Results and Comments

Aroma of pistacia:

The gas chromatogram of basic and neutral-acidic fractions are shown in Fig. (9) , resp. The compounds eluted from G.L.C. analysis and their concentrations are shown in Table (10) .

Basic Fraction:

The separated basic fraction which has a nutty aroma, includes pyrazine and pyrrole derivatives. These compounds were identified by either G.L.C., or G.L.C.-Ms. coupling, as shown in the following.

Peak 8: It was identified as 2-methyl pyrazine by gas chromatographic data and mass spectrum.

From the mass spectrum Fig. (10) , it can be seen that the fragment ion 40 $(C_2H_2N)^+$ is responsible for the base peak. Other peaks at 53 $(C_3H_3N)^+$, 67 $(C_3H_3N_2)^+$ and 94 (M^+) are observed.

Peak 14: It was identified as 2,6-dimethyl pyrazine by the gas chromatographic retention time of the authentic sample Fig. (9) .

Peak 16: It was identified as 2,5-dimethyl pyrazine by the retention time of the authentic sample and mass spectrum data. Fig. (9 , 11).

From the mass spectrum Fig. (11) , it can be seen that 42 is the base peak $(C_2H_4N)^+$ and 108 is the parent peak . All other fragments with their relative abundance are also shown.

Peak 17 and 30 : They were identified as pyrrole and 2-pentyl pyrrole, respectively, by gas chromatographic data. Fig. (9).

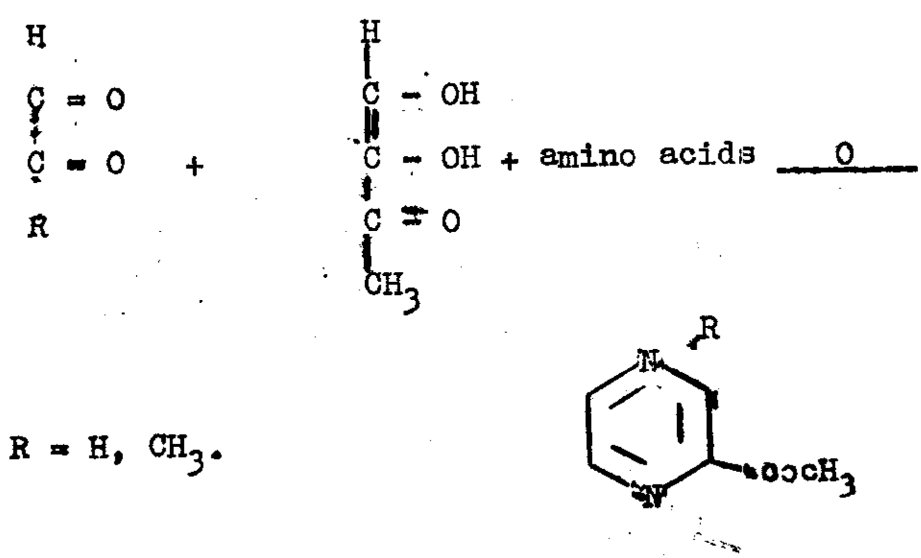
Peak 40: Fig. (12) : It was identified as 2-ethyl-5-acetyl pyrazine by the retention time of the authentic sample and mass spectrum data. It can be seen Fig. (12) that the molecular ion $(M)^+$ 150 is the base peak 43 $(CH_3CO)^+$ 95 is large.

From Table (10) it can be seen that 2,5-dimethyl pyrazine is present in very high concentration (92.91%) and seems to be the key component characteristic to pistacia flavour.

2- Methyl pyrazine and ~~2-ethyl-5-acetylpyrazine~~ are present in relatively equal amounts (2.5%) while pyrrole and 2-pentyl pyrrole are present in very small concentration as shown from Table (10) (0.56and 0.07 respectively). These two components have very strong burnt-like flavour.

