

Comparative Head Space GC/MS Studies of Different Flavored Moâssel in the Egyptian Market (I)

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ABSTRACT

The current study aimed to compare three different types of Egyptian flavored tobacco (Moâssel) used in Hookah smoking. The samples (Apple, Creamy Strawberry and Mix Grapes) were obtained from Al Dandash company (a famous Tobacco company in Egypt). They were analyzed by Head Space GC/MS. There were great differences among the investigated samples. The identified compounds of the Apple sample showed 34 constituents, which represented (93.13%) of the total compounds. The major one was anethole (30.43%). While, the Creamy Strawberry specimen exhibited 27 recognized compounds, which represented (59.61%) of the sample. The chief constituent was acetic acid (15.83%). Finally, the last sample showed 25 identified constituents, which represented (93.16%) of the total compounds and the main compound was 1,2-propanediol (32.74%) of the constituents.

Keywords: Head Space, GC/MS, Egyptian Flavored Moâssel, Al Dandash Company.

INTRODUCTION

Tobacco smoking is an addictive and lethal habit. Moreover, it harms others through passive inhalation of both adults and children to exhaled and side stream smoke^{1,2}. While, smoking in pregnancy impairs fetal development and growth, in some cases reach to the point of fetal death³. Moreover, it causes fires generally reduce economic productivity and social engagement⁴. One of tobacco smoking types is Hookah (syn.: water pipe, shisha or hubble bubble), which is an old form of non-cigarette tobacco smoking that has been commonly practiced in the middle Eastern region contains over 4800 different chemicals out of which 69 are carcinogens and several others are tumor promoters⁵⁻⁷. Another study demonstrated that humectants such as glycerol and propylene glycol have added to tobacco products to facilitate processing of the cured tobacco leaf, retain moisture and increase half shelf life^{8,9}. Furthermore, Cooperation Center for Scientific Research Relative to Tobacco (CORESTA) made experiments focused on the quantitative analysis of these humectants in tobacco and tobacco products¹⁰. Also, CORESTA recommended another method to determine nicotine in tobacco and tobacco products by GC/MS¹⁰. All these data provoked us to make Head space GC/MS analyses on different types of flavored Moâssel used in the Egyptian Hookah.

MATERIALS AND METHODS

Materials

Egyptian flavored Moâssel samples viz., Apple (AFM), Creamy Strawberry (CSFM) and Mix Grapes (MixGFM) were collected from the Egyptian market (June 2016).

These specimens were prepared in Al Dandash Company, Egypt.

Methods

Shimadzu GC/MS with Head Space system provided by FID (Flame Ionization Detector), connected to the Mass Spectrometer Model: QP2010Ultra. Total GLC chromatograms and mass spectra were recorded in the electron impact ionization mode at 70 eV, using ACQ Mode of scan from 35 to 500 m/z in 0.3 s. The used column was 0.25 mm in internal diameter, 30 m length, packed with Rtx-MS and 0.25 µm film thickness. The injected volume was 1.0 µl, using helium as carrier gas at flow rate 40 ml/min. The analyses were carried out at a programmed temperature; the initial temperature was 40 °C (Kept for 2 min), then increased at a rate 30-50 °C to the final temperature 210 °C (kept for 5 min). Injector and detector had the same temperature 230 °C. The total run time was 45 min and split ratio 1:50.

RESULTS

Head Space GC/MS analyses

Identifications of compounds were carried out by direct comparison of retention time and fragmentation patterns with those of reference compounds analyzed under the same conditions^{11,12} and quantitation was based on peak area integration.

Apple Flavored Moâssel (AFM)

Head Space GC/MS analysis of AFM showed 49 compounds. The unidentified compounds represented 06.87% (15 compounds) and identified compounds represented 93.13% (34 compounds). The major one was anethole (30.43%).

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Table 1: Identified compounds of AFM from Head Space GC/MS.

