26. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

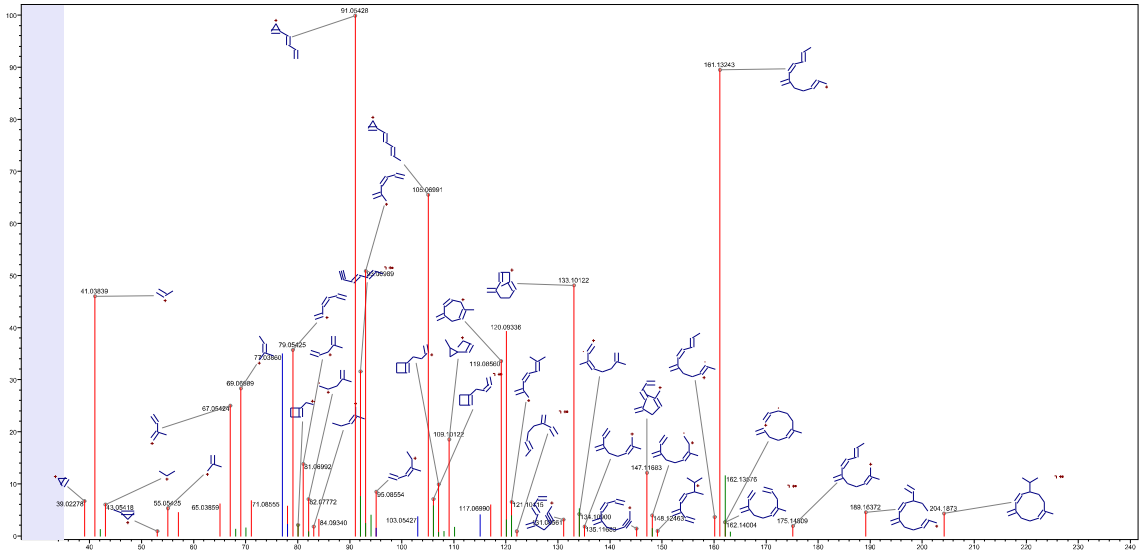

Figure 26. EI m/z spectrum with assigned fragments of cis-β-Farnesene in the Pomegranate extract.

2.9 Peak 9 - Isogermacrene D

EI spectrum of Isogermacrene D in the Pomegranate extract is presented in figure 27.

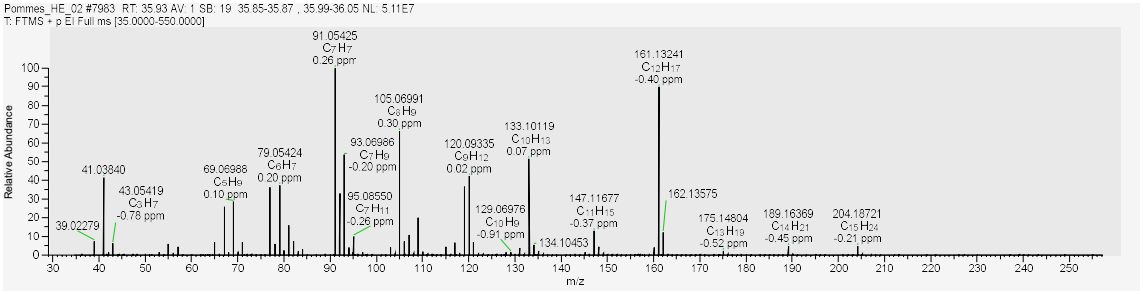

Figure 27. EI m/z spectrum of Isogermacrene D in the Pomegranate extract.

PCI (CH4) spectrum of Isogermacrene D in the Pomegranate extract is presented in figure 28. The adducts of methane are depicted above the corresponding m/z.

