CHAPTER IV

RESULT AND DISCUSSION

4.1 GC-MS Results

The compounds identification was performed by analyzing the MS spectral pattern based on the GC-MS NIST08 database library and comparison with literature data. Most of the compounds identified had similarity index of (50 % - 90 %). The GC-MS chromatogram is shown in Appendices A from figure 17 - 32, and the corresponding compounds with their retention times, peak's area, molecular formula, molecular weights (MW) and similarity index (%) in the Table 8-25.

4.1.1 Methanol Extract (mixed dates)

The methanol extract shown in **Table 8** consists of peaks that have area between 0.17 - 22.58 %. Ten (10) of the peaks have similarity higher than 90 %. Compounds detected are; Furfural ($C_5H_4O_2$) with retention time of 13.673 min and peak area of 1.18 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.392 min and peak area 0.35 %; 9-Octadecene,(E) ($C_{18}H_{36}$) with retention time of 21.685 min and peak area of 0.26 %; 7-Hexadecene, (Z) ($C_{16}H_{32}$) with retention time of 21.798 min and peak area of 0.21 %; Ethyl 9-hexadecenoate ($C_{18}H_{34}O_2$) with retention time of 30.618 min and peak area of 0.25 %; (E)-9-Octadecenoic acid ethyl ester ($C_{20}H_{38}O_2$) with retention time of 34.006 min and peak area of 1.21 %; 5-Hydroxy-methylfurfural ($C_6H_6O_3$) with retention time 34.321 min and peak area of 22.58 %; n-Hexadecanoic acid ($C_{16}H_{32}O2$) with retention time 40.396 min and peak area of 0.84 %; Oleic Acid

($C_{18}H_{34}O_2$) with retention time of 43.651 min and peak area of 0.69 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.345 min and peak area of 0.88 %.

According to the data, there is variation in the percentage of the solvents' impact on the above compounds. The first solvent is methanol where its impact on the first compound which is Glycolaldehyde dimethyl acetal is 74 % and 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl (64 %). On the other hand, the impact of methanol has been similarly significantly with these compounds where it is in the ratio of the nineties , they are Futura (91 %), 2-Furanmethanol (94 %) and 9-Octadecene, (E) (98 %). Moreover, the impact of the methanol on some of the compounds has almost the same percentage like 5-Hydroxymethylfurfural (91 %), n-Hexadecanoic acid (91 %), 9,12-Octadeca-dienoic acid (Z,Z) (99 %). While the percentages have varied simply in these compounds 2-Furanmethanol (94 %) and Ethyl 9-hexadecenoate (95 %), What is noteworthy is that, Methanol has no effect on many compounds, they are 4H-Pyran-4-one, 3,5-dihydroxy, 5-Hydroxymethylfurfural, 9,12-Octadecanoic acid, Hexadecanoic acid, methyl ester and oleic acid.

Table 8: Compounds detected in dates from Methanol extract

peak number	Retention time (min)	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
2	12.802	0.17	Glycolaldehyde dimethyl acetal	030934-97-5	$C_4H_{10}O_3$	106	74
4	13.673	1.18	Furfural	000098-01-1	$C_5H_4O_2$	96 l	91
6	18.3	0.35	2 Furanmethanol	000098-00-0	$C_5H_6O_2$	98	94
10	21.685	0.26	9-Octadecene, (E)	007206-25-9	$C_{18}H_{36}$	252	98
11	21.798	0.21	7-Hexadecene, (Z)	035507-09-6	$C_{16}H_{32}$	224	98
13	24.927	0.24	Orcinol	000504-15-4	$C_7H_8O_2$	124	72
22	30.195	2.85	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	64
23	30.618	0.25	Ethyl 9-hexadecenoate	054546-22-4	$C_{18}H_{34}O_2$	282	95
25	34.006	1.21	(E)-9-Octadecenoic acid ethyl ester	006114-18-7	$C_{20}H_{38}O_2$	310	97
26	34.321	22.58	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	91
32	40.396	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	91
37	43.651	0.69	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	96
39	44.345	0.88	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99

4.1.2 Chloroform Extract (Mixed dates)

The chloroform extract as shown in **Table 9** consist of peaks that have area between 0.17 - 3.49 %. Four of the peaks have similarity higher than 90 %. Compounds detected include; 2-Furanmethanol ($C_5H_6O_2$) with retention time of 18.38 min and peak area 0.17 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time 40.403 min and peak area of 0.84 %; Oleic acid ($C_{18}H_{34}O_2$) with retention time of 43.664 min and peak area of 0.33 %; 9-12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.34 min and peak area of 0.52 %.

The second solvent is chloroform and to compare it with methanol the impacts of both solvents are totally different in some of the compounds such as Furyl-hydroxymethyl ketone and 4-Pyridazinamine where the percentage of the impact of chloroform is (99 %) and (62 %) while as mentioned previously there is no impact of methanol on these compounds at all. On the other hand , there are some compounds that methanol affects on them while the chloroform has no effect on these compounds at all, like (9,12-Octadeceneoic acid, Furfural, 2-Furanmethanol and Oleic Acid)

Furthermore, both the two solvents, methanol and chloroform do not have any impact on some compounds such as (7-Hexadecene, (Z), and (E)-9-Octadecenoic acid ethyl). In contrast, in some compounds, the percentage of the effect of nearly the same or they have simple variances, such as (Futura) 91% / 13.67 with methanol and 86 % / 1 3.64 with chloroform, the same with n-Hexadecanoic acid (91 % / 40.3 impact of methanol) and (99 % / 40.40 impact of chloroform). However, some big variances appeared in the percentage of the effect of the two solvents on the

compounds as in (5-Hydroxymethylfurfural) the percentage of the impact of methanol was (91 % / 34.3) where the percentage with chloroform was (62 % / 34.13).

TABLE 9: Compounds detected in dates from Chloroform extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
3	13.64	0.87	Furfural	000098-01-1	$C_5H_4O_2$	96	86
4	18.38	0.17	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
7	25.23	0.31	Furyl hydroxymethyl ketone	017678-19-2	$C_6H_6O_3$	126	64
7	25.23	0.31	4-Pyridazinamine	020744-39-2	$C_4H_5N_3$	95	64
9	30.138	0.73	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	87
10	34.113	3.49	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	62
12	40.403	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
13	43.66	0.33	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	94
14	44.34	0.52	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99

4.1.3 Hexane Extract (Mixed dates)

The hexane extract in **Table 10** consists of peaks that have area between 19.39 and 76.56 %. Two out of the peaks were prominent and include Acetamide, 2,2,2-trifluoro ($C_2H_2F_3NO$) with retention time of 20.44 min and peak area of 76.56 %; trifluoro acetic acid, ($C_2HF_3O_2$) with retention time of 26.43 min and peak area of 19.39 %. The hexane is non polar solvent, so dates fruit do not have many non polar compounds. For the effect of the third solvent hexane there was not totally any impact on the compounds and the percentage of all was 0 %. In the first phase, each solvent was used separately, and as mentioned previously, some of them have the same impact while the other sometimes has no effect at all.

TABLE 10: Compounds detected in dates from Hexane extract

Peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
1	20.44	76.56	Acetamide, 2,2,2-trifluoro	000354-38-1	$C_2H_2F_3NO$	113	83
2	26.43	19.39	Acetic acid, trifluoro	000076-05-1	$C_2HF_3O_2$	114	70

4.1.4 Methanol : Chloroform Extract (70 % : 30 %) (Mixed dates)

The extract of Methanol (70 %) and Chloroform (30 %) as shown in **Table 11** consist of peaks that have area between 0.13 - 20.3 %. Seven of the peaks have similarity higher than 90 %. Compounds detected include; Furfural ($C_5H_4O_2$) with retention time of 13.68 min and peak area of 1.21 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.40 min and peak area of 0.27 %; 4H-Pyran-4-one,2,3-dihydro-2 ($C_6H_6O_4$) with retention time of 30.52 min and peak area of 13 %; Octadecanoic acid ($C_{18}H_{36}O_2$) with retention time of 43.27 min and peak area of 0.40 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.403 min and peak area of 1.28 %; Octadecanoic acid ($C_{18}H_{36}O_2$) with retention time of 43.27 min and peak area of 0.40 %; 9-Octadecenoic acid ($C_{18}H_{34}O_2$) with retention time of 43.65 min and peak area of 1.37 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.34 min and peak area of 1.77 %.

It has been mixing methanol (70 %) and chloroform (30 %) to see if it is the same effect on the compounds. It has been found that there are some of the compounds are almost has the same percentage with a little difference, (Octadecanoic acid 99 % / 43.26, 9,12-Octadecanoic acid (Z,Z) 99 % / 43.60 and n-Hexadecanoic acid. On the other hand, the percentage has been varied in some of other compounds , such as (Glycolaldehyde dimethyl acetal 83 %, D-Allose 86 % and 2,5-Furandicarbo-xaldehyde 87 %) while there was not any impact on the most of the compounds, like as (7-Hexadecene, (Z), and (E)-9-Octadecenoic acid ethyl).

TABLE 11: Compounds detected in dates from Methanol : Chloroform (70% : 30%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
3	13.01	0.92	Glycolaldehyde dimethyl acetal	030934-97-5	$C_4H_{10}O_3$	106	83
5	13.68	1.21	Furfural	000098-01-1	$C_5H_4O_2$	96	91
8	18.40	0.27	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
13	24.92	0.27	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_2$	124	87
19	30.16	2.32	4H-Pyran-4-one, 2,3-dihydro-3,5	028564-83-2	$C_6H_8O_4$	121	83
20	30.52	0.13	4H-Pyran-4-one, 3,5-dihydroxy-2	001073-96-7	$C_6H_6O_4$	142	96
22	31.35	0.17	2-Propanamine, N-methyl-N-nitroso	030533-08-5	$C_4H_{10}N_2O$	102	64
23	32.88	0.20	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	80
24	34.25	20.3	4-Mercaptophenol	000637-89-8	C_6H_6OS	126	64
32	40.40	1.28	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
35	43.27	0.40	Octadecanoic acid	000057-11-4	$C_{18}H_{36}O_2$	284	99
35	43.27	0.40	Octadecanoic acid, 2-(2-hydroxyethoxy)ethyl ester	000106-11-6	$C_{22}H_{44}O_4$	372	62
36	43.65	1.37	9-Octadecenoic acid	000112-79-8	$C_{18}H_{34}O_2$	282	99
37	44.34	1.77	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O$ 2	280	99
39	45.93	2.10	D-Allose	002595-97-3	$C_6H_{12}O_6$	280	86

4.1.5 Methanol : Chloroform : Hexane Extract (33.33 % : 33.33 % : 33.33%) (Mixed dates)

The extract of Methanol (33.33 %), Chloroform (33.33 %) and Hexane (33.33 %) as shown in **Table 12** consist of peaks that have area between 0.11 - 17.37 %. Eight of the peaks have similarity higher than 90 %. Compounds detected consist of; Furfural ($C_5H_4O_2$) with retention time of 13.69 min and peak area of 1.46 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.40 min and peak area of 0.31 %; Hexadecanoic acid methyl ester ($C_{17}H_{34}O_2$) with retention time of 29.48 min and peak area of 0.17, n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time 40.39 min and peak area 1.07 %; Octadecanoic acid ($C_{18}H_{36}O_2$) with retention time of 43.27 min and peak area of 0.21 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time 44.34 min of and peak area of 1.88 %.

As it has been noticed, the mixture of three solvents (methanol, chloroform and hexane) with equal percentages given almost the same impacts with the methanol 100 % extract, such as in these compounds (Furfural 91 % and 2-Furanmethanol 94 %) that have had approximate percentage. Also, they have not had any effects on the same compounds at all (Ethanone, 1-(2- furanyl); 9-Octadecenoic acid, (E); 2-Furancarboxaldehyde,5, methyl and Maltol.).

TABLE 12: Compounds detected in dates from Methanol : Chloroform : Hexane (33.33% : 33.33% : 33.33%) extract

peak number	Retention time (min)	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
4	13.69	1.46	Furfural	000098-01-1	$C_5H_4O_2$	96	91
6	18.40	0.31	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	94
9	24.92	0.23	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	87
14	29.48	0.17	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	97
15	30.145	1.61	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	028564-83-2	$C_6H_8O_4$	144	87
16	31.34	0.11	2-Propanamine, N-methyl-N-nitroso	030533-08-5	$C_4H_{10}N_2O$	102	68
17	32.851	0.21	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	72
19	34.214	17.3	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	62
23	40.396	1.07	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
26	43.27	0.21	Octadecanoic acid	000057-11-4	$C_{18}H_{36}O_2$	284	96
27	43.65	0.92	9-Octadecenoic acid,	000112-79-8	$C_{19}H_{36}O_2$	196	99
27	43.27	0.92	cis-Vaccenic acid	000506-17-2	$C_{18}H_{34}O_2$	282	99
28	44.34	1.88	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
30	45.91	2.02	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	86

4.1.6 Chloroform : Hexane Extract (70 % : 30 %) (Mixed dates)

The extract of chloroform (70 %) and hexane (30 %) as shown in **Table 13** consist of peaks that have area between 0.19 - 0.39 %. Two of the peaks have similarity higher than 90 %. Compounds detected are; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.390 min and peak area of 0.39 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.339 min and peak area of 0.32 %.

