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Flavoring compounds from tomato hybrids grown in Banat county (Romania)

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Abstract

The paper presents the volatile compounds (flavoring compounds) evaluation of four tomato hybrids grown in Banat county (Romania). The raw tomato samples were subjected to hexane extraction and the extract was analyzed by gas chromatography-mass spectrometry. The composition of volatile compounds in tomatoes samples was determined and the correlation with the hybrid type and fertilizer used for tomatoes crops was established.

Keywords: tomato, flavoring compounds, solvent extraction, gas chromatography-mass spectrometry

1. Introduction

Tomatoes were cultivated by the Incas tousands years ago and tomato seeds were bring to Spain and Portugal by conquistadors in 16th-18th centuries [1,2]; former tomato fruits were yellow-skinned and were used as annual and ornamental plants (apple of gold), being considered poisonous. Now, the tomato is a food of worldwide importance, being cultivated all over the world, even in hydroponic systems [2], where the classical production don't satisfy the necessity of people. Among wild and cultivated tomato species (genus Lycopersicon), some genetically modified crops were developed in order to obtain delayed ripening or for increasing pectin content [3].

Tomatoes are rich in carotenoids (51-85 ppm reported on dry weight basis), especially from C_{40} group (lycopene, α- and β-carotene, which provide the orange-reddish color of tomatoes, depending of the specie and degree of ripeness). For example, β-carotene varies from trace to 36 ppm in High Beta cultivar, where lycopene is almost inexistent, but this last acyclic tetraterpene is in high concentration (44 ppm) in Campbell cultivar and β-carotene is only 1.4 ppm [3-5]. The lycopene content of the tomato increases greatly during ripening [4-7]. Furthermore, after ripening and harvesting of tomato fruits, the respiration rise with the increasing of ethylene production [3].

Degradation of carotenoids conduct to various volatile compounds (aroma compounds, flavoring compounds); thus, degradation of lycopene provide methyl-heptenone and pseudoionone, while degradation of β-carotene provide β-cyclocitral and β-ionone; further, neoxanthin provide β-damascenone

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by oxidative degradation [3,8]. Among the large number of volatile compounds found in tomato aromas, a special importance have (*Z*)-3-hexenal, β-ionone, hexanal, β-damascenone, 1-penten-3-one, and 3-methylbutanal [3,9-12]. Other volatiles identified in fresh or processed (paste) tomatoes are 2-isobutylthiazole, methional, 3/4-hydroxy-4,5/2,5-dimethyl-5/3(2*H*)-furanones, and eugenol [12]; the concentrations of sulfur compounds and furanones increase while those for aldehydes decrease during heating of tomato paste [3,12].

Our study presents the gas cromatographic identification of the raw volatile compounds separed by cold extraction in hydrophobic solvent (non-degradative conditions) from various tomato hybrids grown in the Banat county (Romania) by using different fertilizers.

2. Materials and Method

Materials. Tomato samples (four different hybrids – codes A1-4: Abellus F_1, Birdie F_1, Katerina F_1, and Petula F_1, respectively – grown in the presence of seven fertilizers: Bioplasma with algae base, purchased from Hungary market, and Bionat Plus, Bionex, Elstim, Elrom, Fosfertil, Cropmax, purchased from Romanian market, codes B1-B7, respectively) were grown in 2009 in Banat county (Banat's University of Timisoara basis). Hexane used in the extraction process was purchased from Merck & Co. and was GC grade.

Separation of flavoring compounds. Finelly grounded tomato samples (~10 g) were extracted in hexane (30 mL) in a classical system and the hexane extracts were dryed on anhydrous sodium sulfate (Merck), filtered, and concentrated under vacuum to 1/3 of volume. These tomato extracts were subjected to gas chormatographic analysis, but only the volatile compounds were analyzed.