No.	Name	RT*	RRT**	Base peak	Relative Area %	M. Weight	M. Formula
1	Acetone	01.73	0.086	43	00.27	58	C ₃ H ₆ O
2	2,3-Butanedione	02.13	0.105	43	00.22	86	C ₄ H ₆ O ₂
3	Acetic acid	02.17	0.107	44	00.28	60	C ₂ H ₄ O ₂
4	3-Methyl-1-butanol (Fusel oil)	03.80	0.188	55	00.98	88	C ₅ H ₁₂ O
5	1,2-Propanediol	04.01	0.198	45	01.37	76	C ₃ H ₈ O ₂
6	Dimethyl acetic acid	04.54	0.225	43	00.78	88	C ₄ H ₈ O ₂
7	Butanoic acid	05.13	0.254	60	00.21	88	C ₄ H ₈ O ₂
8	Furfural	06.14	0.304	96	00.65	96	C ₅ H ₄ O ₂
9	Ethyl-1-butanol	06.39	0.316	43	00.23	102	C ₆ H ₁₄ O
10	Ethyl-2-methyl butanoate	06.62	0.327	57	01.64	130	C ₇ H ₁₄ O ₂
11	<i>E</i> -3-hexen-1-ol	06.70	0.331	41	00.19	100	C ₆ H ₁₂ O
12	<i>Z</i> -3-hexen-1-ol	06.82	0.337	41	05.19	100	C ₆ H ₁₂ O
13	<i>n</i> -Hexyl formate	07.24	0.358	56	11.43	130	C ₇ H ₁₄ O ₂
14	3-Methylbutyl acetate (syn.: Isoamyl acetate or Isopentyl acetate)	07.41	0.366	43	00.41	130	C ₇ H ₁₄ O ₂
15	2-Methylbutyl acetate	07.48	0.370	43	00.24	130	C ₇ H ₁₄ O ₂
16	Camphene	09.60	0.475	93	00.18	136	C ₁₀ H ₁₆
17	Benzaldehyde	09.99	0.494	77	00.53	106	C ₇ H ₆ O
18	Isoamyl propionate	10.29	0.509	57	00.20	144	C ₈ H ₁₆ O ₂
19	Hexanoic acid	10.77	0.533	60	00.75	116	C ₆ H ₁₂ O ₂
20	Glycerol	10.95	0.542	61	00.21	92	C ₃ H ₈ O ₃
21	<i>Z</i> -3-Hexenyl acetate	11.48	0.568	43	01.17	142	C ₈ H ₁₄ O ₂
22	<i>n</i> -Hexyl acetate	11.69	0.578	43	05.45	144	C ₈ H ₁₆ O ₂
23	Benzyl alcohol (syn.: Phenylmethanol or Benzenemethanol)	12.45	0.616	79	09.82	108	C ₇ H ₈ O
24	Benzyl acetate	16.40	0.811	108	00.73	150	C ₉ H ₁₀ O ₂
25	Menthol	16.78	0.830	71	04.06	156	C ₁₀ H ₂₀ O
26	Hexyl butanoate (syn.: Hexyl butyrate)	17.27	0.854	43	00.44	172	C ₁₀ H ₂₀ O ₂
27	Anisaldehyde (syn.: 4-Methoxybenzaldehyde)	19.23	0.951	135	00.93	136	C ₈ H ₈ O ₂
28	Anethole	20.22	1.000	148	30.43	148	C ₁₀ H ₁₂ O
29	Benzyl butanoate	21.78	1.077	91	00.19	178	C ₁₁ H ₁₄ O ₂
30	Nicotine	21.89	1.083	84	00.19	162	C ₁₀ H ₁₄ N ₂
31	Hexyl hexanoate	22.80	1.128	43	00.22	200	C ₁₂ H ₂₄ O ₂
32	Vanillin	23.03	1.139	151	00.99	152	C ₈ H ₈ O ₃
33	Ethylvanillin (syn.: Vanilal or 3-Ethoxy-4-hydroxy benzaldehyde)	24.87	1.230	137	06.75	166	C ₉ H ₁₀ O ₃
34	Dihydro methyl jasmonate	29.64	1.466	83	05.80	226	C ₁₃ H ₂₂ O ₃
Unidentified compounds 06.87%							
Oxygenated compounds 92.76%							
Identified compounds 93.13%							
Nitrogenous compounds 00.19%							
Hydrocarbons compounds 00.18%							
*RT: Retention Time. **RRT: Relative Retention Time.							

Creamy Strawberry Flavored Moâssel (CSFM)

The identified compounds are classified into three different classes *viz.*, 92.76% oxygenated, 00.19% nitrogenous and 00.18% hydrocarbons compounds as shown in Figure 1 and enumerated in Table 1.