These pyrazine and pyrrole derivatives were identified in sesame oil (80) , in roasted Spanish peanut (78, 79, 82) , in roasted filbert (81, 82) in roasted almond (Takei et al . 1973), and in the flavour of coffee (83, 84, 85).

The formation of these pyrazines could be explained by Wang et al .(86) mechanism involving the condensation of C-methyl reductone, a browning reaction product with glyoxal or pyruvaldehyde, respectively and amino acids (81).



R = H, CH_3.

Neutral -acidic fraction:

The neutral-acidic fraction has sweet roast flavour. Some aliphatic aldehydes, hetero cyclic aldehydes, acids, alcohols and heterocyclic ketones were identified as shown in the following Fig:(9) .

Peak 2 : It was identified as ethanol by the retention time of the authentic substance.

Peak 3: It was identified as 2-hexenal by the agreement of the mass spectraldata. Fig.(13).

The base peak was observed at 43 $(C_3H_7)^+$.

The peak at 44 $(CH_2-CH = OH)^+$ is approximately 80% and it is predominant peak in the fragmentation of short chain aldehydes and it is formed due to hydrogen rearrangment. The other peaks at 57 , 71 , and 85 are observed and they are due to the cleavage of methylene group (CH_2). The molecular ion is observed at 100.

Peak 7: It was identified as 2-methyl-2-hexenal by mass spectral data . It can be seen from the mass spectrum Fig. (14) that the base peak at both 55 and 83 $(CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-)^+$ is due to the cleavage of the bond adjacent to the double bond, while 83 $(C_6H_{11})^+$ is due to the α -cleavage of the carbonyl group.

The peak at 44 $(CH_2-CH=OH)^+$ is formed due to hydrogen transfere. Other peaks at 29 and 43 are a series of fragments (CH_2).

The molecular ion can be observed at m/e 112.

Peak 13 : It was identified as acetic acid by the gas chromatographic data.

Peak 15 : It was identified as 2-furfural by the mass spectrum and the retention time of the authentic substance Fig. (14) . It can be seen from the mass spectrum that the moleaular ion is observed at $(M)^+$ 96 with 50 % , while the base peak is observed at 81 $(C_5H_5O)^+$. The peaks at mass units 39 $(C_3H_3)^+$ and at 57 $(C_3H_5O)^+$ are abundant in the spectrum of furan.

Peak 18 : It was identified as nonanal by the agreement of retention time of the authentic substence and the mass spectral data . Fig. (15).

Peak 23 , 25 and 26: They were identified as 2-acetyl furan, 5-methyl furfural and furfuryl alcohol. From gas chromatographic data and by matching their mass spectra with those of the authentic one.

Peak 38 : It was identified as 2-nonenal by MS and the retention time of standard reference Fig. (16). It is obvious from the mass spectrum, that the base peak is at 43 $(C_3H_7)^+$. Other peaks with their relative abundance are observed as shown in Fig. (15). The molecular ion can be observed at m/e 140.

Peak 39 : It was identified as trans-2, trans -4-decadienal by the mass spectrum data Fig. (17). It can be seen from the mass spectrum, that the base peak is observed at $(M-2)^+$.

The peak at 44 $(CH_2-CH=OH)^+$ is formed due to the hydrogen transfer, Other peaks at 67 $(C_5H_7)^+$ and 81$(C_6H_9)^+$ are formed by α-cleavage followed by fragmentation of allylic position.

The molecular ion is observed at 152.

From Table (10) it can be seen that furfural is present in large concentration as represented by peak area % (53, 30), followed by 2-hexenal and 2-ethanol (14.20 and 13.53 respectively).

This high concentration of furfural contributes mainly to the pleasent sweet aroma of the neutral-acidic fraction.

All furan derivatives were developed from caramelization of sucrose or any sugar moiety at 190°C (88) . Similar findings were also reported by Bryce and Green wood (87).