GC-MS analysis. For the analysis of flavouring compounds of tomatoes, a gas chromatography-mass spectrometry (GC-MS) system was used. A Hewlett Packard HP 6890 Series coupled with a Hewlett Packard 5973 Mass Selective Detector was used. The GC analysis conditions were: column – HP-5 MS (30 m length, 0.25 mm inner diameter, thickness 0.25 μm), temperature program – 50°C to 250°C with a heating rate of 4°C/min, injector and detector temperatures - 280°C, injection volume – 2 μL, flow gas – He. For the MS detector, it was used an EI energy of 70eV, at a source temperature of 150°C, scanning range of 50-300 amu, scanning rate of 1 s^{-1} for the given mass spectrometry while the recorded spectra were compared with NIST/EPA/NIH Mass Spectral Library 2.0 (2002) database. Acquisition data was performed using a Hewlett Packard Enhanced ChemStation G1701BA ver. B.01.00/1998 program package while the processing of the gas chromatographic and mass spectrometic data were performed by using a Hewlett Packard Enhanced Data Analysis included in the package mentioned above.

3. Results and Discussion

For evaluating the main flavouring compounds (hydrophobic and volatile) in hybrid tomato samples we try to separate these compounds, without significantly affecting the compound integrity and the composition as a result of a degradation due to a high temperature and/or the presence of oxygen and water. Therefore, we use a direct extraction of tomato hybrid volatile compounds (and others soluble compounds in hexane) by solubilizing them in a hydrophobic solvent (hexane).

From the main volatile compounds (slightly volatile compounds, which were extracted and separated by GC-MS, were not used in analysis; examples of these compounds are fatty acids from seeds), unsaturated alcohols, saturated and unsaturated aldehydes, as well as some specific volatile compounds (methyl dihydrojasmone and dihydropseudoionone) appear in the hexane extracts.

The concentrations of these compounds were relatively low, therefore, these could not be quantified for the studied samples. In the case of A1 hybrid, saturated aldehydes were identified in relative concentrations of 0.15-1.33% for nonanal, while only traces of octanal could be found; unsaturated aldehydes were found in higher concentrations: 2-hexanal 0.2%, 2-heptenal 0.1-0.7%, 2,4-decadienal 0.33-2.13%, while other aldehydes were found in traces or not at all (2-octenal, 2-decenal, 2-undecenal); a new ionone was identified (dihydropseudoionone) which is typical to volatiles from tomatoes, in relative concentrations of 0.16-2.87%. Unsaturated alcohools, unsaturated ketone, and furanic derivatives were also identified (Table 1, Figures 1-3).

Table 1. The relative concentrations (%) of the main volatile compounds of A1(*Abellus* F_1) tomato extracts

No	RT (min)	Name	A1B1	A1B2	A1B3	A1B4	A1B5	A1B6	A1B7
1	5.793	2-Nonen-1-ol	0.21	0.31				0.58	
2	6.915	2-Hexenal, (E)-	0.20						
3	7.491	Furan, 2-pentyl- / 2-Heptenal, (Z)-	0.44			0.25			
4	8.078	5-Hepten-2-one, 6-methyl-						0.32	0.31
5	8.161	Octanal							
6	9.553	2-Heptenal, (Z)-	0.10	0.7					
7	9.859	2-Octenal, (E)-							
8	10.535	Nonanal	0.92			0.53	0.15	1.33	0.68
9	12.891	1-Decanol	0.32	0.55		0.76		0.95	
10	14.489	2-Decenal, (E)-							
11	15.558	2,4-Decadienal	0.19						
12	16.205	2,4-Decadienal, (E,E)-	1.05			1.47	0.33	0.98	2.13
13	16.34	2-Nonen-1-ol	0.12					0.24	
14	16.704	2-Undecenal							
15	18.714	Dihydropseudoionone	0.29	2.87		0.16	0.21	0.4	