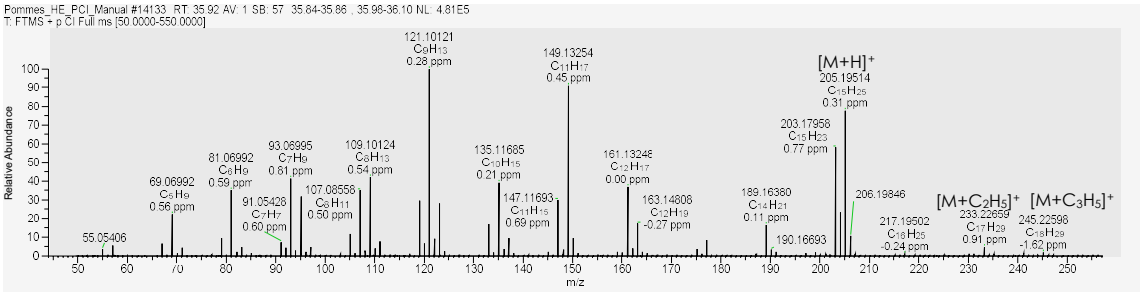

Figure 28. PCI (CH4) m/z spectrum of Isogermacrene D in the Pomegranate extract.

The theoretical fragmentation pattern of Isogermacrene D (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 29. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

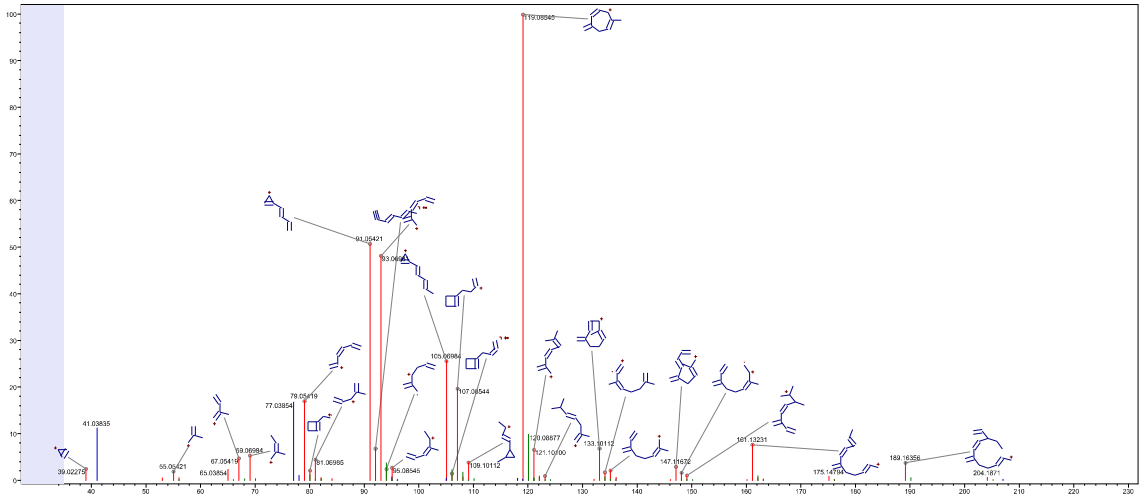

Figure 29. EI m/z spectrum with assigned fragments of Isogermacrene D in the Pomegranate extract.

2.10 Peak 10 - α-Humulene

EI spectrum of α-Humulene in the Pomegranate extract is presented in figure 30.

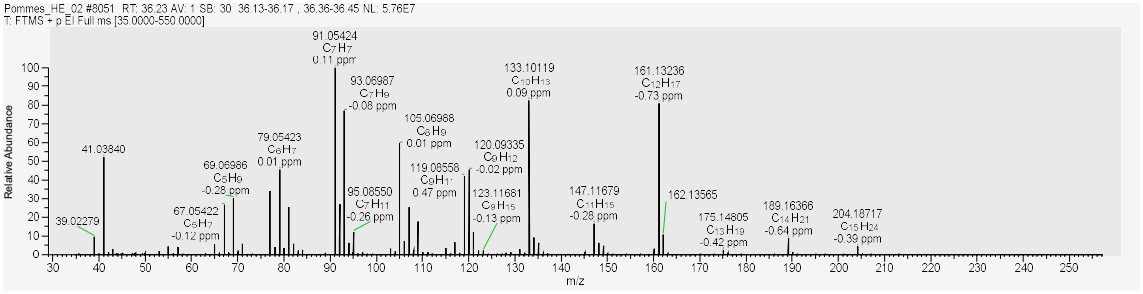

Figure 30. EI m/z spectrum of α-Humulene in the Pomegranate extract.