The mix between the two solvents chloroform (70 %) and hexane (30 %) was a totally different where the effect on some the compounds was with a high percentage in contrast with the previous mix methanol (70 %) and chloroform (30 %) but some compounds were not affected at all. Here are the results: n-Hexadecanoic acid (99%) and Oleic Acid (81%). It has been found a similar impact on this mix on (9,12-Octadeca-dienoic acid (Z,Z) 99%). But the mix does not have effects on the most of those compounds Pentadecanoic acid; 14-methyl-methyl ester; Ethanone,1-(2-furanyl); 9-Octadecenoic acid, (E); 2-Furancarboxaldehyde,5-methyl and Maltol.

TABLE 13: Compounds detected in dates from Chloroform : Hexane (70 % : 30%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
3	34.107	0.26	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	87
4	40.390	0.39	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	265	99
5	43.652	0.19	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	81
6	44.339	0.32	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99

4.1.7 Methanol : Hexane Extract (70 % : 30 %) (Mixed dates)

The extract of methanol (70 %) and hexane (30 %) as presented in **Table 14** consist of peaks that have area between 0.11 - 23.47 %. Seven out of the peaks have similarity higher than 90 %. Compounds detected include; Furfural ($C_5H_4O_2$) with retention time of 13.717 min and peak area of 1.46 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.404 min and peak area of 0.31 %; 2,5-Furandicarboxaldehyde ($C_6H_4O_3$) with retention time of 24.91 min and peak area of 0.28 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.390 min and peak area of 0.96 %; Octadecanoic acid ($C_{13}H_{26}O_2$) with retention time of 43.279 min and peak area of 0.18 %; 9-Octadecenoic acid, (E) ($C_{18}H_{34}O_2$) with retention time of 43.652 min and peak area of 0.78 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.346 min and peak area of 1.08 %.

The mixture of methanol (70 %) and hexane (30 %) shown the same impact with the previous mixes, for some compounds, for examples, 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl- and Furfural (91 %) and no impact on some compounds such as Pentadecanoic acid; 14-methyl-methyl ester; Ethanone, 1-(2-furanyl); 9-Octadecenoic acid, (E); 2-Furancarboxaldehyde,5-methyl and Maltol.

TABLE 14: Compounds detected in dates from Methanol : Hexane (70 % : 30 %) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
9	13.717	1.46	Furfural	000098-01-1	$C_5H_4O_2$	96	91
12	18.404	0.31	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
18	24.915	0.28	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	90
28	30.176	2.61	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	028564-83-2	$C_6H_8O_4$	144	83
30	31.343	0.11	2-Propanamine, N-methyl-N-nitroso	030533-08-5	$C_4H_{10}N_2O$	102	74
31	32.864	0.09	2-Furancarboxylic acid	000088-14-2	$C_5H^4O_3$	112	80
32	34.315	23.47	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	91
40	40.396	0.96	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
44	43.279	0.18	Octadecanoic acid	000057-11-4	$C_{13}H_{26}O_2$	214	72
45	43.652	0.78	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	99
46	44.346	1.08	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
49	45.954	1.45	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	86

4.1.8 Methanol : Chloroform Extract (30 % : 70%) (Mixed dates)

The extract of methanol (30 %) and chloroform (70 %) as shown in **Table 15** consist of peaks that have area between 0.13 -10.91 %. Four of the peaks have similarity higher than 90 %. Compounds detected are; Furfural ($C_5H_4O_2$) with retention time of 13.667 min and peak area of 0.54 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.392 min and peak area of 0.16 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.384 min and peak area of 0.29 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{34}O_2$) with retention time of 44.339 min and peak area of 0.29 %. When methanol (30 %) was mixed with Chloroform (70%), then the percentage of them (70 %, 30 %) was changed, the results converged in some compounds Furfura (91) %, 2-Furanmethanol (94 %), 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl (83 %) and n-Hexadecanoic acid (91 %).

TABLE 15: Compounds detected in dates from Methanol : Chloroform (30 % : 70 %) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
4	13.667	0.54	Furfural	00098-01-1	$C_5H_4O_2$	96	91
5	18.392	0.16	2-Furanmethanol	00098-00-0	$C_5H_6O_2$	98	94
9	24.915	0.15	2,5-Furandicarboxaldehyde	00823-82-5	$C_6H_4O_4$	124	86
10	25.230	0.13	2-Furancarboxylic acid, hydrazide	03326-71-4	$C_5H_4N_2O_2$	126	80
12	30.138	0.91	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	28564-83-2	$C_6H_8O_4$	144	83
13	34.182	10.91	5-Hydroxymethylfurfural	00067-47-0	$C_6H_6O_3$	126	62
15	40.384	0.29	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	91
16	43.645	0.20	Oleic Acid	00112-80-1	$C_{18}H_{34}O_2$	282	72
17	44.339	0.29	9,12-Octadecadienoic acid (Z,Z)	00060-33-3	$C_{18}H_{34}O_2$	282 l	99

4.1.9 Chloroform : Hexane Extract (30 % : 70 %) (Mixed dates)

The extract of chloroform (30 %) and hexane (70 %) as shown in **Table 16** of peaks that have area of 0.79 – 1.41 %. Only one of the peaks has similarity higher than 90 %. Compound detected include; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.333 min and peak area of 1.17 %.

The findings showed nearly the same impact when it has mixed chloroform and hexane but exchanged their ratio chloroform (30 %) and hexane (70 %) and these results are n-Hexadecanoic acid (87 %), cis-Vaccenic acid (60 %) and 9,12-Octadeca-dienoic acid (Z,Z) (99 %), while some of the compounds have not affected at all, such as Furfural; 3-Furaldehyde; 2-Furanmethanol; 9-Octadecene,(E); 3-Octadecene,(E); 9-Octad-ecenoic acid, (E); 2-Furancarboxaldehyde,5-methyl and Maltol

.

TABLE 16: Compounds detected in dates from Chloroform : Hexane (30 % : 70%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
4	40.390	1.41	n-Hexadecanoic acid	000057-10-3	$C_{15} H_{30} O_2$	256	87
5	43.652	0.79	cis-Vaccenic acid	000506-17-2	$C_{18} H_{34} O_2$	282	60
6	44.333	1.17	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18} H_{32} O_2$	280	99

4.1.10 Methanol : Hexane Extract (30 % : 70 %) (Mixed dates)

The extract of methanol (30 %) and hexane (70 %) is shown in **Table 17** and consists of peaks that have area between 0.05 - 28.72 %. Six of the peaks have similarity higher than 90 %. Compounds detected include; Furfural ($C_5H_4O_2$) with retention time of 13.686 min and peak area of 2.30 %; 2-Furancarboxaldehyde, 5-methyl ($C_6H_6O_2$) with retention time of 16.619 min and peak area of 0.20 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.373 min and peak area of 0.62 %; 4H-Pyran-4-one,3,5-dihydro-2-methyl ($C_6H_6O_4$) with retention time of 30.498 min and peak area of 0.16 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.359 min and peak area of 0.43%; 9-Octadecenoic acid, (E) ($C_{18}H_{34}O_2$) with retention time of 43.608 min and peak area of 0.31 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time 44.301 min and peak area 0.64 %.

On the other side, the findings of mix methanol (30 %) and hexane (70 %) with exchanging their ratios, show a little of similarities with the first mix methenol (70 %) and hexane (30 %), and the results are Furfural (91 %) and 2-Furanmethanol (95 %).

TABLE 17: Compounds detected in dates from Methanol : Hexane (30 % : 70%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
8	13.686 min	2.30	Furfural	000098-01-1	$C_5H_4O_2$	96	91
14	16.619 min	0.20	2-Furancarboxaldehyde, 5-methyl	000620-02-0	$C_6H_6O_2$	110	93
16	18.373 min	0.62	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
19	20.714 min	0.14	1,2-Cyclopentanedione	003008-40-0	$C_5H_6O_2$	98	53
23	24.455 min	0.05	Maltol	000118-71-8	$C_6H_6O_3$	128	76
24	24.890 min	0.36	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	87
39	30.183 min	4.24	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	83
40	30.498 min	0.16	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl	001073-96-7	$C_6H_6O_4$	142	91
46	32.813 min	0.17	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	80
49	34.353 min	28.72	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	86
69	40.396 min	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	74
83	43.608 min	0.31	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	99
85	44.301 min	0.64	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
92	45.910 min	1.37	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	86

4.1.11 Methanol : Chloroform Extract (50 % : 50 %) (Mixed dates)

The extract of Methanol (50 %) and Chloroform (50 %) as shown in **Table 18** consist of peaks that have area between 0.03 - 21.30 %. Ten of the peaks have similarity higher than 90 %. Compounds detected include: Furfural ($C_5H_4O_2$) with retention time 13.654 of min and peak area of 1.34 %; 2-Furancarbxaldehhde, 5-methyl ($C_6H_6O_2$) with retention time of 16.512 min and peak area of 0.03 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.367 min and peak area of 0.34 %. Other peaks have area higher than 0.03 %. 13 of those peaks are prominent and include: Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) with retention time of 29.457 min and peak area of 0.08 %; 4-Mercaptophenol ($C_6H_6O_2$) with retention time of 34.239 min and peak area of 21.30 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.359 min and peak area of 0.84 %; Octadecanoic acid ($C_{18}H_{36}O_2$) with retention time of 43.229 min and peak area of 0.09 %; 9-Octadecenoic acid, (E) ($C_{18}H_{34}O_2$) with retention time of 43.608 min and peak area of 0.44 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.301 min and peak area of 0.67 %.

In this part, the discussion will be on the impacts of the three solvents when mixed them equally with ratio 50 %. Firstly, the mixing of methanol (50 %) chloroform and (50 %) and the findings are Furfural (93 %), 2-Furanmethanol (95 %) and Orcinol (86 %).

TABLE 18: Compounds detected in dates from Methanol : Chloroform (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
5	13.654	1.34	Furfural	000098-01-1	$C_5H_4O_2$	96	93
8	16.512	0.03	2-Furancarboxaldehyde, 5-methyl-	000620-02-0	$C_6H_6O_2$	110	95
9	18.367	0.34	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
16	24.896	0.28	Orcinol	000504-15-4	$C_7H_8O_2$	124	86
18	25.205	0.29	Furyl hydroxymethyl ketone	017678-19-2	$C_6H_6O_3$	126	72
24	29.457	0.08	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	98
24	29.457	0.08	Pentadecanoic acid, 14-methyl	005129-60-2	$C_{17}H_{34}O_2$	270	96
26	30.120	1.72	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	87
28	32.807	0.07	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	72
30	34.239	21.30	4-Mercaptophenol	000637-89-8	C_6H_6OS	126	99
31	34.510	0.01	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	96
36	40.359	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
39	43.229	0.09	Octadecanoic acid	000057-11-4	$C_{18}H_{36}O_2$	284	68
40	43.608	0.44	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	99
41	44.301 min	0.67	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
45	45.879	1.34	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	86

4.1.12 Chloroform : Hexane Extract (50 % : 50 %) (Mixed dates)

The extract of chloroform (50 %) and Hexane (50 %) is presented in **Table 19** and consists of peaks that have area between 0.09 - 0.84 %. Four of the peaks have similarity higher than 90 %. Compounds detected include; n-Hexadecanoic ($C_{16}H_{32}O_2$) with retention time of 40.346 min and peak area of 0.31 %; 9-Octadecenoic acid, (E) ($C_{18}H_{34}O_2$) with retention time of 43.607 min and peak area of 0.21 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{19}H_{34}O_2$) with retention time of 44.301 min and peak area of 0.33 %.

The mixing of chloroform (50 %) and hexane (50 %) and its impact on the compounds is a follow 5-Hydroxymethylfurfural (80 %), n-Hexadecanoic acid (99 %) and Oleic Acid (97 %) while some of the compounds have not affected at all, such as Furfural; 3-Furaldehyde; 2-Furanmethano; 9-Octadecene,(E); 3-Octadecene,(E); 9-Octadecenoic acid,(E); 2-Furancarboxaldehyde,5-methyl and Maltol.

TABLE 19: Compounds detected in dates from Chloroform : Hexane (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
2	34.069	0.09	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	80
3	40.346	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
4	43.607	0.21	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	97
4	43.607	0.21	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	97
5	44.301	0.33	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{19}H_{34}O_2$	294	99

4.1.13 Methanol : Hexane Extract (50 % : 50 %) (Mixed dates)

The extract of Methanol (50 %) and Hexane (50 %) as shown in **Table 20** consist of peaks that have area between 0.09 - 22.61 %. Eight of the peaks have similarity higher than 90 %. Compounds detected include; Furfural ($C_5H_4O_2$) with retention time of 13.692 min and peak area of 2.04 %; 2-Furancarboxaldehyde, 5-methyl ($C_6H_6O_2$) with retention time of 16.682 min and peak area of 0.22 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.379 min and peak area of 0.74 %; Hexadecanoic acid methyl ester ($C_{17}H_{34}O_2$) with retention time of 29.451 min and peak area of 0.09 5; 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-2-methyl ($C_6H_6O_4$) with retention time of 30.183 min and peak area of 4.14 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.396 min and peak area of 0.48 %; Oleic acid ($C_{18}H_{34}O_2$) with retention time of 43.614 min and peak area of 0.70 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.308 min and peak area of 1.08 %.