Head Space GC/MS analysis of CSFM exhibited 37 compounds. The unidentified compounds represented 40.39% (10 compounds) and identified compounds represented 59.61% (27 compounds). The major one was

acetic acid (15.83%). The identified compounds are classified into three diverse classes *viz.*, 57.44% oxygenated, 00.90% nitrogenous and 01.27% hydrocarbons compounds as demonstrated in Figure 2 and listed in Table 2.

Mix Grapes Flavored Moâssel (MixGFM)

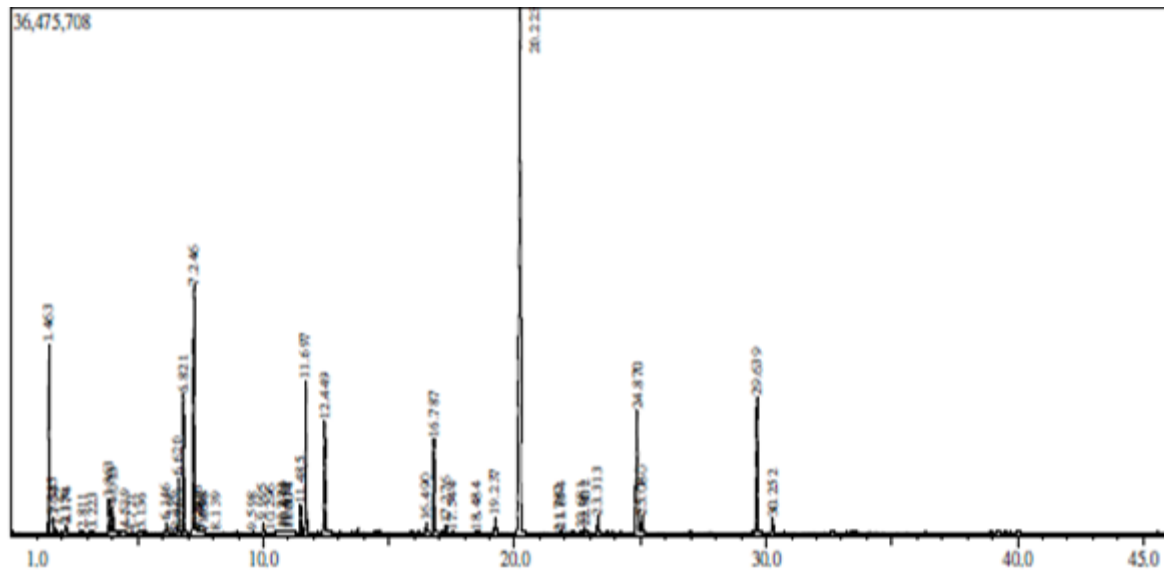


Figure 1: Total GC chromatogram of AFM.

Table 2: Identified compounds of CSFM from Head Space GC/MS.

No.	Name	RT*	RRT**	Base peak	Relative Area %	M. Weight	M. Formula
1	Acetic acid	2.26		43	15.83		C ₂
2	Butanoic acid	5.10		60	01.49		C ₂
3	Furfural	6.15		96	00.94		C ₂
4	Ethyl-2-methyl butanoate	6.61		57	01.97		C ₂ O ₂
5	Ethyl isovalerate	6.71		88	00.46		C ₂ O ₂
6	Z-3-hexen-1-ol	6.81		41	00.79		C ₂ O
7	Camphene	9.59		93	00.50		C ₁₆
8	Benzaldehyde	9.99		77	00.61		C ₇
9	Glycerol	10.48		43	00.94		C ₃
10	Hexanoic acid	10.71		60	01.85		C ₂ O ₂
11	Limonene	12.16		68	00.39		C ₁₆
12	Benzyl alcohol (syn.: Phenylmethanol or Benzenemethanol)	12.40		79	03.54		C ₇
13	Benzyl acetate	16.40		108	01.58		C ₂ O ₂
14	Ethyl maltol (syn.: 2-Ethylpyromeconic acid)	17.52		140	02.70		C ₃
15	Benzyl butanoate	21.78		91	00.43		C ₁₄ O ₂
16	Nicotine	21.86		84	00.90		C ₁₄ N ₂
17	Z-Methylcinamate	22.84		131	00.71		C ₁₀ O ₂
18	Vanillin	23.30		151	00.68		C ₃
19	α -Ionone	24.00		121	00.96		C ₂₀ O
20	Ethylvanillin (syn.: Vanilal or 3-Ethoxy-4-hydroxy benzaldehyde)	24.80		137	04.70		C ₃
21	γ -Decalactone	25.06		85	02.35		C ₁₈ O ₂
22	β -Ionone	25.56		177	01.22		C ₂₀ O
23	δ -Decalactone	25.80		99	00.89		C ₁₈ O ₂
24	γ -Undecalactone	27.70		85	00.92		C ₂₀ O ₂
25	α -Amylcinnamic aldehyde (syn.: Z-Jasminaldehyde)	29.50		129	10.21		C ₁₈ O
26	Dihydro methyl jasmonate	29.61		83	01.67		C ₂₂ O ₃
27	Neophytadiene	33.55		68	00.38		C ₃₈