PCI (CH4) spectrum of α-Humulene in the Pomegranate extract is presented in figure 31. The adducts of methane are depicted above the corresponding m/z.

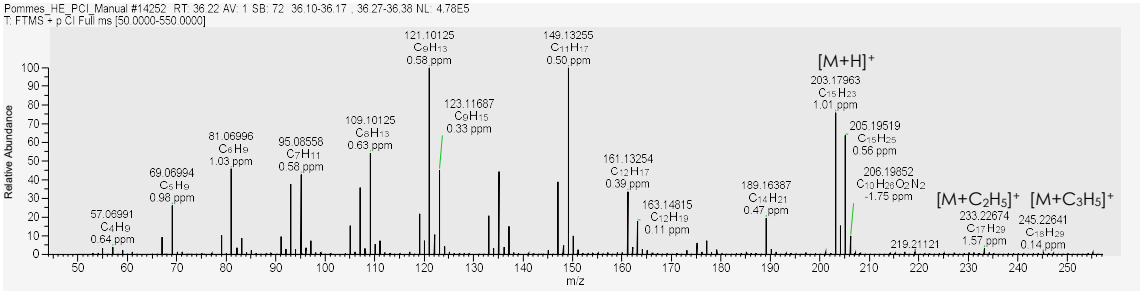

Figure 31. PCI (CH4) m/z spectrum of α-Humulene in the Pomegranate extract.

The theoretical fragmentation pattern of α-Humulene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 32. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

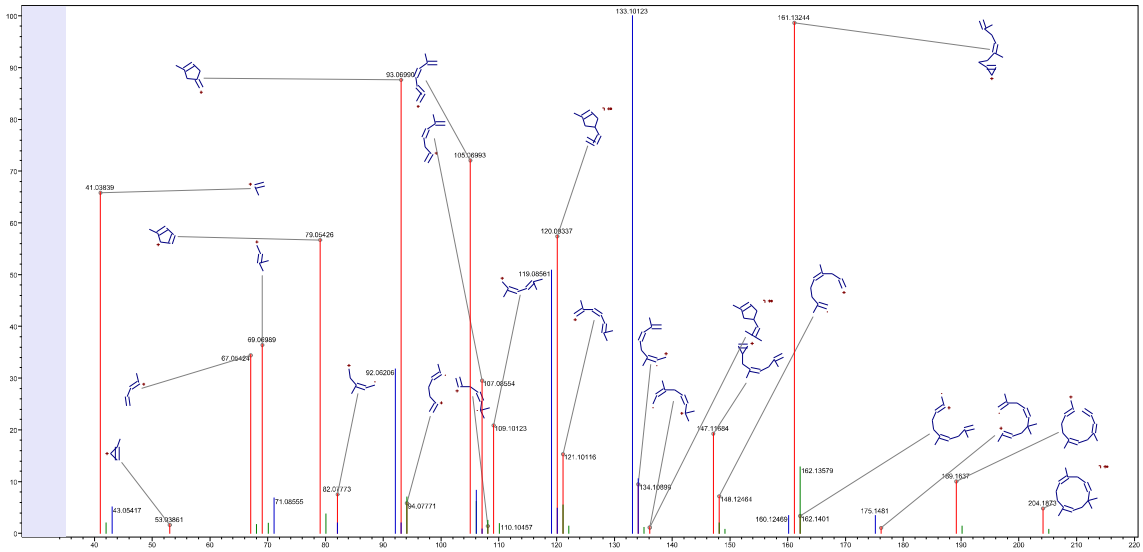

Figure 32. EI m/z spectrum with assigned fragments of α-Humulene in the Pomegranate extract.