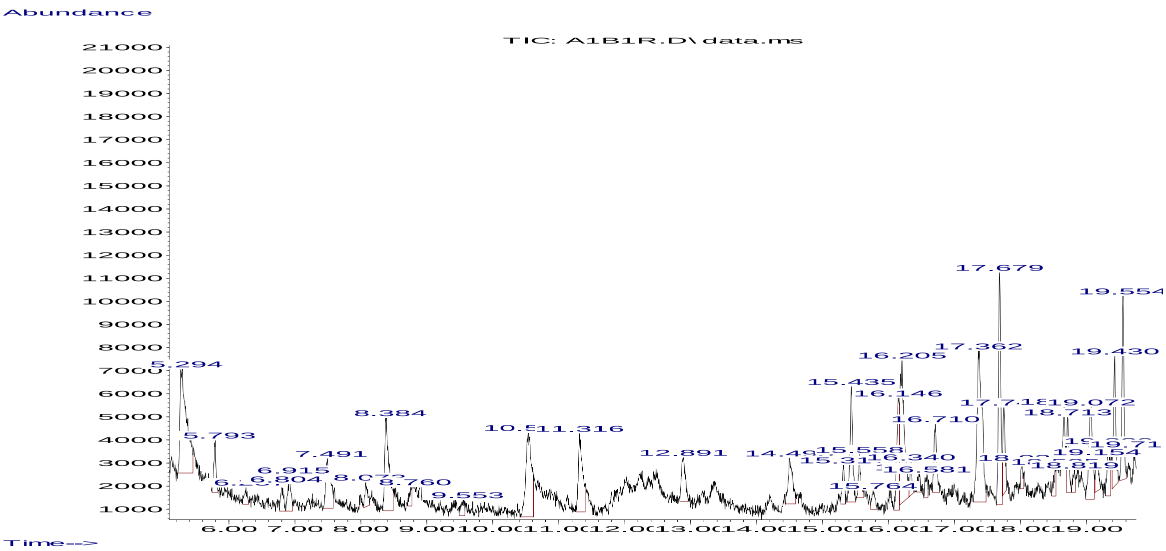


Figure 1. Gas chromatogram from the GC-MS analysis for the A1B1 tomato volatiles

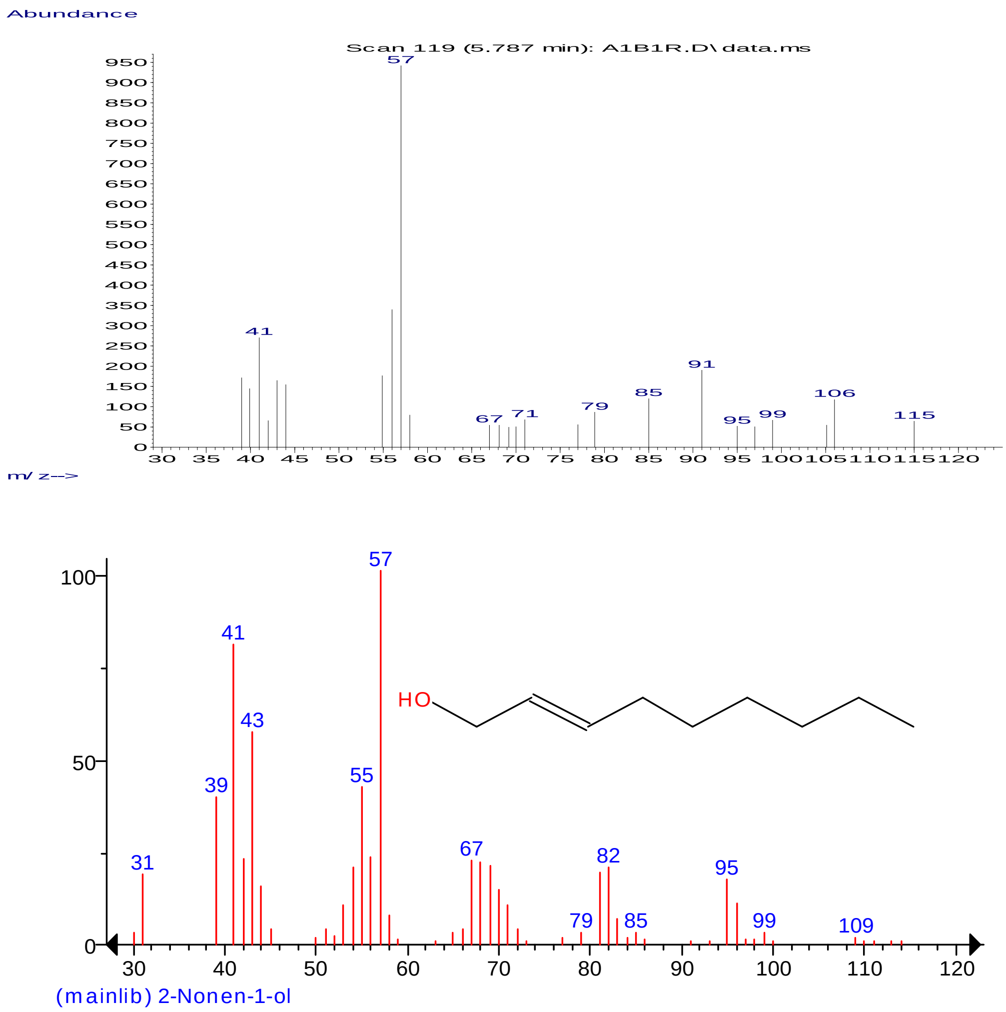
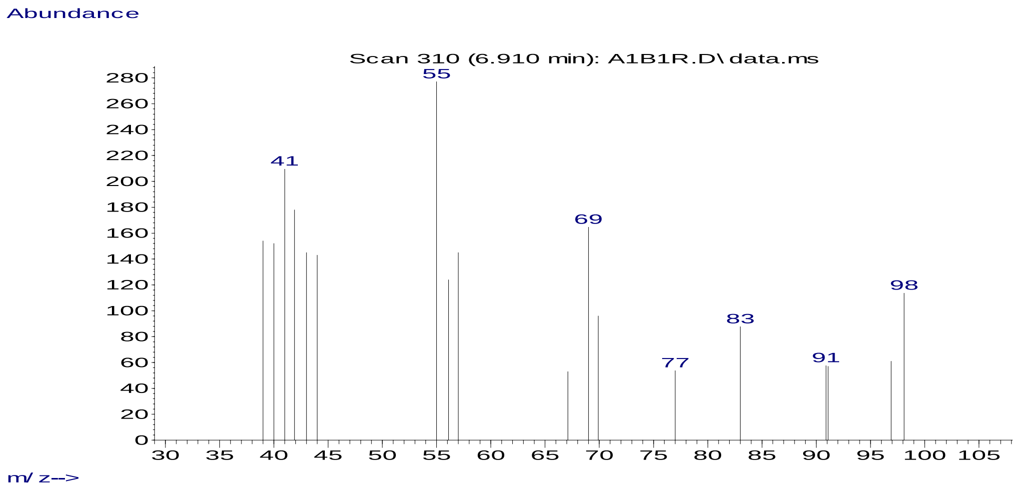


Figure 2. The MS experimental (up) and from the NIST database (down) spectra for 