Unidentified compounds 40.39%

Identified compounds 59.61%

Oxygenated compounds 57.44%

Nitrogenous compounds 00.90%

Hydrocarbons compounds 01.27%

*RT: Retention Time. **RRT: Relative Retention Time.

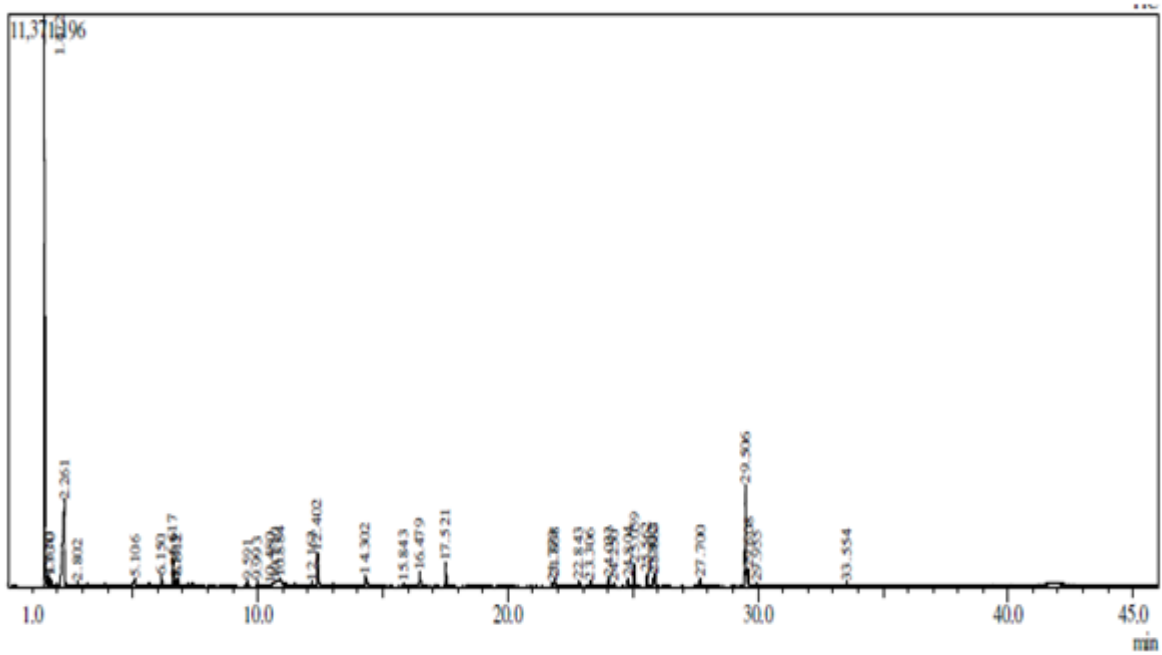


Figure 2: Total GC chromatogram of CSFM.