2.11 Peak 11 - 9-epi-(E)-Caryophyllene

EI spectrum of 9-epi-(E)-Caryophyllene in the Pomegranate extract is presented in figure 33.

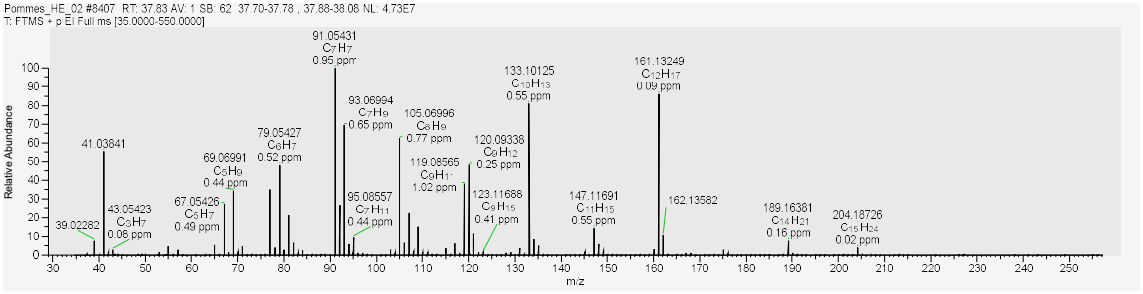

Figure 33. EI m/z spectrum of 9-epi-(E)-Caryophyllene in the Pomegranate extract.

PCI (CH4) spectrum of 9-epi-(E)-Caryophyllene in the Pomegranate extract is presented in figure 34. The adducts of methane are depicted above the corresponding m/z.

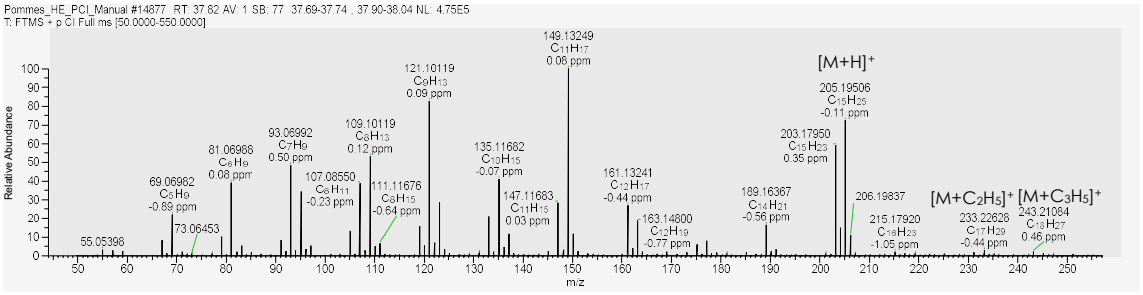

Figure 34. PCI (CH4) m/z spectrum of 9-epi-(E)-Caryophyllene in the Pomegranate extract.

The theoretical fragmentation pattern of 9-epi-(E)-Caryophyllene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 35. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