The mixing methanol (50 %) and hexane (50 %) and the results show follow Glycolaldehyde dimethyl acetal (83 %) Furfural (91 %) and 2-Furanmethanol (95 %) while some of the compounds have not affected at all, such as Furfural; 3-Furaldehyde; 2-Furanmethanol; 9-Octadecene,(E); 3-Octadecene,(E); 9-Octadecen-oicacid, (E); 2-Furancarboxaldehyde,5–methyl and Maltol.

Table 20: Compounds detected in dates from Methanol : Hexane (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
5	12.916	0.67	Glycolaldehyde dimethyl acetal	030934-97-5	$C_4H_{10}O_3$	106	83
7	13.692	2.04	Furfural	000098-01-1	$C_5H_4O_2$	96	91
13	16.682	0.22	2-Furancarboxaldehyde, 5-methyl	000620-02-0	$C_6H_6O_2$	110	91
15	18.379	0.74	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
23	24.454	0.05	Maltol	000118-71-8	$C_6H_6O_3$	126	76
25	24.890	0.20	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124 l	80
30	29.451	0.09	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	99
39	30.183	4.14	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	83
40	30.498	0.16	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl	001073-96-7	$C_6H_6O_4$	142	90
44	32.807	0.17	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	86
49	34.302	22.61	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	86
69	40.396	0.84	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
81	43.614	0.70	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	99
85	44.308	1.08	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
91	45.898	0.91	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	86

4.1.14 Methanol : Chloroform Extract Khesab (Tamar) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) as shown in **Table 21** consist of peaks that have area between 0.09 - 11.19 %. Ten of the peaks have similarity higher than 90 %. Compounds detected include: Furfural ($C_5H_4O_2$) with retention time of 13.376 min and peak area of 0.28 %; 2-Furancarboxaldehyde, 5-methyl ($C_6H_6O_2$) with retention time of 16.556 min and peak area of 0.16 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.341 min and peak area of 0.28 %; Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) with retention time of 29.451 min and peak area of 0.09 %; 5-Hydroxymethylfurfural ($C_6H_6O_3$) with retention time of 34.132 min and peak area of 11.19 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.396 min and peak area of 0.30%; cis-Vaccenic acid ($C_{18}H_{34}O_2$) with retention time of 43.601 min and peak area of 0.31 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{34}O_2$) with retention time of 44.289 min and peak area of 0.40 %.

TABLE 21: Compounds detected in dates Khesab (Tamar) from Methanol : Chloroform (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
5	13.376	0.28 %	Furfural	000098-01-1	$C_5H_4O_2$	96	91
9	16.556	0.16 %	2-Furancarboxaldehyde, 5-methyl	000620-02-0	$C_6H_6O_2$	110	93
10	18.341	0.28 %	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	94
16	24.877	0.15 %	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	87
17	25.092	0.07 %	2H-Pyran-2,6(3H)-dione	005926-95-4	$C_{10}H_{18}O$	154	72
22	29.451	0.09 %	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	92
23	30.088	1.03 %	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	87
26	32.801	0.09 %	2-Furancarboxylic acid	000088-14-2	$C_6H_8O_4$	144	72
28	34.132	11.19 %	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	91
34	40.396	0.30 %	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
36	43.601	0.31 %	cis-Vaccenic acid	000506-17-2	$C_{18}H_{34}O_2$	282	99
36	43.601	0.31 %	Oleic Acid	000112-80-1	$C_{18}H_{34}O_2$	282	99
36	43.601	0.31 %	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	98
37	44.289	0.40 %	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{34}O_2$	282	99
42	45.841	0.95 %	D-Allose	002595-97-3	$C_{18}H_{34}O_2$	282	86

4.1.15 Methanol : Chloroform Extract Segae (Rutab) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) as shown in **Table 22** consist of peaks have area of between 0.09 - 17.20 %. Nine of the peaks have similarity higher than 90 %. Compounds detected include; Furfural ($C_5H_4O_2$) with retention time of 13.597 min and peak area of 0.97 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.335 min and peak area of 0.48 %; Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) with retention time of 29.451 min and peak area of 0.09 %; 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-2-methyl ($C_6H_6O_4$) with retention time of 30.486 min and peak area of 0.10 %; (E)-9-Octadecenoic acid ethyl ester ($C_{20}H_{38}O_2$) with retention time of 33.898 min and peak area of 0.24 %; 5-Hydroxymethylfurfural ($C_6H_6O_3$) with retention time of 34.195 min and peak area of 17.20 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.346 min and peak area of 0.55%; 9-Octadecenoic acid, (E)- ($C_{18}H_{34}O_2$) with retention time of 43.607 min and peak area of 0.35 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.301 min and peak area of 0.77 %.

TABLE 22: Compounds detected in dates Segae (Rutab) from Methanol : Chloroform (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
10	13.597	0.97	Furfural	000098-01-1	$C_5H_4O_2$	96	91
14	18.335	0.48	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	95
20	24.883	0.19	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	80
30	29.451	0.09	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	98
31	30.107	2.02	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	78
32	30.486	0.10	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl	001073-96-7	$C_6H_6O_4$	142	96
40	33.898	0.24	(E)-9-Octadecenoic acid ethyl ester	006114-18-7	$C_{20}H_{38}O_2$	310	95
41	34.195	17.20	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	91
53	40.396	0.55	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
62	43.607	0.35	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	99
64	44.301	0.77	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
70	45.866	1.11	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	72

4.1.16 Methanol : Chloroform Extract Khalas (Tamar) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) is shown in **Table 23** and it consists of peaks that have area between 0.07 - 18.84 %. Eleven of the peaks have similarity higher than 90 %. Compounds detected include: Furfural ($C_5H_4O_2$) with retention time of 13.629 min and peak area of 0.93 %: 2-Furancarboxaldehyde, 5-methyl ($C_6H_6O_2$) with retention time of 16.60 min and peak area of 0.21 %; 2-furanmethanol ($C_5H_6O_2$) with retention time of 18.341 min and peak area of 0.33 %; Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) with retention time 29.451 min and peak area 0.12 %; 9-Octadecenoic acid (Z)-, methyl ($C_{19}H_{36}O_2$) with retention time of 33.305 min and peak area of 0.13 %; trans-13-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$) with retention time of 33.305 min and peak area of 0.13 %; n-Hexadecanoic acid ($C_{16}H_{32}O_2$) with retention time of 40.396 min and peak area of 0.60 %; 9-Octadecenoic acid, (E)- ($C_{18}H_{34}O_2$) with retention time of 43.601 min and peak area of 0.62 %; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 44.289 min and peak area of 0.80 %.

TABLE 23: Compounds detected in dates khalas (tamar) from Methanol : Chloroform (50 % : 50%) extract

peak number	Retention time min	Peak's area %	Compound	CAS	Molecular formula	Molecular weight (MW) g/mol	Similarity index (%)
9	13.629	0.93 %	Furfural	000098-01-1	$C_5H_4O_2$	96	91
12	16.600	0.21 %	2-Furancarboxaldehyde, 5-methyl	000620-02-0	$C_6H_6O_2$	110 g	91
14	18.341	0.33 %	2-Furanmethanol	000098-00-0	$C_5H_6O_2$	98	94
20	24.877	0.24 %	2,5-Furandicarboxaldehyde	000823-82-5	$C_6H_4O_3$	124	87
30	29.451	0.12 %	Hexadecanoic acid, methyl ester	000112-39-0	$C_{17}H_{34}O_2$	270	98
31	30.101	1.59 %	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	028564-83-2	$C_6H_8O_4$	144	80
32	30.485	0.07 %	4H-Pyran-4-one, 5-hydroxy-2-(hydroxymethyl)	001073-96-7	CH_6O_4	142	96
36	32.801	0.08 %	2-Furancarboxylic acid	000088-14-2	$C_5H_4O_3$	112	72
37	33.305	0.13 %	9-Octadecenoic acid (Z)-, methyl	000112-62-9	$C_{19}H_{36}O_2$	296	93
38	33.401	0.12 %	trans-13-Octadecenoic acid, methyl ester	1000333-61-3	$C_{19}H_{36}O_2$	296	93
39	34.201	18.84 %	5-Hydroxymethylfurfural	000067-47-0	$C_6H_6O_3$	126	91
49	40.346	0.60 %	n-Hexadecanoic acid	000057-10-3	$C_{16}H_{32}O_2$	256	99
55	43.601	0.62 %	9-Octadecenoic acid, (E)	000112-79-8	$C_{18}H_{34}O_2$	282	99
56	44.289	0.80 %	9,12-Octadecadienoic acid (Z,Z)	000060-33-3	$C_{18}H_{32}O_2$	280	99
63	45.853	1.18 %	D-Allose	002595-97-3	$C_6H_{12}O_6$	180	68

4.1.17 Discussion of the Compounds Detected Using GC-MS

In the GC-MS analyses of dates extracts, the identified compounds in the different extracts are tabulated in **Table 24**. In general, the results showed that some compounds were identified in all extracts as n-Hexadecanoic acid was found in all extract but in extracted hexane, all was not found. Some compounds were extracted with specific solvent for example (E)-9-Octadecenoic acid ethyl ester was extracted with methanol and Maltol was extracted with methanol, hexane (50 %; 50 %). The mixture of the three solvents extracted 6-methyl-3, 5-dihydroxy, 2, 3-dihydro-4H-Pyran-4-one; 9, 12-Octadecadienoic acid (Z, Z); Furfural and Orcinol. Most of these compounds have been previously reported in this plant (Cechovska et al., 2011). The compounds in the solvent mixture extract all possess benefits to human health.

Based on the data in the tables above, three types of solvents: methanol, chloroform and hexane were used to extract compounds in dates, each solvent was used separately at first and was then mixed at certain percentages where a total of 38 compounds were detected.

Table 24: Summary of compounds detected in mixture dates extracts

No	Compounds	M 100%	CH100%	He100%	70%M+30 CH	70%ch+30 %H	70%M+30 %H	H+M+CH= 33.3%	30%M+70 %CH	30%CH+70 %H	30%M+70%H	50%M+50%C H	50%CH+50 %H	50%M+50%H
1	Glycolaldehyde dimethyl acetal	74% /12.8	-	-	83%/13.0	-	83%/12.88	-	-	-	78 % /12.88	-	-	83 %/12. 9
2	Furfural	91% /13.67	86%/13.64	-	93%/13.68	-	91%/13.65	91%/13.65	91%/13.65	-	91 % /13.68	91 %/13.65	-	91 %13.69
3	3-Furaldehyde	86% /13.67	96%/13.64	-	78%/13.68	-	86%/13.68	94%/13.68	86%/13.67	-	78 % /13.68	-	-	-
4	2 Furanmethanol	94% /18.3	98%/18.64	-	95%/18.40	-	95%/18.36	-	94%/18.36	-	95 %/ 18.37	95 %/18.36	-	95%/18.37
5	9-Octadecene, (E)	98% /21.68	-	-	-	-	-	-	-	-	-	-	-	-
6	3-Octadecene, (E)	96%/21.6	-	-	-	-	-	-	-	-	-	-	-	-
7	Cyclodecane, octyl	70%/12.6	-	-	-	-	-	-	-	-	-	-	-	-
8	Orcinol	72%/24.9	-	-	72%/24.92	-	90%/24.89	80%/24.90	-		86 % /24.89	86 %/24.89	-	80 %/24.89
9	2-Furancarboxylic acid,hydrazide	58%/25.2	-	-	59%/25.23	-	53%/25.24	-	-	-	-		-	-
10	Furyl hydroxylmethyl ketone	58%/25.2	64%/25.23	-	-	-	-	59%/25.20	72%/25.21	-	59 %/25.20	72%/25.20	-	-
11	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	64%/30.1	87%/30.13	-	83%/30.18	-	83%/30.18	87%/30.18	83%/30.18	-	83 % /30.18	87%/30.12	-	83 %/30.18
12	Ethyl 9-hexadecenoate	95%/30.6	-	-	-	-	-	-	-	-	-	-	-	
13	Ethyl Oleate	99%/34.0	-	-	-	-	-	-	-	-	-	-	-	-
14	(E)-9-Octade-cenoic acid ethyl ester	97% /34.00	-	-	-	-	-	-	-	-	-	-	-	-
15	5-Hydroxyme-thylfurfural	91%/34.3	62%/34.13	-	-	-	-	-	-	-	86 % /34.35	76 %/34.51	80 %/34.06	86 %34.30
16	n-Hexadecanoic acid	91%/40.3	99%/40.40	-	91%/40.39	99%/40.390	99%/40.39	99%/40.39	91%/40.38	99%/40.390	74 %/40.390	99%/40.359-	99%/40.34	99%/ 40.39
17	Octadec-9-enoic acid	99%/43.6	-	-	-	-	-	-	-	-	-	-	-	-
18	cis-Vaccenic acid	97%/43.	93%/43.66	-	99%/43.65	-	-	99%/43,65	87%/43.66	60%/43.65	99%/43.60	99 %/43.60	-	99%/43.61
19	Oleic Acid	96%/43.6	94%/43.66	-	-	81%/43.60	-	-	72%/43,66	-	-	99 %/43.60	97 %/43.60	99%/43.61
20	9,12-Octadeca-	99%/44.3	99%/44.34	-	99%/44.34	99%/44.34	-	99%/44.33	99%/44.34	99%/44.34	99 %/ 44.30	99 %/44.30	99 %/44.30	99 %/44.30