2-nonen-1-ol (from GC-MS analysis of the hexane extract of tomato variant A1B1)



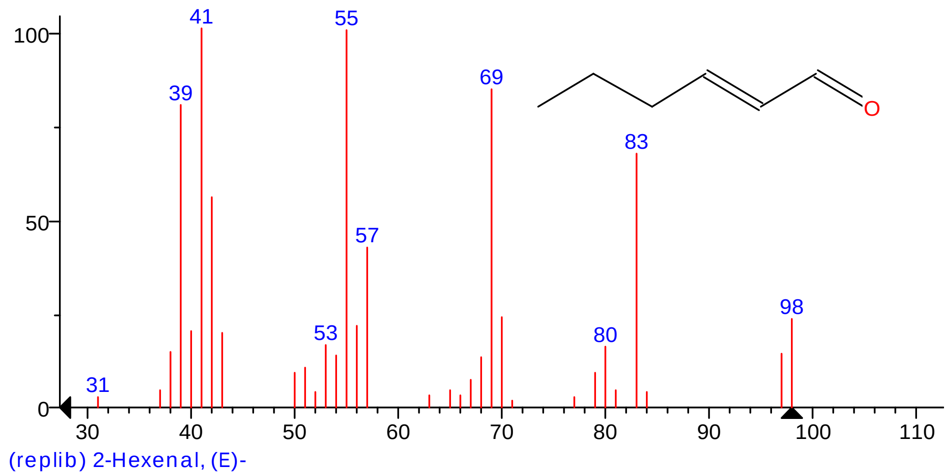


Figure 3. The MS experimental (up) and from the NIST database (down) spectra for 2-hexen-1-ol (from GC-MS analysis of the hexane extract of tomato variant A1B1)