2-Hexenal, nonanal and 2-nonenal might be developed from lipid oxidation (77).

Ethanol and acetic acid were developed via maillard reaction (as reported by Rossi <u>et</u> <u>al</u> . 1962). These components were identified in sesame oil (80), roasted coffee (83 , 84 ,85).and roasted Spanish peanut (78, 79, 82).

<u>Fatty acid analysis:</u>

The G.L.C. analysis of fatty acids of pistacia lipid beforeand after roasting is shown in Table (11,12) . From the data obtained, it is obvious that there is no significant change in the fatty acid composition of pistacia oil before and after roasting and that there are other synergetic compounds in lipid which may be considered responsible for producing pistacia aroma.

Table (10)

Identified Corponents and Their Composition in Basic and Neutral-Acidic Fractions from Roasted <u>Pistacia Atlantica</u> Seeds.

Peak No.	Reference to Fig. (9) peak composition (peak area %)* Basic F.	Acidic-Neutral F.	Identified compound	Evidence
1	-	-	Ether	
2	-	13.53	Ethanol	Rt
3	-	14.20	2-Hexenal	MS
4	-	1.30	-	-
5	-	1.50	-	-
6	0.05	-	-	-
7	-	8.85	2-Methyl-2-hexenal	MS
8	2.30	-	2-Methyl pyrazine	MS&Rt
9	0.11	-	-	-
10	-	trace	-	-
11	-	trace	-	-
12	0.70	-	-	-
13	-	1.13	Acetic acid	Rt
14	0.80	-	2,6-Dimethyl pyrazine	MS$^{\phi}$&Rt
15	-	53.30	2-Furfural	MS&Rt
16	92.91	-	** 2,5-Dimethyl	MS&Rt
17	0.56	-	pyrazine	Rt
18	-	trace	Nonanal	MS&Rt
19	trace	-	-	-
20	-	-	-	-
21	-	trace	-	-
22	trace	-	-	-
23	-	0.14	2-Acetyl furan	MS$^{\phi}$& Rt
24	trace	-	-	-

Cont. Table (10).

Peak No.	Reference to Fig. (9) peak composition (peak area %)* Basic F.	Acidic-Neutral F.	Identified compound	Evidence
25	-	0.14	5-Methyl fur-	MS^ø&Rt
26	-	2.24	Furfuryl alcohol	MS^ø&Rt
27	-	0.14	-	-
28	-	trace	-	-
29	-	trace	-	-
30	0.07	-	2-Pentyl pyrrole	Rt
31	trace	-	-	-
32	-	0.14	-	-
33	-	1.05	-	-
34	-	trace	-	-
35	-	trace	-	-
36	trace	-	-	-
37	-	0.58		-
38	-	0.70	2-Nonenal	MS
39	-	1.06	Trans-2,trans-4-decadienal	MS
40	2.50	-	2-Ethyl-5-acetyl pyrazine	MS

* For each fraction, sum of all peak areas (peak No. 2 to 40) = 100 %

ø Maching the mass spectral data with those of authentic specimens.

** = 2-5-Dimethyl pyrazine is present in very high concentration and seems to be the key compound characteristic to Pistacia flavour.

Table (11)

Fatty acid content of unroasted pistacia lipid.

Peak No.	Peak area	Peak %	Compounds
1	3.32	21.67	Palmitic acid
2	8.00	52.21	Oleic acid
3	4.00	26.12	Linoleic

Table (12)

Fatty acid content of roasted pistacia lipid.