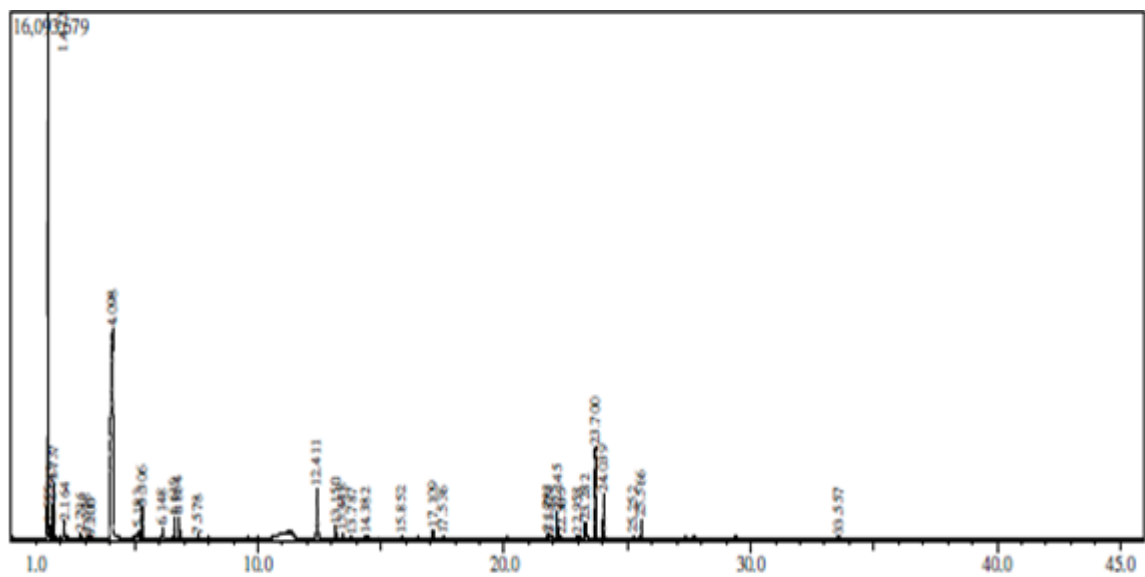


Figure 3: Total GC chromatogram of MixGFM.

Head Space GC/MS analysis MixGFM displayed 34 compounds. The unidentified compounds represented 06.84% (9 compounds) and recognized compounds represented 93.16% (25 compounds). The major one was 1,2-propanediol (32.74%). The identified compounds are classified into three various classes *viz.*, 92.51% oxygenated, 00.37% nitrogenous and 00.28% hydrocarbons compounds as shown in Figure 3 and recorded in Table 3.

DISCUSSION

The present study investigated three different Egyptian flavored Moâssels *viz.*, Apple, Creamy Strawberry and Mix Grapes by Head Space GC/MS analyses. The

samples showed very high percentage of oxygenated compounds and traces of (nitrogenous & hydrocarbons) constituents. Therefore, they have strong flavored odors.

The three samples had six common compounds *viz.*, acetic acid, butanoic acid, furfural, Z-3-hexen-1-ol, benzyl alcohol and nicotine.

Furthermore, AFM and CSFM had also ten common compounds *viz.*, ethyl-2-methyl butanoate, camphene, benzaldehyde, hexanoic acid, glycerol, benzyl acetate, benzyl butanoate, vanillin, ethylvanillin and Dihydro methyl jasmonate. But, AFM and MixGFM had an another common compound; 1,2-propanediol. Finally, CSFM and MixGFM had also three common

Table 3: Identified compounds of MixGFM from Head Space GC/MS.