In the case of A2 hybrid, the concentrations of these compounds were lower; for A2B1 and A2B2 these were observed only in traces. Saturated aldehydes were identified in traces (octanal) and up to 1.8% for nonanal, while unsaturated aldehydes were found in relatively low quantities or in traces (2,4-decadienal was a little bit more concentrated with values of relative concentrations up to 3%). Pseudoionone was determined in concentrations up to 1% while furanic derivatives up to 5% (Table 2, Figure 4).

Table 2. The relative concentrations (%) of the main volatile compounds of A2 (*Birdie* F_1) tomato extracts

No	RT (min)	Name	A2B1	A2B2	A2B3	A2B4	A2B5	A2B6	A2B7
1	5.793	2-Nonen-1-ol							0.08
2	6.915	2-Hexenal, (E)-							0.01
3	7.491	Furan, 2-pentyl- / 2-Heptenal, (Z)-			0.15	0.47	0.6		
4	8.078	5-Hepten-2-one, 6-methyl-			0.36	2.49	0.36		0.01
5	8.161	Octanal							
6	9.553	2-Heptenal, (Z)-							
7	9.859	2-Octenal, (E)-							
8	10.535	Nonanal			1.15	0.55	0.76	1.81	0.02
9	12.891	1-Decanol			0.73	0.81	1.43		0.03
10	14.489	2-Decenal, (E)-							
11	15.558	2,4-Decadienal				1.23	1.12	1.85	0.18
12	16.205	2,4-Decadienal, (E,E)-		1.07	1.19	0.68	2.03	2.98	0.08
13	16.34	2-Nonen-1-ol							0.05
14	16.704	2-Undecenal							
15	18.714	Dihydropseudoionone			0.4	0.93	0.45		0.04

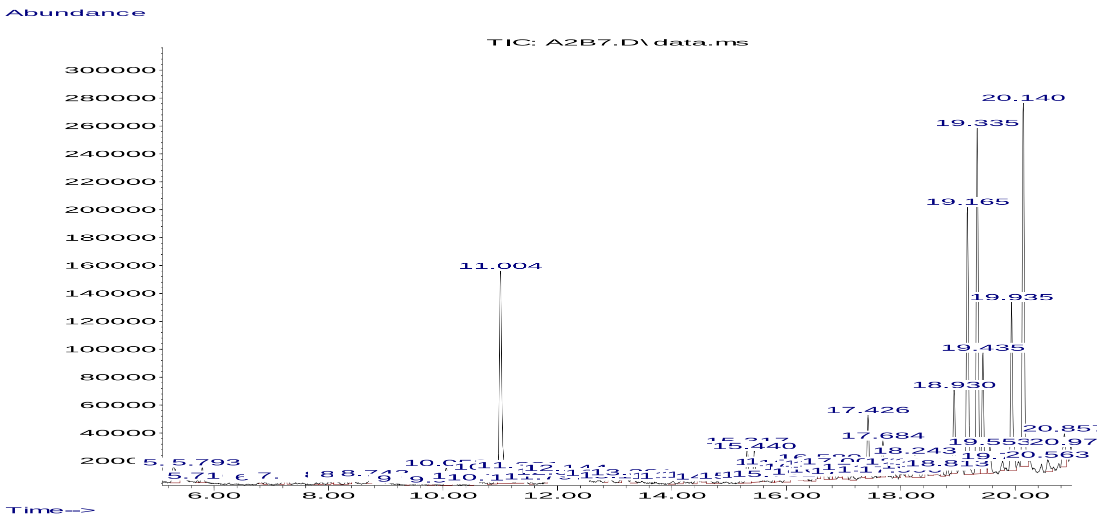


Figure 4. Gas chromatogram from the GC-MS analysis for the A2B7 tomato volatiles

In the case of A3 hybrid, it was identified and quantified mainly the same volatile compounds and the monounsaturated aldehydes were found in low quantities (decenal <0.5%) or even just traces; out of the saturated, the highest found was nonanal (up to 0.57%); 2,4-decadienal was found in significant quantities (up to 2.5%). The ionone derivative was below 0.3% in all cases (Table 3, Figure 5).