Peak No.	Peak area	Peak %	Compounds
1	7.86	22.87	Palmitic acid
2	17.10	49.76	Oleic acid
3	9.4	27.35	Linoleic acid

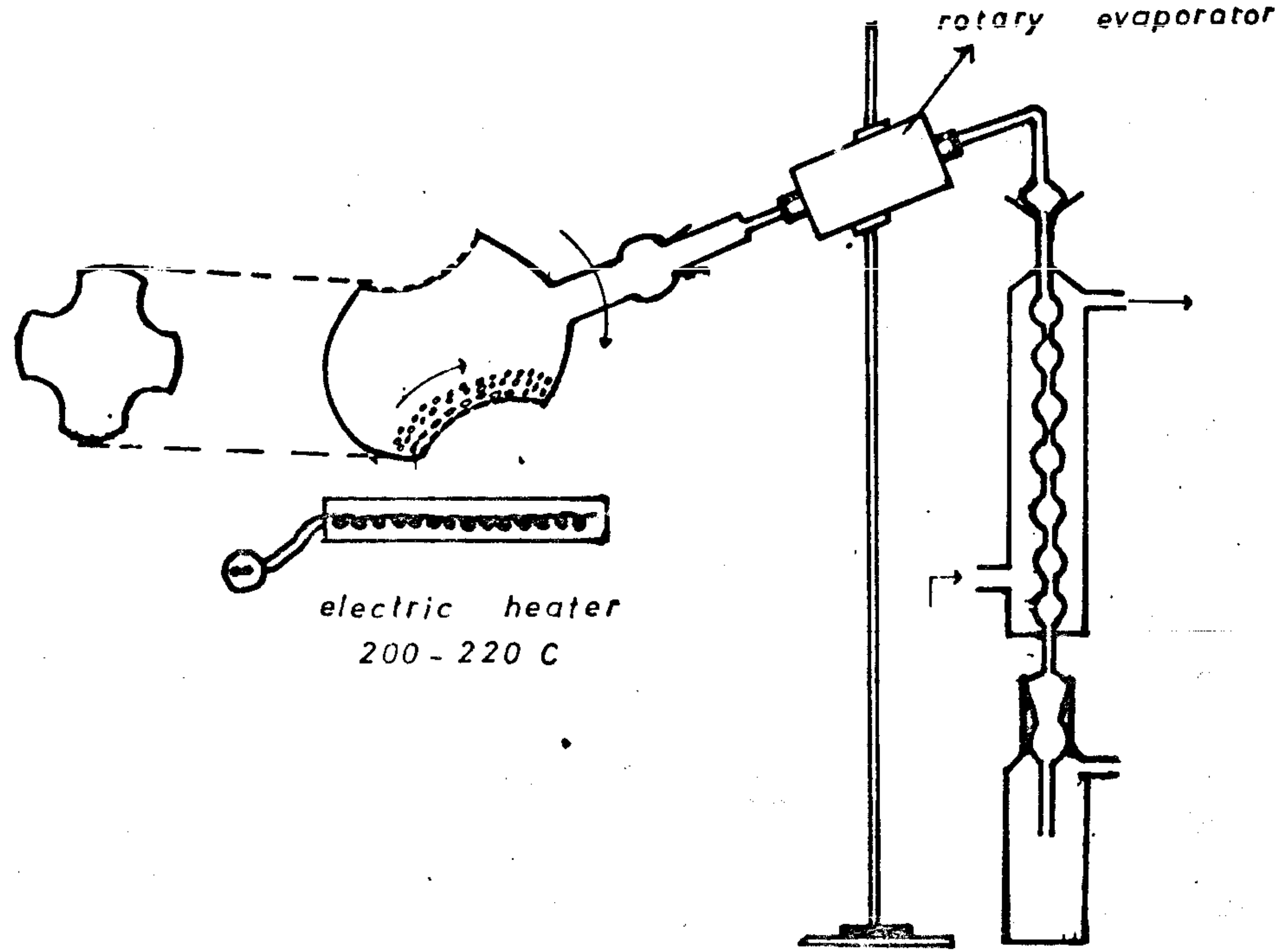