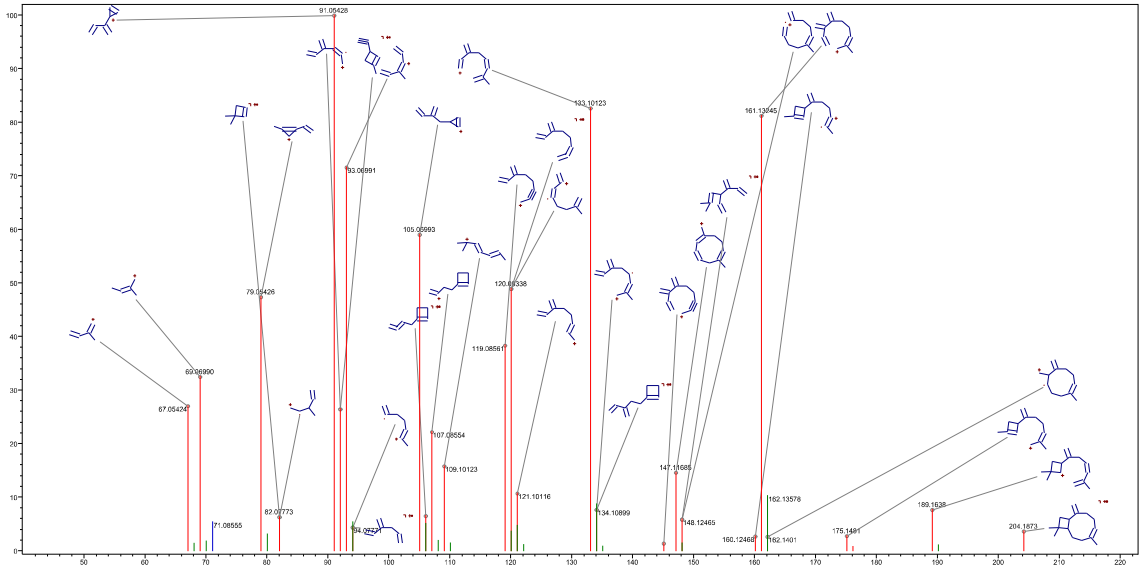

Figure 35. EI m/z spectrum with assigned fragments of 9-epi-(E)-Caryophyllene in the Pomegranate extract.

2.12 Peak 12 - Pentadecane

EI spectrum of Pentadecane in the Pomegranate extract is presented in figure 36.

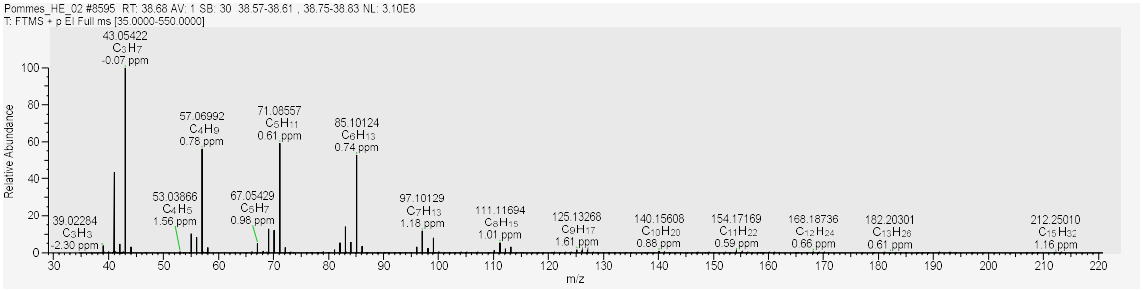

Figure 36. EI m/z spectrum of Pentadecane in the Pomegranate extract.

The molecular ion and corresponding adducts in the PCI (CH4) spectrum are not visible for Pentadecane.

The theoretical fragmentation pattern of Pentadecane (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 37. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