No.	Name	RT*	RRT**	Base peak	Relative Area %	M. Weight	M. Formula
1	5,6-Epoxy- β -ionone	01.47	0.359	40	26.82	208	C ₁₃ H ₂₀ O ₂
2	2-Propanol (syn.: Isopropanol)	01.73	0.423	45	02.41	60	C ₃ H ₈ O
3	Acetic acid	02.16	0.528	43	01.55	60	C ₂ H ₄ O ₂
4	1-Hydroxy-2-propanone (syn.: Acetol)	02.79	0.682	43	00.27	74	C ₃ H ₆ O ₂
5	2,4-Dimethyl-1,3-dioxolane	03.07	0.751	43	00.21	102	C ₅ H ₁₀ O ₂
6	1,2-Propanediol	04.09	1.000	45	32.74	76	C ₃ H ₈ O ₂
7	Butanoic acid	05.18	1.267	60	01.85	88	C ₄ H ₈ O ₂
8	Ethyl butanoate	05.30	1.296	71	01.98	116	C ₆ H ₁₂ O ₂
9	Furfural	06.14	1.501	96	00.77	96	C ₅ H ₄ O ₂
10	Z-3-Hexen-1-ol	06.80	1.663	41	01.50	100	C ₆ H ₁₂ O
11	Propylene glycol 1-acetate (syn.: 1-Acetoxy-2-propanol or 2-Hydroxypropylacetate)	07.50	1.834	43	00.28	118	C ₅ H ₁₀ O ₃
12	Benzyl alcohol (syn.: Phenylmethanol or Benzenemethanol)	12.41	3.034	79	04.33	108	C ₇ H ₈ O
13	Butanoic acid anhydride	13.44	3.286	71	00.40	158	C ₈ H ₁₄ O ₃
14	Heptanoic acid	13.78	3.369	60	00.33	130	C ₇ H ₁₄ O ₂
15	Ethyl acetoacetate (syn.: Ethyl 3-oxobutanoate)	14.38	3.516	43	00.23	130	C ₆ H ₁₀ O ₃
16	3-Hydroxy-2,3-dihydromaltol (syn.: 2,3-Dihydro-3,5 dihydroxy-6-methyl 4H pyran-4-one)	15.80	3.863	43	00.32	144	C ₆ H ₈ O ₄
17	Z-3-Hexenyl butyrate	17.10	4.181	67	00.63	170	C ₁₀ H ₁₈ O ₂
18	Ethyl maltol (syn.: 2-Ethylpyromeconic)	17.53	4.286	140	00.29	140	C ₇ H ₈ O ₃
19	Phenyl-3-methylbutanote	21.78	5.325	91	00.52	178	C ₁₁ H ₁₄ O ₂
20	Nicotine	21.80	5.330	84	00.37	162	C ₁₀ H ₁₄ N ₂
21	3-Allyl-2-methoxyphenol	22.14	5.413	164	02.19	164	C ₁₀ H ₁₂ O ₂
22	Z-Jasmone	23.28	5.692	79	01.82	164	C ₁₁ H ₁₆ O
23	E- β -Damascone	23.70	5.795	177	07.46	192	C ₁₃ H ₂₀ O
24	α -Ionone	24.03	5.875	121	03.61	192	C ₁₃ H ₂₀ O
25	Neophytadiene	33.55	8.203	68	00.28	278	C ₂₀ H ₃₈
Unidentified compounds		06.84%					
Identified compounds		93.16%					
			Oxygenated compounds 92.51%				
			Nitrogenous compounds 00.37%				
			Hydrocarbons compounds 00.28%				

*RT: Retention Time. **RRT: Relative Retention Time

compounds viz., ethyl maltol, α -ionone and neophytadiene. From these data, there are relatively differences between the three studied samples specially between (AFM & MixGFM) and (CSFM & MixGFM). While, AFM and CSFM samples are the most similar. The AFM exhibited that anethole was the main compound (30.43%). It is an organic compound, which was widely used as a flavouring agent, showing a reduction *in vitro* and *in vivo* leucocytes migration induced by formyl-methionyl-leucyl-phenylalanine (fMLP), leukotriene B₄ (LTB₄) and carrageenan¹³. In addition to, it suppressed cell survival and induced apoptosis in human breast cancer cell independent on estrogen receptor status¹⁴. Furthermore, it demonstrated an inhibitory effect in non-immune acute inflammation¹⁵. However, it was associated with a slight increase in liver cancer in rats¹⁶. Moreover, it was a slightly toxic and irritant substance in large quantities¹⁷.

While, the CSFM showed that acetic acid (15.83%) was the chief identified constituent. It has many synonyms as ethanoic acid or methane carboxylic acid or ethylic acid or methane carboxylic acid¹⁸. It is used in pharmaceutical, plastics and chemical industries. During controlled exposure to vapours of acetic acid, it caused a mild nasal irritation at 10 ppm¹⁹. It demonstrated an anticancer activity since the 1800s²⁰. Moreover, it possessed a broad antibacterial spectrum against *Streptococci*, *Staphylococci*, *Pseudomonas*, *Enterococci* and others^{21,22}. Also, it can treated skin infections caused by *Pseudomonas* resistant to ideal antibiotics²³. Furthermore, it can be also used to treat obesity-linked type 2 diabetic Otsuka Long-Evans Tokushima Fatty rats²⁴. Finally, the third one MixGFM displayed that 1,2-propanediol (32.74%) was the major secondary metabolite. The undiluted 1,2-propanediol was minimally

irritating to the eye and producing slight transient conjunctivitis. The eye recovered after the exposure removed²⁵. Its concentration increased the hazard of respiratory and immune ailments in children including asthma, hay fever, eczema and allergies from 50% to 180%^{26,27}.

CONCLUSION

By comparing three different samples of Moâssel (Apple, Creamy Strawberry and Mix Grapes) from one of the most popular company in Egypt (Al Dandash Company), showed pronounced difference in the identified constituents. Therefore, it is possible for researchers to predict the physiological effects for these samples.

CONFLICT OF INTEREST

We declare that no conflict of interest.

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