Table 3. The relative concentrations (%) of the main volatile compounds of A3 (*Katerina* F_1) tomato extracts

No	RT (min)	Name	A3B1	A3B2	A3B3	A3B4	A3B5	A3B6	A3B7
1	5.793	2-Nonen-1-ol	0.05						
2	6.915	2-Hexenal, (E)-							
3	7.491	Furan, 2-pentyl- / 2-Heptenal, (Z)-	0.44			0.06		0.18	0.07
4	8.078	5-Hepten-2-one, 6-methyl-	0.04			0.13	0.14	0.08	0.25
5	8.161	Octanal						0.09	
6	9.553	2-Heptenal, (Z)-							
7	9.859	2-Octenal, (E)-	0.06						
8	10.535	Nonanal	0.55		0.43	0.17	0.19	0.57	0.06
9	12.891	1-Decanol	0.11		0.5	0.39		0.24	
10	14.489	2-Decenal, (E)-	0.54			0.07		0.09	
11	15.558	2,4-Decadienal	0.84	1.09	1.66	0.4	0.41	0.14	
12	16.205	2,4-Decadienal, (E,E)-	2.53	0.85	0.88	0.41		0.25	0.23
13	16.34	2-Nonen-1-ol							
14	16.704	2-Undecenal	0.35					0.14	
15	18.714	Dihydropseudoionone	0.1			0.26		0.08	0.07

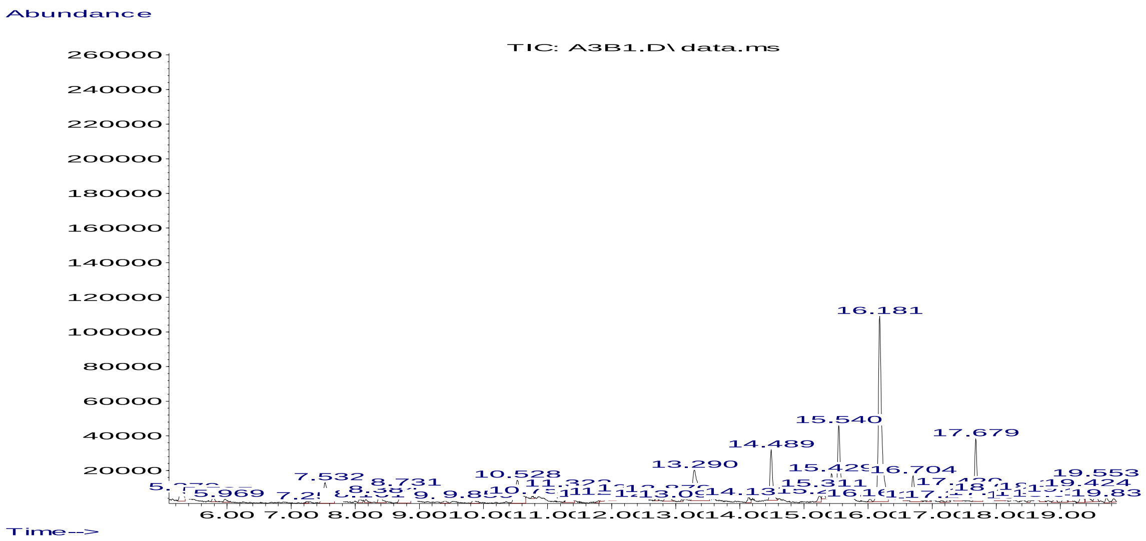


Figure 5. Gas chromatogram from the GC-MS analysis for the A3B1 tomato volatiles

In the last case presented, for hybrid A4, the concentrations for these compounds were usually higher; neither 2-hexenal, 2-heptenal, 2-octenal nor 2-decenal were identified in high concentrations. However, the nonanal and 2,4-decadienal were identified in concentrations reaching 1% and 1.1% respectively. In this last case, the pseudoionone was more concentrated (reaching even a relative concentration of 14%) (Table 4, Figure 6).