	dienoic acid (Z,Z)													
21	Tridecanoic acid	-	91% /40.40	-	-	-	91%/40.40	-	-	-	-	90%/40.35	-	-
22	D-Allose	-	53%/45.89	-	86%/45.89	-	-	86%/45.90	85%/45.90	-	86 %/45.91	86 %/45.89	-	86 %/45.89
23	2,5-Furandicarbo-xaldehyde	-	-	-	87%/24.92	-	64%/24.90	87%/24.92	86%/24.29	-	87 %/24.89	-	-	80 %/24.89
24	4H-Pyran-4-one, 3,5-dihydroxy-2-..	-	-	-	96%/30.52	-	-	-	-	-	91 % /30.49	-	-	-
25	2-Propanamine, N-methyl-N-nitroso-	-	-	-	64%31.35	-	74%/31.33	68%/31.35	-	-	-	-	-	73 %/31.31
26	2-Furancarboxylic acid	-	-	-	80%/32.88	-	80%/32.88	72%/32.83	-	-	80 % /32.81	72 %/32.80	-	86 %/32.80
27	5-Hydroxyme-thylfurfural	-	-	-	58%/34,21	87%/34.21	91%/34.21	62%/34.21	59%/34.21	-			-	-
28	Octadecanoic acid	-	-	-	99%/43,26	-	72%/43.26	96%/43.23	-	-	-	68 %/43.22	-	62%/43.23
29	9-Octadecanoic acid	-	-	-	99%/43.60	-	99%/43.60	-	-	-	-	97 %/43.60	-	-
30	6-Octadecenoic acid	-	-	-	99%/43.65	-	-	-	-	-	-	-	-	-
31	Hexadecanoic acid, methyl ester	-	-	-	72%/45.93	-	-	72%/45.93	-	-	74 %/45.91	64 %/45.87	-	72 %/45.89
32	Acetamide, 2,2,2-trifluoro	-	-	-	-	76%/43,65	-	-	-	55%/43.65	-	-	-	-
33	Acetic acid, trifluoro	-	-	-	-	-	-	-	97%/29.45	-	98 %/29.45	-	-	-
34	Pentadecanoic acid, 14-methyl-, methyl ester	-	-	-	-	-	-	-	97%/29.45	-	96 % /29.45	-	-	-
35	Ethanone, 1-(2-furanyl)-	-	-	-	-	-	-	-	-	-	64 % /14.83	-	-	-
36	9-Octadecenoic acid, (E)-	-	-	-	-	-	-	-	-	-	99 %/43.60	99%/34.60	-	99%/34.61
37	2-Furancarboxaldehyde,5-methyl	-	-	-	-	-	-	-	-	-	-	-	-	91%/16.68
38	Maltol	-	-	-	-	-	-	-	-	-	-	-	-	76 %/24.45

This study highlights the presence of many biochemical compounds in the aerial parts of date fruits that may affect pharmacological activities. The extraction of biochemical compounds is mainly dependent on the mixture design of solvents. The GC-MS analysis of extracts showed the presence of various types of compounds in date fruits. For global metabolomics approach, the combination of solvents such as methanol / water or methanol / chloroform/ water is favoured (Rowan, 2011; Rohloff, 2015). Combination of polar (water) and nonpolar (organic solvent) increases the metabolite coverage and could also reduce variations that can occur when trying to combine metabolite information from separate samples (Tambellini et al., 2013; Mushtaq et al., 2014).

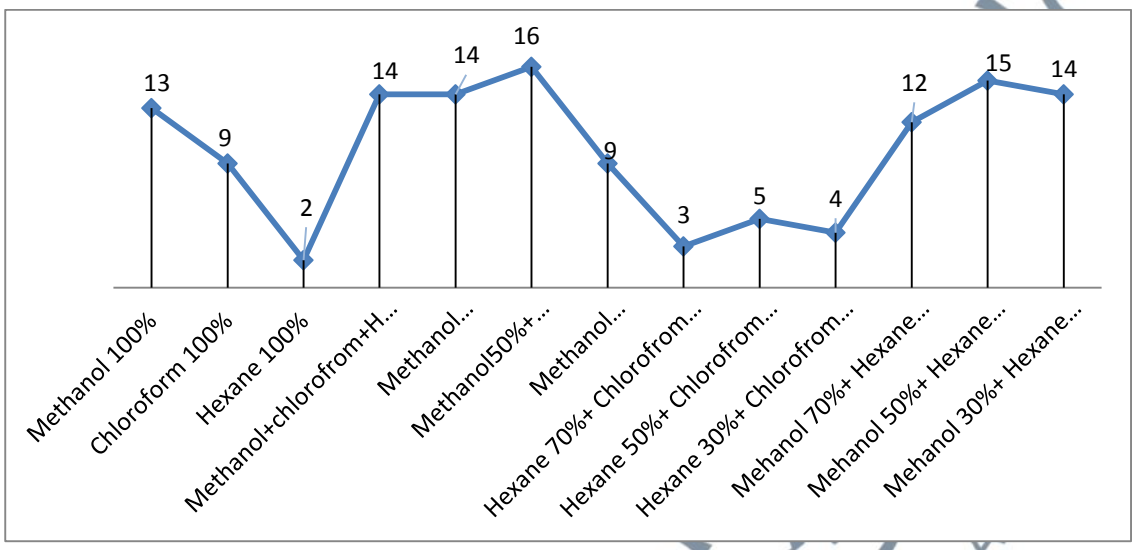
The following compounds appear in all solvents except in hexane solvent; n-Hexadecanoic (Palitic acid) acid, antioxidant, lubricant, hemolytic, nematicide, antiandrogenic, flavor, pesticide, hypocholesterolemic, 5-alpha reductase inhibitor (Rajeswari et al., 2012). Certain compounds appear in specific solvent; for example, 2-Propanamine, N-methyl-N-nitroso- in extraction using three mixture design, the mixture of solvents exhibited the biochemical compounds compared to the other extracts. The possible explanation of this is that most of these compounds are semi polar by mixing the polar and non-polar solvents (Methanol, hexane and chloroform).

The Pentadecanoic acid, 14-methyl found in extraction using methanol : chloroform (50 % : 50 %) is antifungal and antimicrobial in action (Akpuaka et al., 2013) While the best extraction process was using methanol : chloroform (50 % : 50 %). Hexadecanoic acid; ethyl ester, Oleic Acid (9-Octadecenoic acid (Z)) are 5-alpha reductase inhibitor, allergenic, alpha reductase inhibitor, anemiagenic,

antialopecic, antiandr-ogenic, antiinflamatory, antileukotriene-D4 (Anti-platelet activating factor), cancer preventive, choleretic, dermatitigenic flavor, hypocholesterolemic, insectifuge irritant, percutaneostimulant perfumery, propecic, (Rajeswari & Srinivasan, 2015). 9-Octadecenoic acid, (E)- and 9,12-Octadecadienoic acid (Z,Z) are fatty acid, which showed many functions such as Anti-inflammatory, hypocholesterolemic, cancer preventive, hepatoprotective, nematicide, insectifuge, antihistaminic antieczemic, antiacne, 5-Alpha reductase inhibitor, antiandrogenic, antiarthritic, anticoronary, insectifuge (Mathavi et al., 2013).

The **Fig 6** shows the most important biochemical compounds with similarity index (SI) above 80 % with solvents type shown in the Tables 7 to 20. Methanol (50 %) and chloroform (50 %) is best design in extraction biochemical compounds because it extracted 16 compounds and methanol (50 %) and hexane (50 %) extracted 15 compounds and methanol : chloroform : hexane, methanol (70 %) and chloroform (30 %) and methanol (30 %) and hexane (70 %) extracted 14 compounds, while the three mixture design was the best design because have eight compounds higher than 90 % (SI) and methanol (30%) and hexane (70 %) extracted have six compounds higher than 90 % (SI). In the other mixture of solvents, less number of compounds were extracted as compound with the previous mixture.

Figure 6: Graph of Biochemical Compounds with Solvents Type



The 6-methyl 3,5-dihydroxy-4H-Pyran-2,3-dihydro 4-one which was found in most of the extractions has been reported to have antioxidants property (Xiangying et al., 2013). Furfural; Oleic Acid; D-Allose; Hexadecanoic acid, methyl ester; n-Hexadecanoic acid; and 6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one all of them found in tamar, rutab and khalas but different ratio . Hexadecanoic acid, methyl ester; Oleic Acid and n-Hexadecanoic acid are fatty acid and 6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one is antioxidant activity these major compounds found in three dates Other compounds were detected at small percentage of area such as 5-methyl-2-Furancarboxaldehyde; cis-Vaccenic acid; 9,12-Octadecadienoic acid (Z,Z); and D-Allose.

During the mixture of the three types of dates, some high percentage of compounds that were low in the dates in a separate case; for example Furfural; 2-Furancarboxaldehyde, 5-methyl, and some compounds were not present in the dates in the event of a separate while it was present in the case of mixing dates such as;

Orcinol, Furyl hydroxymethyl ketone and Octadecanoic acid. Some compounds were present in the same proportion or close to the compounds found in a separate case or mixed for example; Hexadecanoic acid, methyl ester; 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methy; 2-Furancarboxylic acid; n-Hexadecanoic acid and 9-Octadecenoic acid, (E).

In the GC-MS analyses of dates extracts, the identified compounds in the different extracts are presented in **Table 25**. The results showed that some compounds were identified in all extracts of the mixture dates, Tamar, Kalas and Rutab. The compounds are; Furfural (93 %, 91 %, 91 % and 91 % respectively), 6-methyl--3,5-dihydroxy,2,3-dihydro-4H-Pyran-4-one (87 %, 87 %, 80 % and 78 respectively), 5-Hydroxymethyl-furfural (96 %, 91 %, 91 % and 91 % respectively), n-Hexadecanoic acid (99 %, 99 %, 99 % and 99 % respectively), 9-Octadecenoic acid, (E)- (99 %, 98 %, 93 % and 99 % respectively).

In summary, the effect of three solvents (methanol , chloroform and hexane) on the compounds extracted from dates, has shown good results where a total of 38 compounds were identified.

TABLE 25: Comparison between mixture dates, Khesab (Tamar), Kalas (Tamar) and Segae (Rutab)

Compounds	Mixture Similarity index (%)	Tamar Similarity index (%)	Kalas Similarity index (%)	Rutab Similarity index (%)
Furfural	93	91	91	91
2-Furancarboxaldehyde, 5-methyl	95	93	-	52
2-Furanmethanol	95	94	94	95
Orcinol	86	-	-	-
Furyl hydroxymethyl ketone	72	-	-	-
Hexadecanoic acid, methyl ester	98	92	98	98
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	87	87	80	78
2-Furancarboxylic acid	72	72	72	-
4-Mercaptophenol	99	-	-	-
5-Hydroxymethylfurfural	96	91	91	91
n-Hexadecanoic acid	99	99	99	99
9-Octadecenoic acid, (E)	99	98	93	99
9,12-Octadecadienoic acid (Z,Z)	99	99	99	99
D-Allose	86	86	86	72

4.2 Results and Discussion of compounds detected using LC-TOF-MS

The compounds identification was performed by analyzing the LC, TOF and MS spectral pattern based on micro TOF-Q 86 source type ESI database library and comparison with literature data. Most of the possible compounds identified have intensity of about 23 - 283. The LC-TOF-MS results is shown in Appendices B from figure 33-35, and the corresponding compounds with their retention times, peak's area, molecular formula, molecular weights (MW), and Intensity in the tables from 26-28, when the best mixture design in extraction (Methanol : Chloroform extract (50 % : 50 %) was used.

4.2.1 Methanol : Chloroform Extract Khesab (Tamar) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) is shown in **Table 26** and consist of intensity higher than 30. Thirteen of the intensity are prominent of which are 4H-6-methyl-3,5-dihydroxy-2,3-dihydro-Pyran-4-one ($C_6H_8O_4$) with retention time of 2.14 min and intensity of 50; Narinerin methyl ether ($C_{16}H_{13}O_{15}$) with retention time of 14.99 min and intensity of 93; O-dicaffeoyl shikimic acid ($C_{22}H_{25}O_{13}$) with retention time of 14.99 min and intensity of 50; Luteolin rhamnosyl hexoside ($C_{27}H_{29}O_{13}$) with retention time of 14.99 min and intensity of 30; 4-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 22.35 min and intensity of 64.