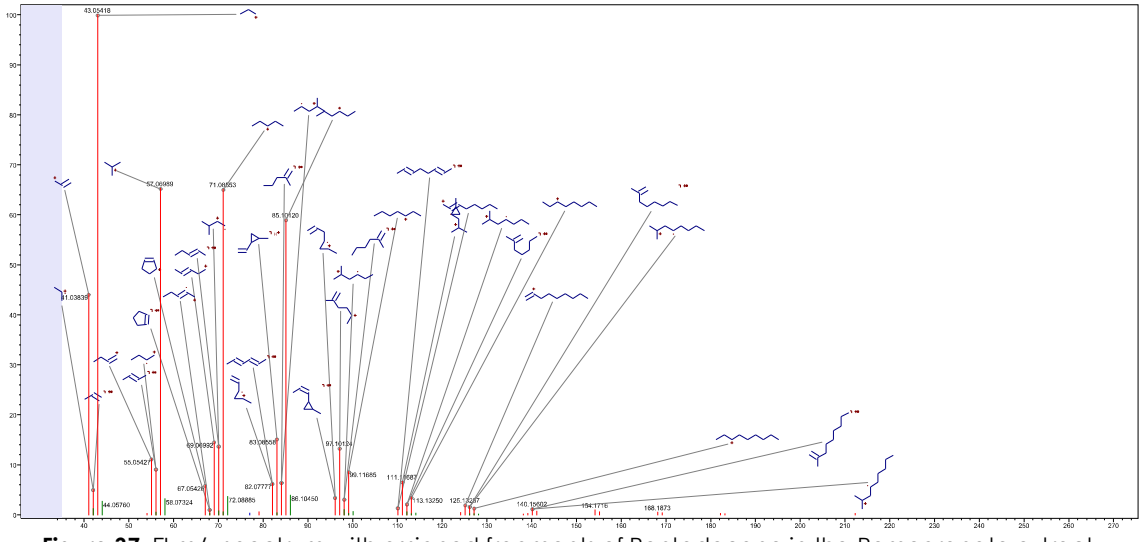

Figure 37. EI m/z spectrum with assigned fragments of Pentadecane in the Pomegranate extract.

2.13 Peak 13 - Valencene

EI spectrum of Valencene in the Pomegranate extract is presented in figure 38.

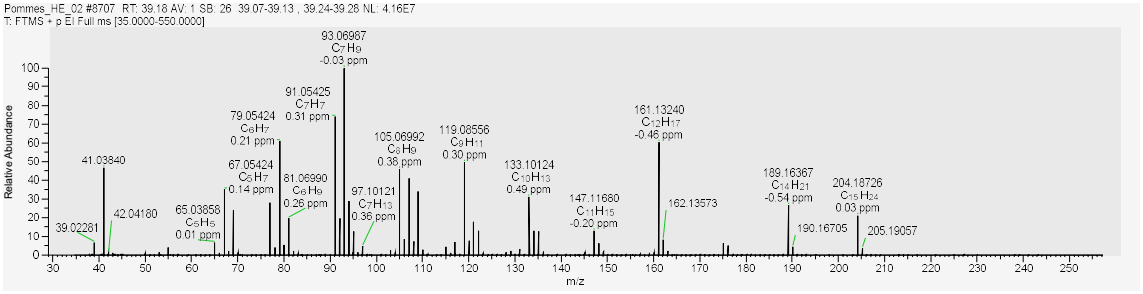

Figure 38. EI m/z spectrum of Valencene in the Pomegranate extract.

PCI (CH4) spectrum of Valencene in the Pomegranate extract is presented in figure 39. The adducts of methane are depicted above the corresponding m/z.

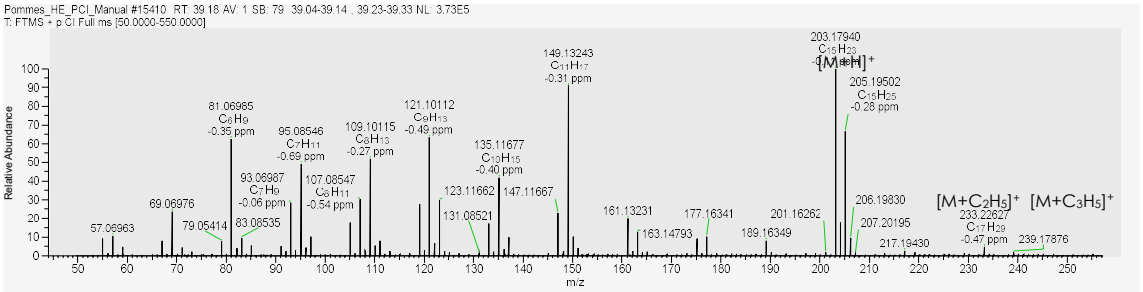

Figure 39. PCI (CH4) m/z spectrum of Valencene in the Pomegranate extract.