Table 4. The relative concentrations (%) of the main volatile compounds of A4 (*Petula* F_1) tomato extracts

No	RT (min)	Name	A4B1	A4B2	A4B3	A4B4	A4B5	A4B6	A4B7
1	5.793	2-Nonen-1-ol							
2	6.915	2-Hexenal, (E)-	0.35						0.02
3	7.491	Furan, 2-pentyl- / 2-Heptenal, (Z)-	0.09	0.03			0.08		0.38
4	8.078	5-Hepten-2-one, 6-methyl-		0.11	0.06	0.08	0.15		0.13
5	8.161	Octanal	0.16	0.08			0.07		0.04
6	9.553	2-Heptenal, (Z)-		0.14					
7	9.859	2-Octenal, (E)-							0.08
8	10.535	Nonanal	0.94	0.33	0.65	0.4	0.22	0.15	0.39
9	12.891	1-Decanol	0.33		0.74	0.55	0.36	0.45	0.25
10	14.489	2-Decenal, (E)-	0.19					0.1	0.3
11	15.558	2,4-Decadienal	0.63	0.12	1.08	0.65	0.24	0.52	0.59
12	16.205	2,4-Decadienal, (E,E)-	0.51	0.27	0.71	0.45	0.49	0.42	0.49
13	16.34	2-Nonen-1-ol							0.09
14	16.704	2-Undecenal	0.07	0.06	0.06	0.04		0.06	0.09
15	18.714	Dihydropseudoionone	1.43	0.2	0.49	0.31	0.13	0.2	14.4

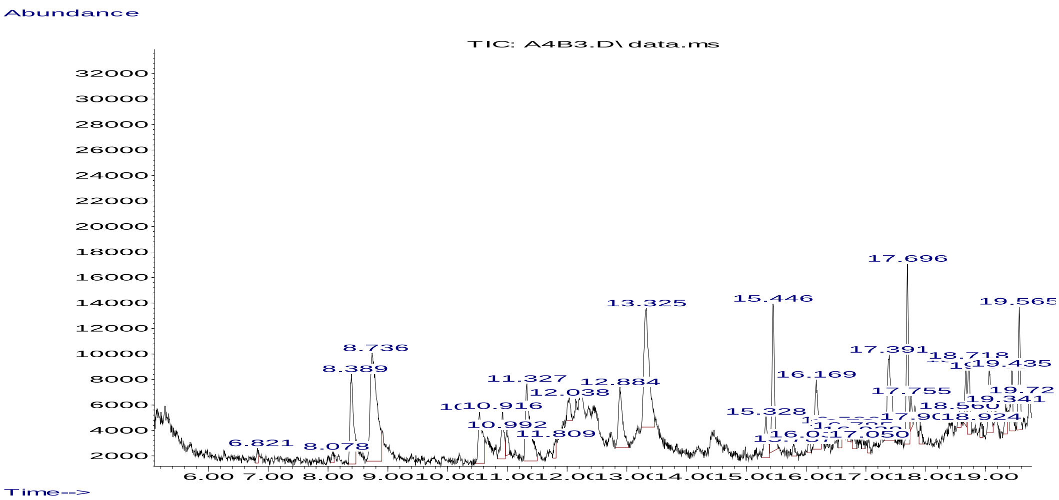


Figure 6. Gas chromatogram from the GC-MS analysis for the A4B3 tomato volatiles

4. Conclusion

The following conclusions can be drawn among the analysis of volatile compounds from tomato hybrids grown by using natural fertilizers: (1) total concentration of volatile compounds were lower than 20% in hydrophobic extract, while attempts to separate these volatile compounds by classical steam distillation did not conduct to concludent results; (2) the main volatile compounds which provide the tomato aroma were saturated and unsaturated aldehydes (especially nonanal and 2,4-decadienal) and ionone derivatives (dihydropseudoionone); (3) more concentrated in volatile compounds is *Petula* hybrid in comparation with other hydrophobic compounds with lower volatility.

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