The LC-TOF-MS analysis of extracts showed the presence of various types of compounds in date fruits. Some compounds appeared in all type dates Khesab (Tamar), Segae (Ruteb) and Khalas (Tamar) for example; 6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one which is antioxidant activity (Farag, M. A et al 2014).

Stearic acid biological activities include, 5-α reductase inhibitor, hypo cholesterolemic, suppository, cosmetic, lubricant, surfactant and softening agent, perfumery, propecic, flavor (Mathavi et al., 2013). Tridecanoic acid biological activities include; antioxidant, lubricant, Hypercholesterolemic, Cancer preventive, Cosmetic (Rajeswari & Srinivasan, 2015). 9, 12-Octadecadienoic acid (Z, Z) and (E)-9-Octade-cenoic acid ethyl ester biological activities include; Antioxidant, hypocholesterolemic nematicide, pesticide, anti-androgenic flavor, hemolytic. 5-Alpha reductase inhibitor (Rajeswari & Srinivasan, 2015) was found only in Rutab using LC-TOF-MS.

TABLE 26: Compounds detected in dates Khesab (Tamar) from Methanol : Chloroform (50 % : 50%) Extract using LC-TOF -MS

Peak	Retention time min	Intense	Possible compounds	Type	Molecular formula	Molecular weight (MW) g/mol	Reference
1	2.14	50	6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one	antioxidant activity	$C_7 H_6 O_3$	146	(Farag, M. A et al 2014)
5	2.14	187	Un	-	$C_{15} H_{20} O_{10}$	360	(No ref)
6	2.14	63	O-Feruloyl quinic acid	Fatty acid	$C_{17} H_{18} O_{10}$	318	(Farag, M. A et al 2014)
7	2.14	330	Un	-	$C_{30} H_{38} O_{20}$	702	(no ref)
10	2.14	100	Un	-	$C_{30} H_{42} H_{20}$	723	(Farag, M. A et al 2014)
2	1.99	93	Narinerin methyl ether	Fatty acid	$C_{16} H_{13} O_{15}$	286	(Farag, M. A et al 2014)
3	14.99	15	Catechin / epicatechin	Antioxidant	$C_{15} H_{13} O_{16}$	287	(Farag, M. A et al 2013)
6	14.99	50	O-dicaffeoyl shikimic acid	Phenolic acid	$C_{22} H_{25} O_{13}$	497	(Farag, M. A et al 2014)
10	14.99	30	Luteolin rhamnosyl hexoside	Flavanoids	$C_{27} H_{29} O_{13}$	593	(Farag, M. A et al 2014)
2	22.35	64	4-o-caffeoylquinic acid	Phenol acid	$C_{16} H_{17} O_9$	353	(Farag, M. A et al 2013)

4.2.2 Methanol : Chloroform Extract Segae (Rutab) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) is presented in **Table 27** with intense higher than 40. Eight of the intensity are prominent and include 4H-6-methyl-3,5-dihydroxy-2,3-dihydro-Pyran-4-one ($C_6H_8O_4$) with retention time of 2.13 min and intensity of 170; Tridecanoic acid ($C_{13}H_{26}O_2$) with retention time of 2.13 min and intensity of 63; Stearic acid ($C_{18}H_{33}O_2$) with retention time of 2.13 min and intensity of 193; 9,12-Octadecadienoic acid (Z,Z) ($C_{18}H_{32}O_2$) with retention time of 3.08 min and intensity of 82; 5-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 12.86 min and intensity of 253; 3-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 13.53 min and intensity of 254; 4-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 22.38 min and intensity of 193; Sucrose ($C_{12}H_{20}O_{11}$) with retention time of 22.95 min and intensity of 64.

The process of identifying in LC-TOF-MS; the extracted compounds have high molecular weight (MW) between 146-757 g / m such as Narinerin methyl ether Fatty acid (Farag et al., 2013); Catechin / epicatechi antioxidant (Farag et al., 2013); O-dicaffeoyl shikimic acid Phenolic acid (Farag et al., 2014); Luteolin rhamnosyl hexoside and 4-o-caffeoylquinic acid which were found in Khesab (Tamar) (Farag et al., 2013).

TABLE 27: Compounds detected in dates Segae (Rutab) from Methanol : Chloroform Extract (50 % : 50 %) using LC-TOF -MS

Peak	Retention time	Intense	Possible compounds	Type	Molecular formula	Molecular weight (MW)	Reference
2	2.13	170	6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one	antioxidant activity	$C_6H_8O_4$	146 g / mol	(Farag, M. A et al 2014)
4	2.13	63	Tridecanoic acid	Fatty acid	$C_{13}H_{26}O_2$	214	(Farag, M. A et al 2014)
5	2.13	193	Stearic acid	Fatty acid	$C_{18}H_{33}O_2$	219	(Farag, M. A et al 2013)
7	2.13	104	Un	-	$C_{15}H_{21}O_2$	233	(no ref)
8	2.13	237	Un	-	$C_{16}H_{24}O_2$	248	(no ref)
10	2.13	40	Compesterol	Natural steroids	$C_{28}H_{48}O$	400	(Farag, M. A et al 2014)
8	3.08	82	9,12-Octadecadienoic acid (Z,Z)-	Fatty acid	$C_{18}H_{32}O_2$	280	(Rajeswari. B & Srinivasan. M., 2015)
9	3.08	40	Hydroxy octedecadienoic acid	Fatty acid	$C_{18}H_{31}O_3$	294	(Mathavi. P et al., 2013)
10	3.08	40	(E)-9-Octade-cenoic acid ethyl ester	Fatty acid	$C_{20}H_{38}O_2$	310	(Rajeswari. B & Srinivasan. M., 2015)
5	12.86	253	5-o-caffeoylquinic acid	Phenolic acid	$C_{16}H_{17}O_9$	353	(Farag, M. A et al 2014)
3	13.53	254	3-o-caffeoylquinic acid	Phenolic acid	$C_{16}H_{17}O_9$	353	(Farag, M. A et al 2014)
2	17.86	283	Un	-	$C_{17}H_{18}O_{10}$	318	(Farag, M. A et al 2014)
5	18.97	110	Un	-	$C_{20}H_{24}O_{11}$	441	(no ref)
1	20.90	195	Un	-	$C_{13}H_{15}O_{10}$	331	(Farag, M. A et al 2013)
2	22.38	193	4-o-caffeoylquinic acid	Phenolic acid	$C_{16}H_{17}O_9$	353	(Farag, M. A et al 2013)
1	22.95	64	Sucuroso	Sugar	$C_{12}H_{20}O_{11}$	340	(Farag, M. A et al 2014)
4	22.95	116	Un	-	$C_{16}H_{27}O_{10}$	379	(Farag, M. A et al 2014)

4.2.3 Methanol : Chloroform Extract Khalas (Tamar) (50 % : 50 %)

The extract of Methanol (50 %) and Chloroform (50 %) is shown in **Table 28** and consist of intensity higher than 50. Fifteen of the peak are prominent which are 4H-6-methyl-3,5-dihydroxy-2,3-dihydro-Pyran-4-one ($C_6H_8O_4$) with retention time of 2.21 min and intensity of 354; Stearic acid ($C_{18}H_{34}O_2$) with retention time of 2.21 min and intensity of 105; Apigenin ($C_{15}H_{10}O_5$) with retention time of 2.21 min and intensity of 65; Tridecanoic acid ($C_{13}H_{26}O$) with retention time of 3.20 min and intensity of 50; phingolipid conjugate with retention time of 12.68 of min and intensity of 146; 5-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 12.93 min and intensity of 72; 3-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time 13.45 min and intensity of 87; Luteolin rhamnosyl hexoside ($C_{27}H_{29}O_{15}$) with retention time of 16.52 min and intensity of 80; Isoqurcetrin ($C_{21}H_{20}O_{12}$) with retention time of 18.21 min and intensity of 157; 4-o-caffeoylquinic acid ($C_{16}H_{17}O_9$) with retention time of 22.65 min and intensity of 157; Sucrose ($C_{12}H_{21}O_{11}$) with retention time of 23.13 min and intensity of 93; Luteolin rhamonsyl dihexoside ($C_{33}H_{39}O_{20}$) with retention time of 23.13 min and intensity of 66.

The Khalas (Tamar) the date was the best type of date in this study because it has many compounds which give several benefits to human health such as Apigenin, Corchori fatty acid, Hydroxy octadecadienoic acid, Sphingolipid conjugate, Chiysoeriol hexosyl, 5-o-caffeoylquinic acid, 3-o-caffeoylquinic acid, 4-o-caffeoylquinic acid, and Luteolin rhamonsyl dihexoside. Stearic acid biological activities include, 5-α reductase inhibitor, hypo cholesterolemic, suppository, cosmetic, lubricant, surfactant and softening agent, perfumery, propecic, flavor

(Mathavi et al., 2013). Tridecanoic acid biological activities include; antioxidant, lubricant, Hypercholesterolemic, Cancer preventive, Cosmetic (Rajeswari & Srinivasan, 2015). 9, 12-Octadecadienoic acid (Z, Z) - was also found in GC-MS analysis of compounds in Khalas (Tamar) and Segae (Rutab). (E)-9-Octade-cenoic acid ethyl ester biological activities include; Antioxidant, hypocholesterolemic nematicide, pesticide, anti-androgenic flavor, hemolytic. 5- Alpha reductase inhibitor (Rajeswari & Srinivasan, 2015) was found only in Rutab using LC-TOF-MS.

TABLE 28: Compounds detected in dates Khalas (Tamar) from Methanol : Chloroform Extract (50 % : 50%) using LC-TOF -MS

Peak	Retention time min	Intense	Possible compounds	Type	Molecular formula	Molecular weight (MW) g/mol	Reference
2	2.21	354	6-methyl-3,5-dihydroxy-2,3-dihydro-4H-Pyran-4-one	antioxidant activity	$C_6 H_8 O_4$	146	(Farag, M. A et al 2014)
4	2.21	105	Stearic acid	Fatty acid	$C_{18} H_{34} O_2$	219	(Farag, M. A et al 2014)
5	2.21	72	Un	-	$C_{14} H_{14} O_3$	230	(Farag, M. A et al 2014)
10	2.21	65	Apigenin	flavanoid	$C_{15} H_{10} O_5$	266	(Farag, M. A et al 2014)
4	3.20	100	Un	-	$C_{14}H_{11}O_5$	262	(Farag, M. A et al 2014)
5	3.20	109	Linolenic acid	-	$C_{18}H_{29}O_2$	277	(Farag, M. A et al 2014)
1	3.20	50	Tridecanoic acid	Fatty acid	$C_{13} H_{26} O_2$	214	(Farag, M. A et al 2014)
6	3.20	32	9,12-Octadecadienoic acid (Z,Z)-	Fatty acid	$C_{18} H_{32} O_2$	280	(Rajeswari. B & Srinivasan. M., 2015)
7	3.20	61	Un	-	$C_{10} H_{27} O_{11}$	294	(Farag, M. A et al 2014)
8	3.20	23	Corchori ftty acid	Fatty acid	$C_{18} H_{25} O_4$	304	(Farag, M. A et al 2014)
9	3.20	44	Hydroxy octadecadienoic acid	Fatty acid	$C_{18} H_{31} O_3$	312	(Mathavi. P et al., 2013).
6	12.68	146	Sphingolipid conjugate	Fatty acid	$C_{23}H_{47} NO_7P$	480	(Farag, M. A et al 2014)
10	12.68	51	Chiysoeriol hexosyl	Phenolic acid	$C_{28}H_{31} O_5$	607	(Farag, M. A et al 2014)
5	12.93	72	5-o-caffeoylquinic acid	Phenol acid	$C_{16} H_{17} O_9$	353	(Farag, M. A et al 2014)
3	13.45	87	3-o-caffeoylquinic acid	Phenol acid	$C_{16} H_{17} O_9$	353	(Farag, M. A et al 2014)
6	13.45	50	Un	-	$C_{17} H_{29} O_5$	427	(Farag, M. A et al 2014)
5	16.52	71	Un	-	$C_{17}H_{26}O_{15}$	421	(no ref)
9	16.52	80	Luteolin rhamnosyl hexoside	Flavanoids	$C_{27} H_{29} O_{15}$	593	(Farag, M. A et al 2014)
5	18.21	157	Isoqurcetrin	Antioxidant	$C_{21}H_{20}O_{12}$	465	Mathavi. P et al., 2013)
2	18.95	114	Un	-	$C_{20}H_{24}O_{11}$	441	(no ref)

6	20.89	77	Un	-	$C_{17}H_{21}O_{10}$	385	(no ref)
1	22.65	157	4-o-caffeoylquinic acid	Phenolic acid	$C_{16}H_{17}O_9$	353	(Farag, M. A et al 2014)
6	22.65	60	Un	-	$C_{27}H_{22}O_{13}$	554	(no ref)
1	23.13	93	Sucrose	sugar	$C_{12}H_{21}O_{11}$	340	(Mathavi. P et al., 2013).
5	23.13	198	Un	-	$C_{15}H_{23}O_{11}$	379	(no ref)
6	23.13	57	Un	-	$C_{15}H_{24}O_{11}$	380	(no ref)
8	23.13	66	Luteolin rhamonsyl dihexoside	Flavanoids	$C_{33}H_{39}O_{20}$	757	(Farag, M. A et al 2014)

4.3 Results and Discussion of GC-MS using Principal Component Analysis (PCA)

Results of GC-MS (retention time and peak area) for 13 design mixtures were tabulated in from of multvaiate data set. Principal Component Analysis (PCA) was peformed on the data using unscrambler X 10.1 Scores and Loading were obtained and plots of Scores and Loadings were studied.