The theoretical fragmentation pattern of Valencene (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 40. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

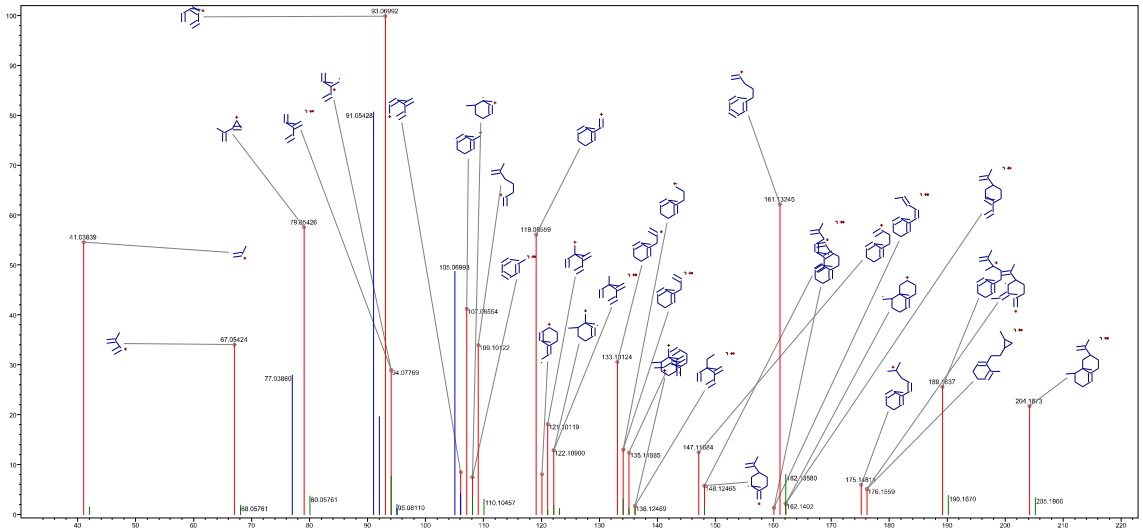

Figure 40. EI m/z spectrum with assigned fragments of Valencene in the Pomegranate extract.

2.14 Peak 14 - Ethyl-4-ethoxy benzoate

EI spectrum of Ethyl-4-ethoxy benzoate in the Pomegranate extract is presented in figure 41.

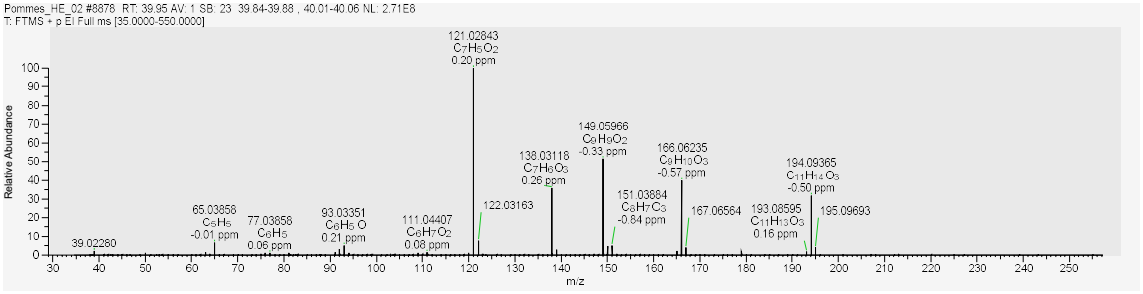

Figure 41. EI m/z spectrum of Ethyl-4-ethoxy benzoate in the Pomegranate extract.