4.3.1 Compounds with Mixture Design and Retention Time (Raw Data)

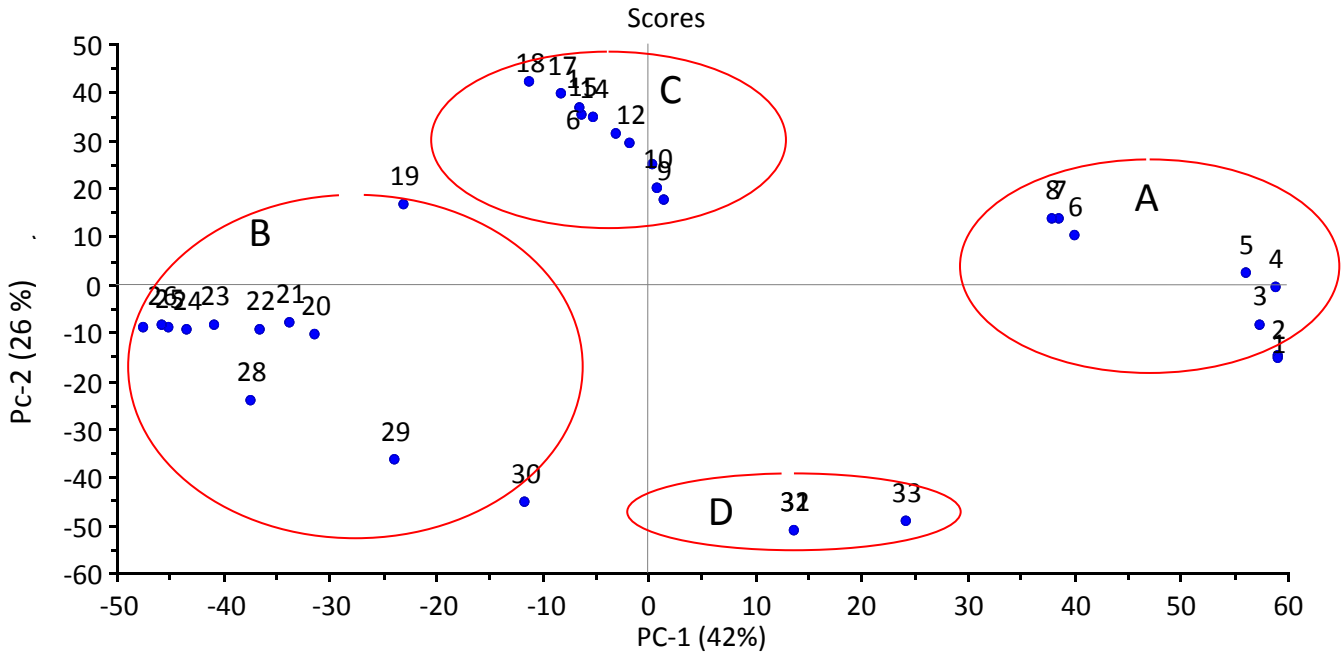
4.3.1.1 Scores

The score plot is a two dimensional scatter plot (or map) of scores for two specified components (PCs) for PCA. The score plots show how well the data is distributed and gives information in the samples (Wise et al., 2006). The scores plot (PC1, PC2) was used in this study because the two components which reveals more disparity in the data than any other pair of components. Figure 8 describes the PCA score plot of different solvents extractions and are represented in four clusters (A, B, C and D) on the graph.

The compounds with positive and high scores are denoted as A. Compounds 1 (Glycolaldehyde dimethyl acetal), 2 (Furfural), 3(3-Furaldehyde), 4 (2 – Furanmethanol), and 5 (9-Octadecene) are closer to one another. Compounds 6 (3-Octadecene, (E)), 7 (Cyclodecane, octyl) and 8 (Orcinol) are also loaded and closely packed on PC 1. On the other hand, the compounds with high and negative impact on PC1 (B) include 27 (Octadecanoic acid), 26 (5-Hydroxyme-thylfurfural), 25 (Propanamine, N-methyl-N-nitroso-), 24 (4H-Pyran-4-one, 3,5-dihydroxy-2-), 23 (2,5-Furandicarbo-xaldehyde), 22 (D-Allose), 21 (Tridecanoic acid) and 20 (9,12-Octadeca-dienoic acid (Z,Z)). These compounds are superimposed to one another.

Also, on PC 1, compound 19 (Oleic acid) was negative and quite separate from the other samples. On PC 2, the compounds with the most influence are labeled D and include compounds 29 (9-Octadecanoic acid), 30 (6-Octadecenoic acid), 32 (cis-9-Hexadecenoic acid) and 33 (cis-13-Octadecenoic acid). Also positively loaded on PC 2 are 9 (Furancarboxy-lic acid, hydrazide), 10 (Furyl hydroxyl-methyl ketone), 11 (4H-Pyran-4-one, 2,3-dihydro-3,5- dihydroxy-6-methyl), 12 (Ethyl 9-hexadecenoate), 13 (Ethyl Oleate), 14 ((E)-9-Octade-cenoic acid ethyl ester), 15 (5-Hydroxy-methylfurfural), 16 (n-Hexadecanoic acid), 17 (Octadec-9-enoic acid) and 18 (cis-Vaccenic acid).

Figure 7: PCA Scores plot for the compounds extracted



the components concerned (i.e. they have close values for the corresponding variables). On the other hand, samples for which scores differ greatly are quite different from each other with respect to the variables. The score describes the major

features of the sample, relative to the variables with high loadings on the PC (CAMO, 2011).

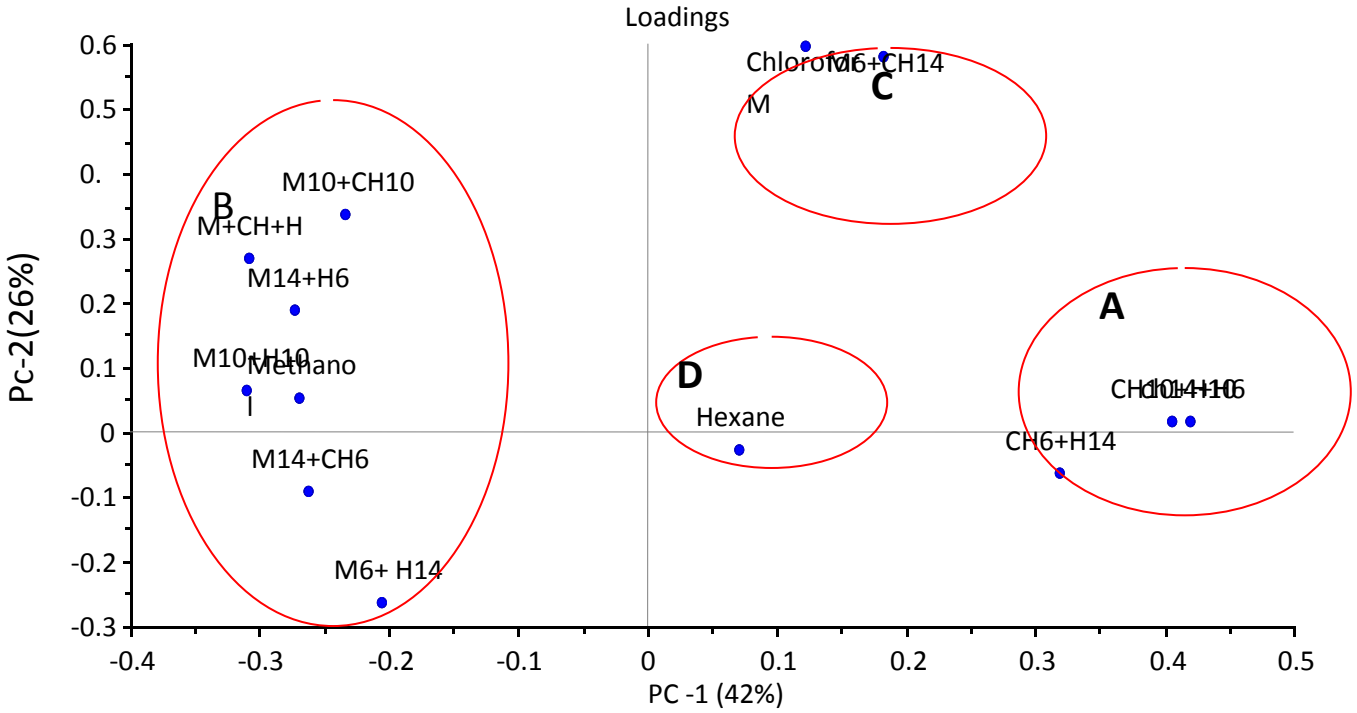
4.3.1.2 Loadings

Fig.8 the separation between solvents system was achieved using the first two principal components (PCs) (PC1 versus PC2) with a total variance of 68 % (the mixture design used is as shown in APPENDIX D). PC1 was the highest variance (42 %) while PC2 was the greatest variance (28 %) in subspace perpendicular to PC1 (Figure 9 & 10). On PC 1, (A) CH_{10} + H_{10}, CH_{14} + H_6 and (D) hexane were positively loaded. CH_{10} + H_6 and CH_{14} + H_{10} were highly loaded and overlapped, indicating shared similarities. This shows that the best mixture designs are CH_{10} + H_{10} (50 % Chloroform + 50 % Hexane), CH_{14} + H_6 (70 % Chloroform +30 % Hexane) and hexane. Also on PC 1, (B) M_{10} + CH_{10}, M + CH + H, M_{14} + H_6, M_{10} + H_{10} and methanol were negatively loaded, with M_{10} + H_{10} and methanol superimposed on each other. Furthermore, the mixtures which are positive and those that are negative on PC 1 are both anti-correlated, indicating that the increase in one will lead to the decrease on the other. On PC 2, chloroform and M_6 + CH_{14} were positively loaded and packed together while (C) M_{14}+ CH_6 and M_6 + H_{14} were negatively loaded.

The segregation observed in PCA score plot can be explained in terms of the identified compounds with regards to different mixture design, using the loading plots for PC1 signals that expose those peaks (mixture design) that have the largest effect on the respective principle component. Examination of the mixture designs in A shows that 50 % Chloroform + 50 % Hexane, 70 % Chloroform +30 % Hexane and hexane are best for extraction of group A on the scores plot (Figure 8) which include,

Glycolaldehyde dimethyl acetal, Furfural, 3-Furaldehyde, 2 –Furanmethanol, 9-Octadecene, 3-Octadecene, (E), 7 Cyclodecane, octyl and Orcinol. Methanol and chloroform extracts grouped in B on the loading plot are best suited in extracting carbohydrates as majorly represented in group B on the scores plot. Results from PCA shows that mostly phenolic, carbohydrates and fatty acids contribute to the date variety. In previous study of Mohamed et al. (2014), Principal component and clustering analyses reveal that flavonols and sugars, contribute the most to variety classification of the date studied.