PCI (CH4) spectrum of Ethyl-4-ethoxy benzoate in the Pomegranate extract is presented in figure 42. The adducts of methane are depicted above the corresponding m/z.

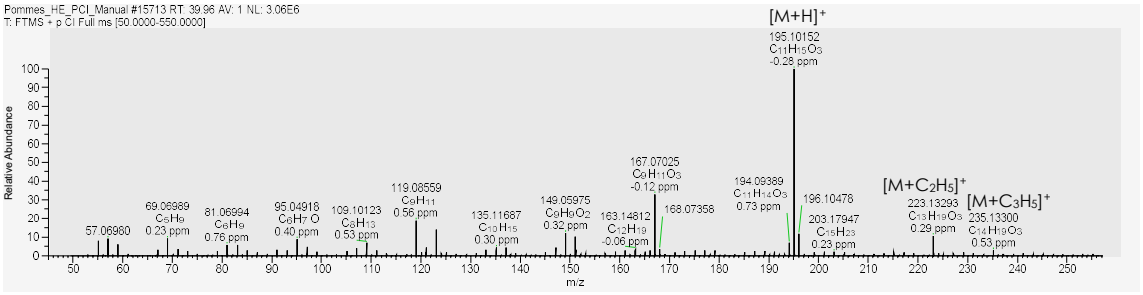

Figure 42. PCI (CH4) m/z spectrum of Ethyl-4-ethoxy benzoate in the Pomegranate extract.

The theoretical fragmentation pattern of Ethyl-4-ethoxy benzoate (using common fragmentation and rearrangement rules) is matched to the EI spectrum of hexanal using MassFrontier 8.1 in figure 43. The measured fragments provide detailed information with respect to the proposed chemical formula with <1 ppm mass accuracy.

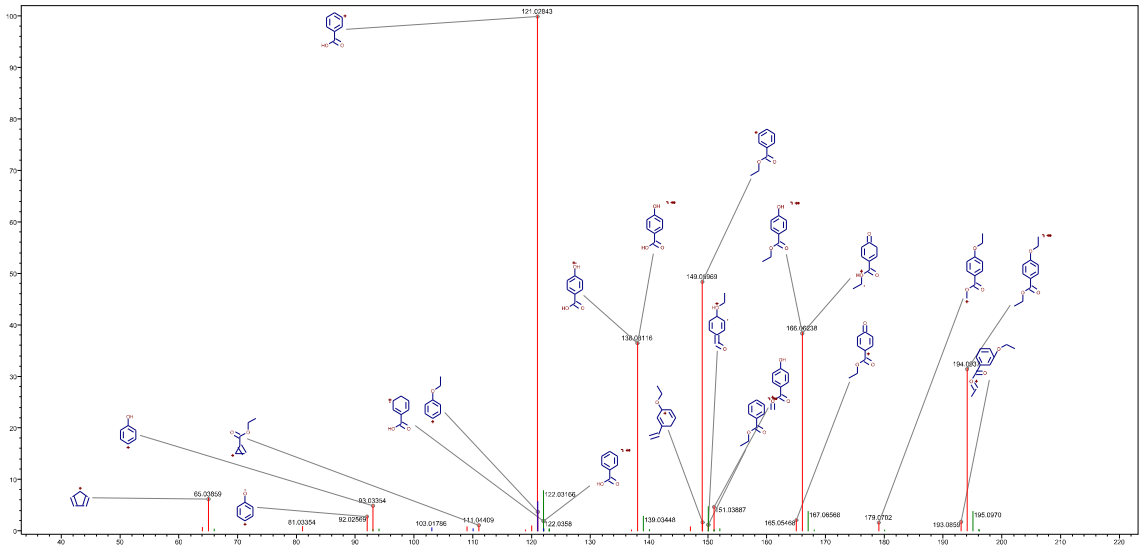

Figure 43. EI m/z spectrum with assigned fragments of Ethyl-4-ethoxy benzoate in the Pomegranate extract.