Figure 8: Loading plot of all variables on PC1 and PC2

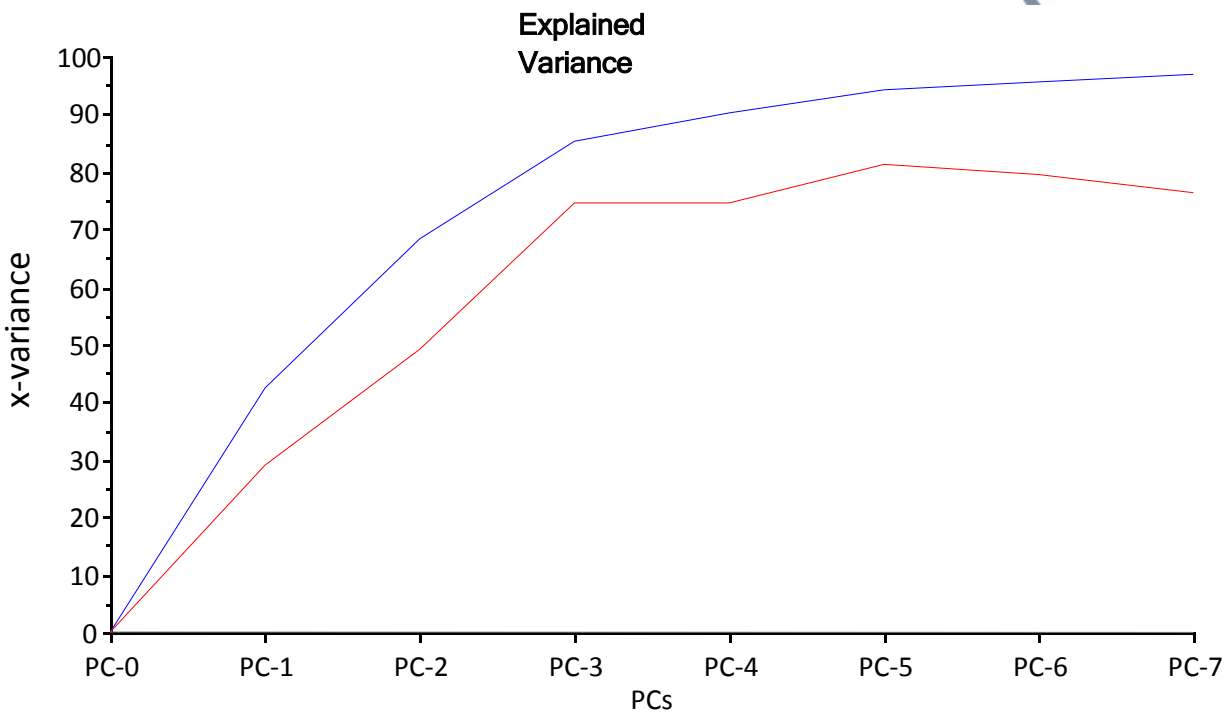


4.3.1.3 Explained variance

Fig.9 shows the blue curve indicates the calibrated variance while the red indicates the validated variance. From the validated curve, it shows that PC 1 and PC 2 are enough

to explain most variance as a sharp slope is encountered after the PC 2, after which a decline is visible**.**

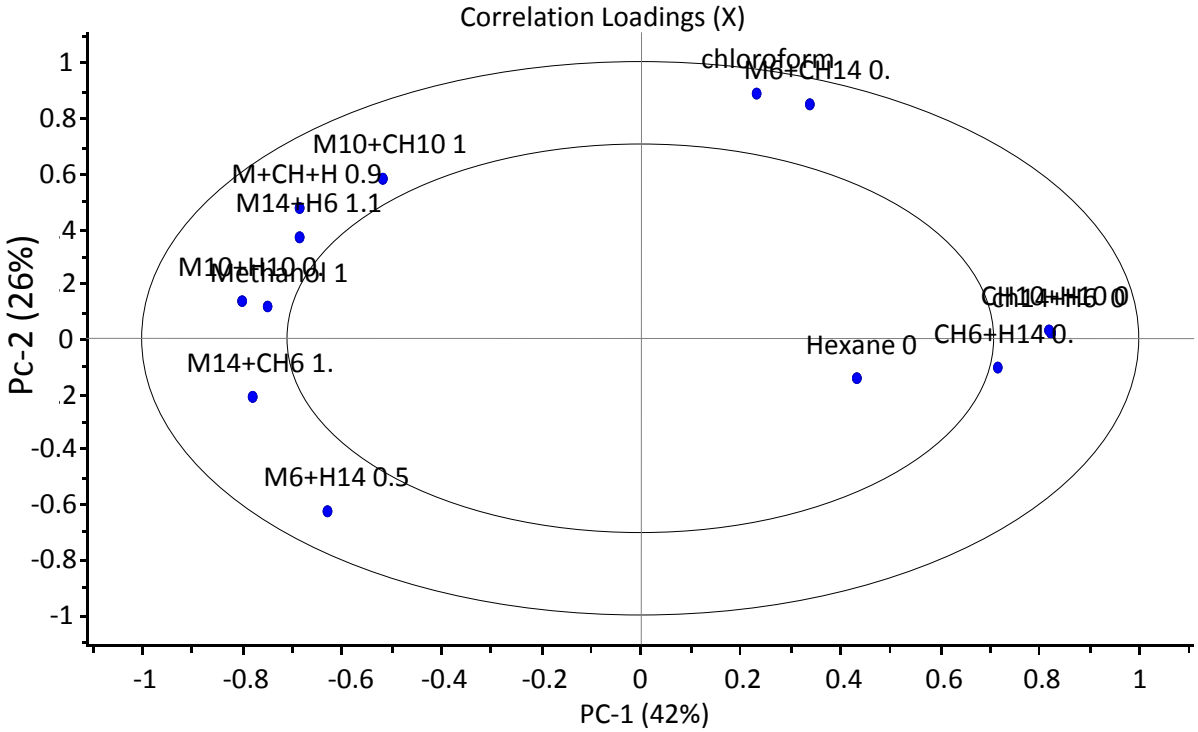
Figure 9: Cumulative variance.



4.3.1.4 Correlation loadings

Fig.10 shows the correlation loadings contain two ellipses, the inner and outer ellipses. The variables in the inner circle indicate 50 % of explained variance while those in the outer ellipse indicate 100 % variance and have high contribution to PC1.

Figure 10: Correlation loadings plot of all variables along PC1 and PC2



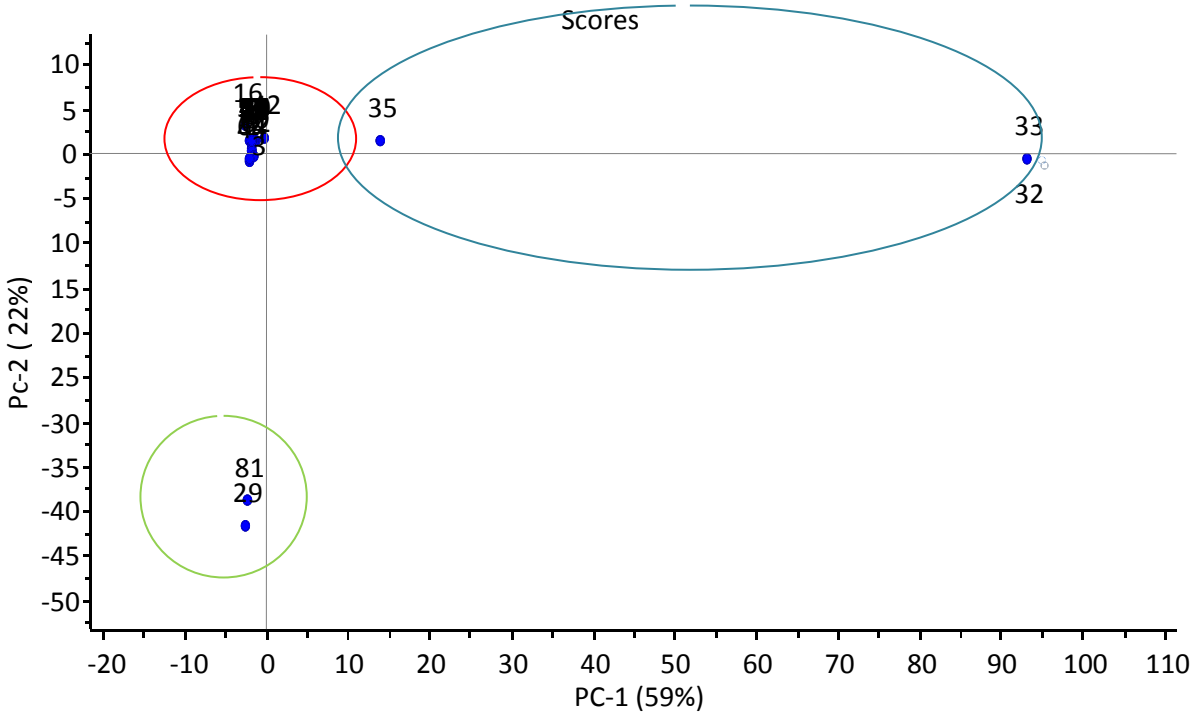
Every variable analyzed has a loading on each PC and this reflects how much the individual variable contributes to that PC, and how well the PC takes into accounts the variation in the variable (Wise et al., 2006). The magnitude of the loadings indicates the relative contribution of the individual variable to each PC based on the interrelationships among the variables, and the biological meaning is determined by eigenvectors (weight) and the PC scores. Variables on the component 1 vs. component 2 represent the largest variations in the data set. PC 1 is generally better correlated with the variables than PC 2; this is expected as PCs are extracted successively, each one accounting for as much of the remaining variance as possible (CAMO, 2011).

4.3.2 Compound with Mixture Design and Peak Area (Raw Data)

4.3.2.1 Scores

Fig.11 shows on PC 1, 33, 32 and 35 had positive scores and far apart from one another. 18 and 29 had negative scores and were superimposed on each other. On PC 2, majority of the compounds were superimposed on one another.

Figure 11: PCA Scores plot for the compounds extracted



18 (cis-Vaccenic acid) and 29 (9-Octadecanoic acid) had negative scores and were superimposed on each other. On PC 2, majority of the compounds were superimposed on one another.

4.3.2.2 Loadings

Fig.12 & 13 show PC 1 and PC 2 explained 81 % of the total variation. PC 1 made up 59 % while PC 2 made up 22 %. H100 % and M 100 % were positive and had high loadings on PC 1. Both mixture designs were far away from each other. On the other hand, 70 % M + 30 % CH contributed highly to PC 2. Other mixture designs were densely packed at the centre.

Figure 12: Loading plot of all variables on PC1 and PC2

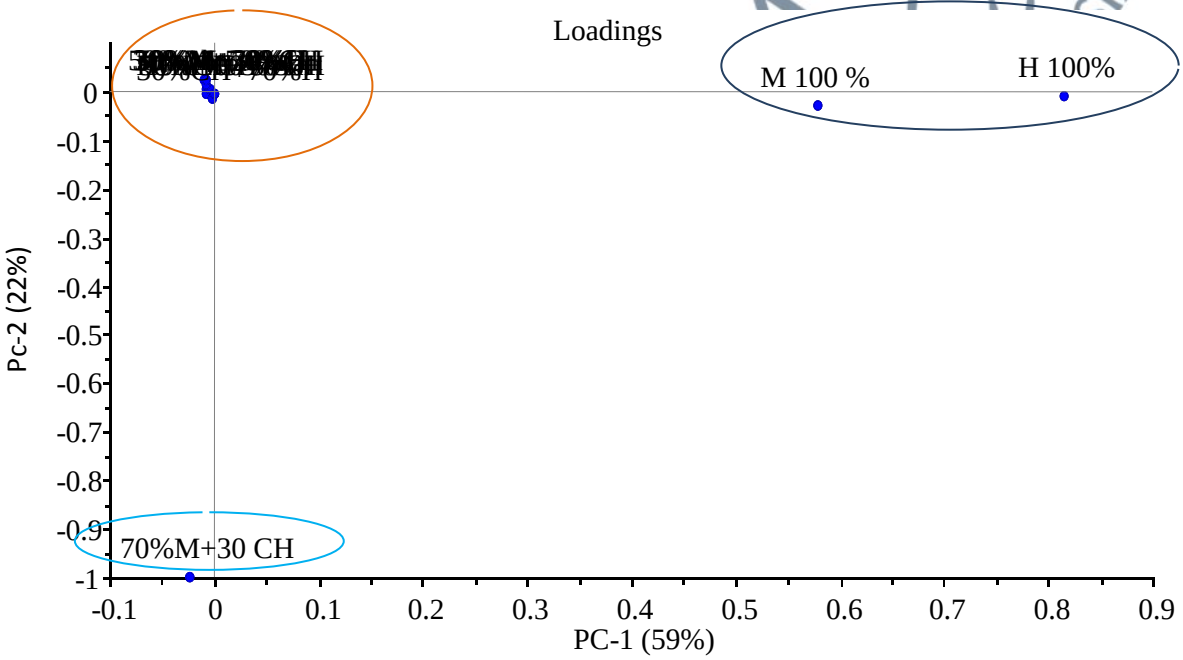
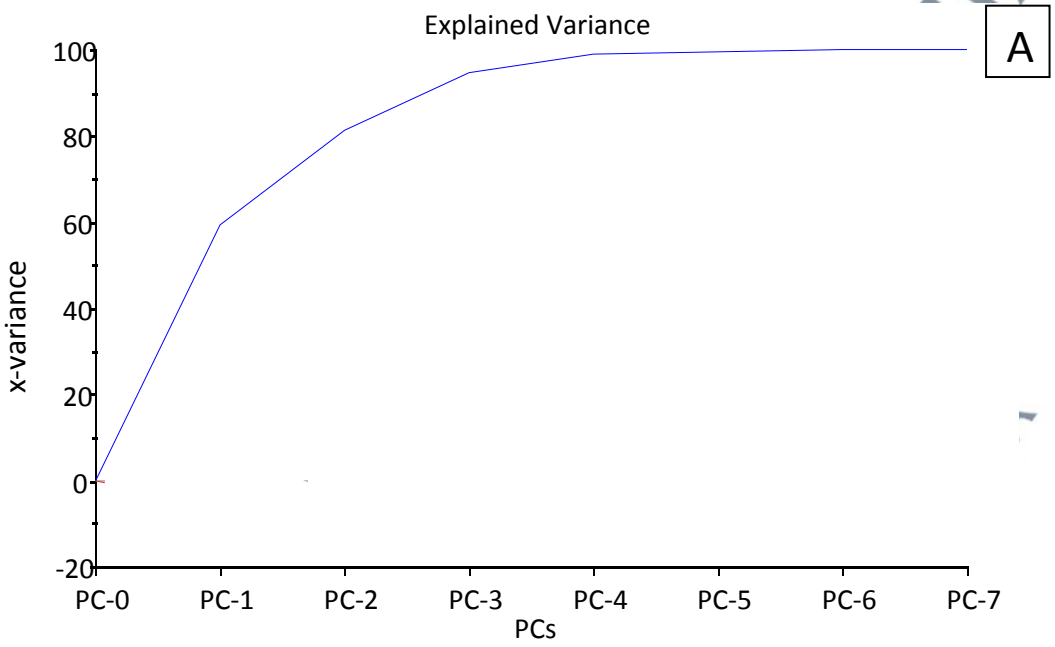


FIGURE 13: Cumulative variance



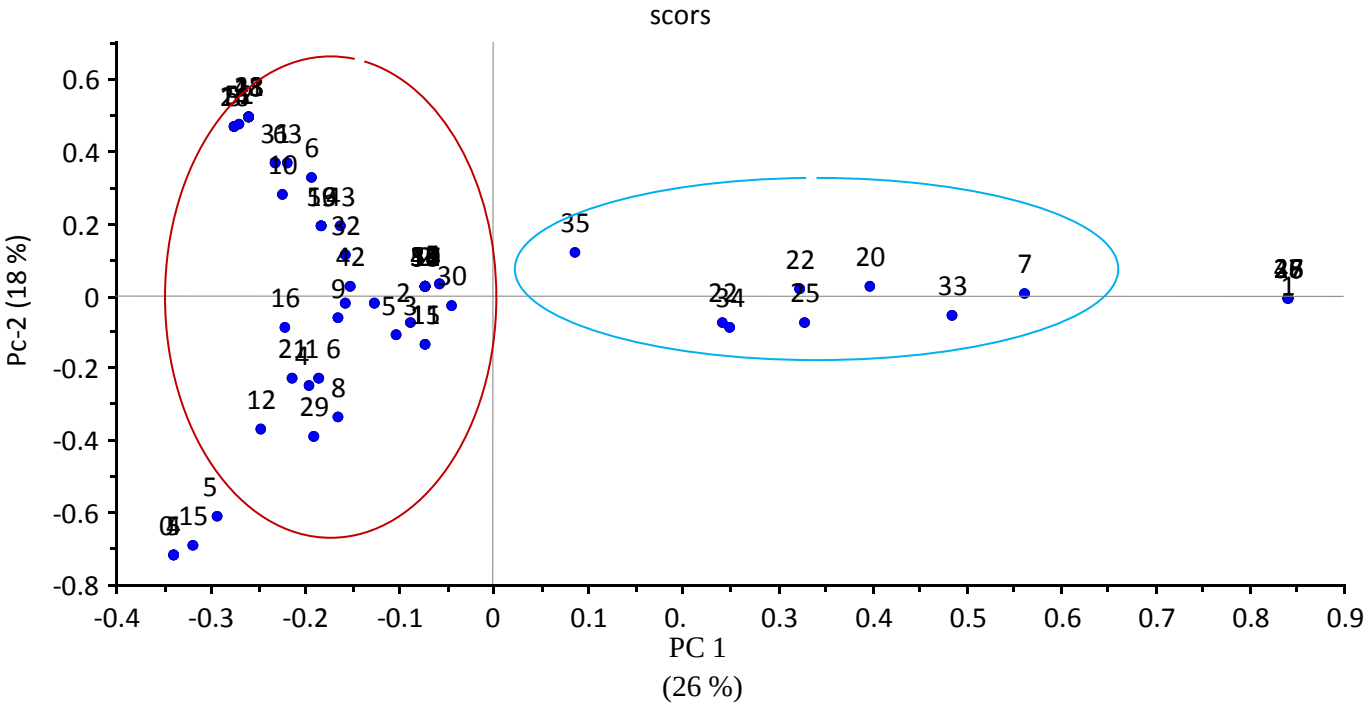
4.3.3 Compound with Mixture Design and Peak Area (Normalized Data)

4.3.3.1 Scores

Fig.14 shows on PC 1, the compounds with positive and high loadings include 20 (9, 12-Octadeca-dienoic acid (Z,Z)) and 27 (Octadecanoic acid) and are superimposed on each other. 7 (Cyclodecane), 33 (cis-13-Octadecenoic acid) and 20 (9, 12-Octadeca-dienoic acid (Z,Z)) were slightly separated; 25 (Propanamine, N-methyl-N-nitroso), 26 (5-Hydroxyme-thylfurfural), 34 (Hexadecanoic acid, methyl ester) and 17 (Octadec-9-enoic acid) were densely packed while 41 were far afar from the others. Also on PC 1, the ones with negative scores include 28 (Octadecanoic acid, 2-(2-hydroxyetho-xy) ethyl ester), 5 (9-Octadecene), 16 (n-Hexadecanoic acid), 13 (Ethyl oleate), 6 (3-Octadecene), 10 (Furyl hydroxyl-methyl ketone), 30 (6-Octadecenoic acid), 12 (Ethyl 9-hexadecenoate), 3 (3-Furaldehyde), 9 (Furancarboxy-lic acid,

hydrazide), 15 (5-Hydroxy-methylfurfural), 1 (Glycolaldehyde dimethyl acetal), 6 (3-Octadecene), 4 (2 –Furanmethanol), 14 ((E)-9-Octade-cenoic acid ethyl ester), 29 (9-Octadecanoic acid) and 8 (Orcinol). On PC 2, 18 (cis-Vaccenic acid), 19 (Oleic acid) and 24 (4H-Pyran-4-one, 3,5-dihydroxy-2-) were with negative scores and overlapped on one another.

Figure 14: PCA Scores plot for the compounds extracted

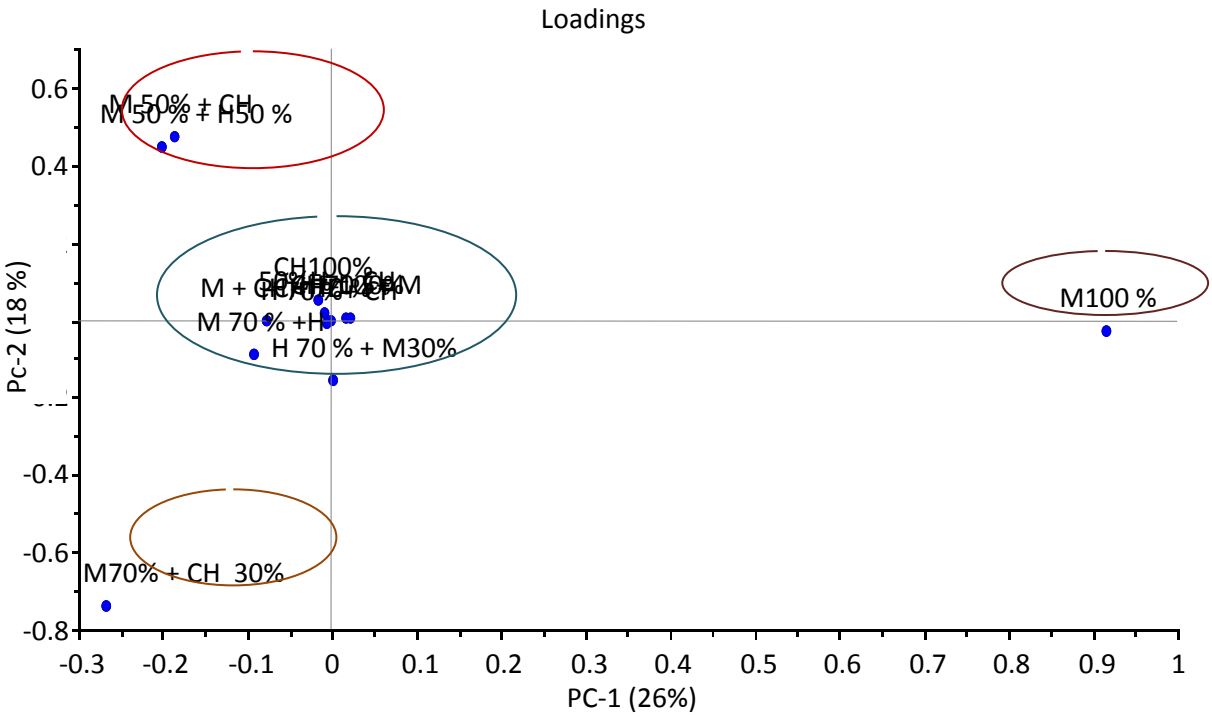


4.3.3.2 Loadings

Fig.15 shows PC 1 and PC 2 explained 44 % of the total variations with 26 % and 22 % respectively. M100 % was positive and highly loaded on PC 1 while M50 % + CH50 % and M50 % + H50 %. On PC 2, M70 % + CH30 % are at the centre, other mixtures were densely packed and do not influence the variation. The correlation loadings contain two ellipses, the inner and outer ellipses. The variables in the inner

circle indicate 50 % of explained variance while those in the outer ellipse indicate 100% variance and have high contribution to PC1.

Figure 15: Loading plot of all variables on PC1 and PC2

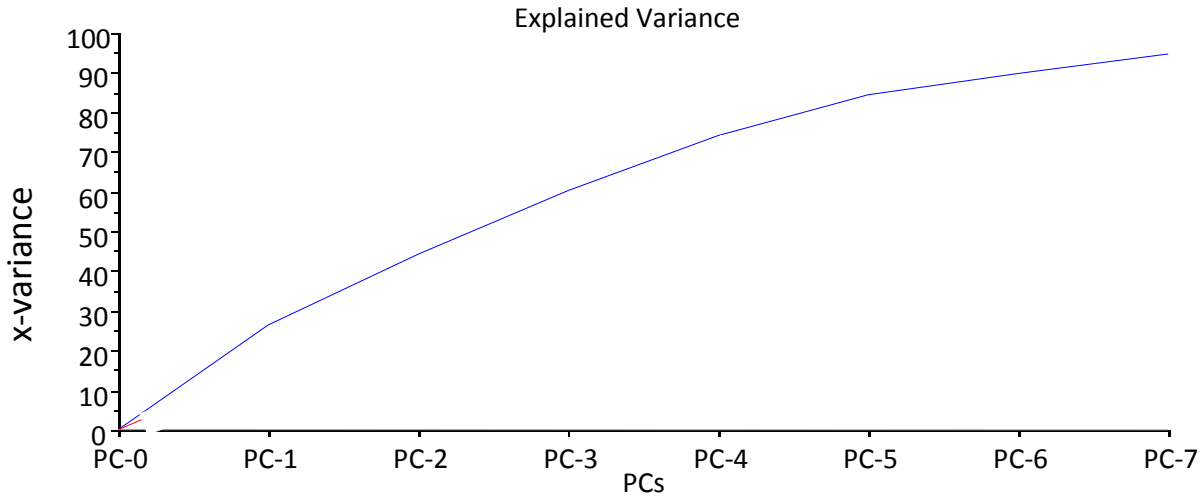


4.3.3.3 Explained variance

Fig.16 explained variance graph, which is often measured as percentage of the total variance in the data is a measurement of the proportion in the data accounted for by the individual principal component (PC). It gives an indication of how much of the variation in the data is described by the different components (CAMO, 2011). The calibration variance indicates the number of PC that was selected for this research based on the eigenvalue one criterion and is based on fitting the calibration data to the model while the validation variance is the proof of the optimum number of principal

components needed to describe the PCA model and is computed by testing the model on data that were not used to build the PCA model (CAMO, 2011)

Figure 16: Cumulative variance



4.3.4 Summary of PCA on GC-MS Data

Data from the GC-MS were subjected directly (raw data) and normalized (standardized) to get varying results. The raw data did not show much variation as that of the normalized data. According to Hendriks et al. (2005), Normalization (object-wise standardization) of analytical profiles is an important step in the preprocessing of metabolic profiling data. The difference in biological extract concentrations can be quite large and multivariate analyses of unprocessed signals could lead to results that are strongly biased. Normalization procedures might have a strong impact on data clustering and therefore influence any final interpretation.

PCA has enabled easy visualization of the compounds dispersal based on the different mixture design used. It has successfully shown which mixture design most influenced the variations of the compounds extracted from the mixed dates. Boccard

et al. (2007) in their research concluded that the multivariate analysis of TMS spectra obtained with a rapid gradient LC-TOF/MS analysis has demonstrated to be an attractive approach for the ion detection linked to significant markers of the wound response in *Arabidopsis thaliana*. Mohamed et al. (2014) also in their study reported that UPLC/PDA/ESI–qTOF-MS & GC–MS approach coupled with multivariate data analysis adopted to revealed compositional differences in secondary and primary metabolites among date fruits. The approach which allowed for the tentative identification and monitoring of 49 metabolites, most of them belonging to the flavonoid class with absolute quantification of the major peaks.