FIG 1A Schematic Diagram of the Roasting Apparatus

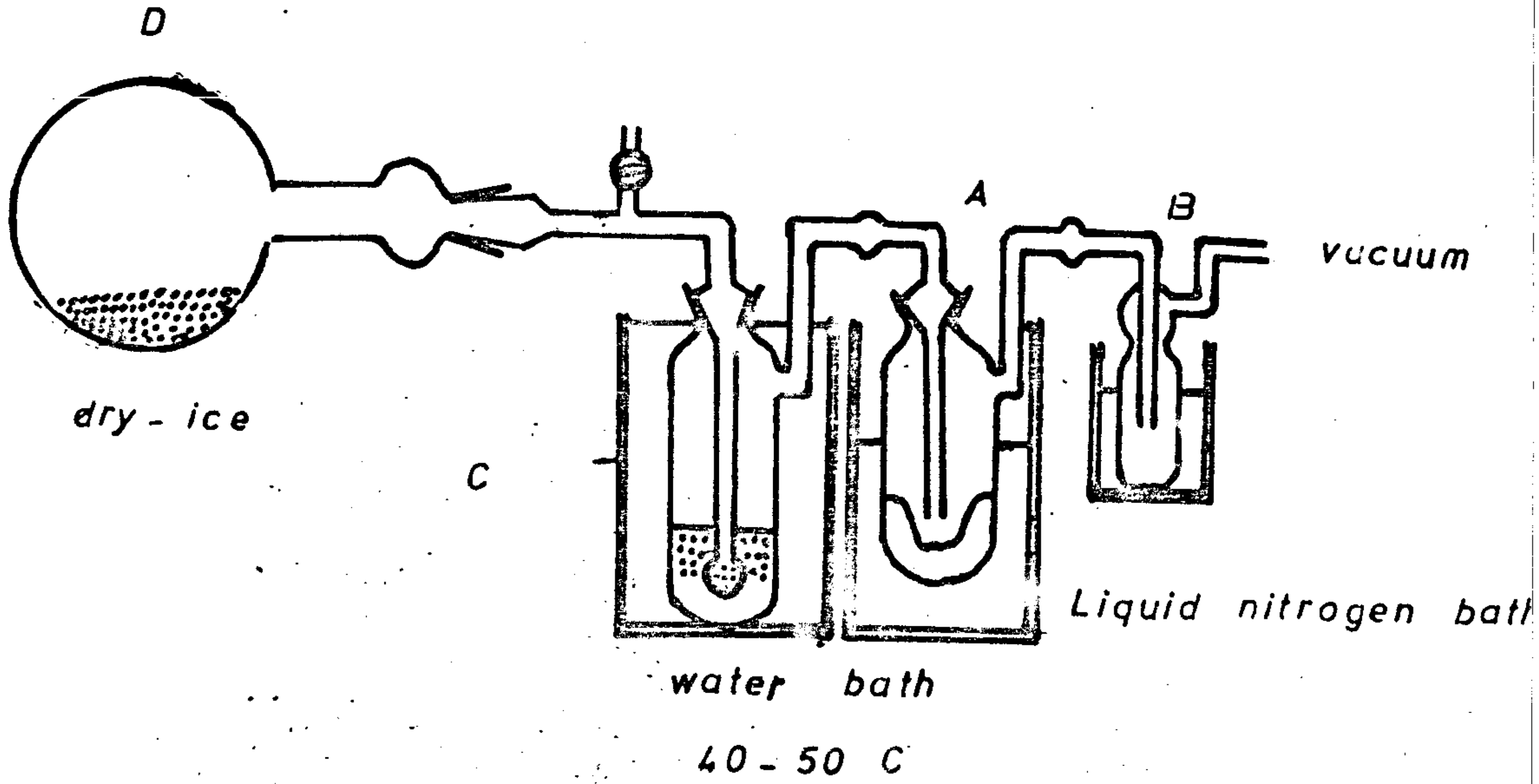


FIG 8 A Sch matic Diagram of the Carbon Dioxide Distillation Apparatus

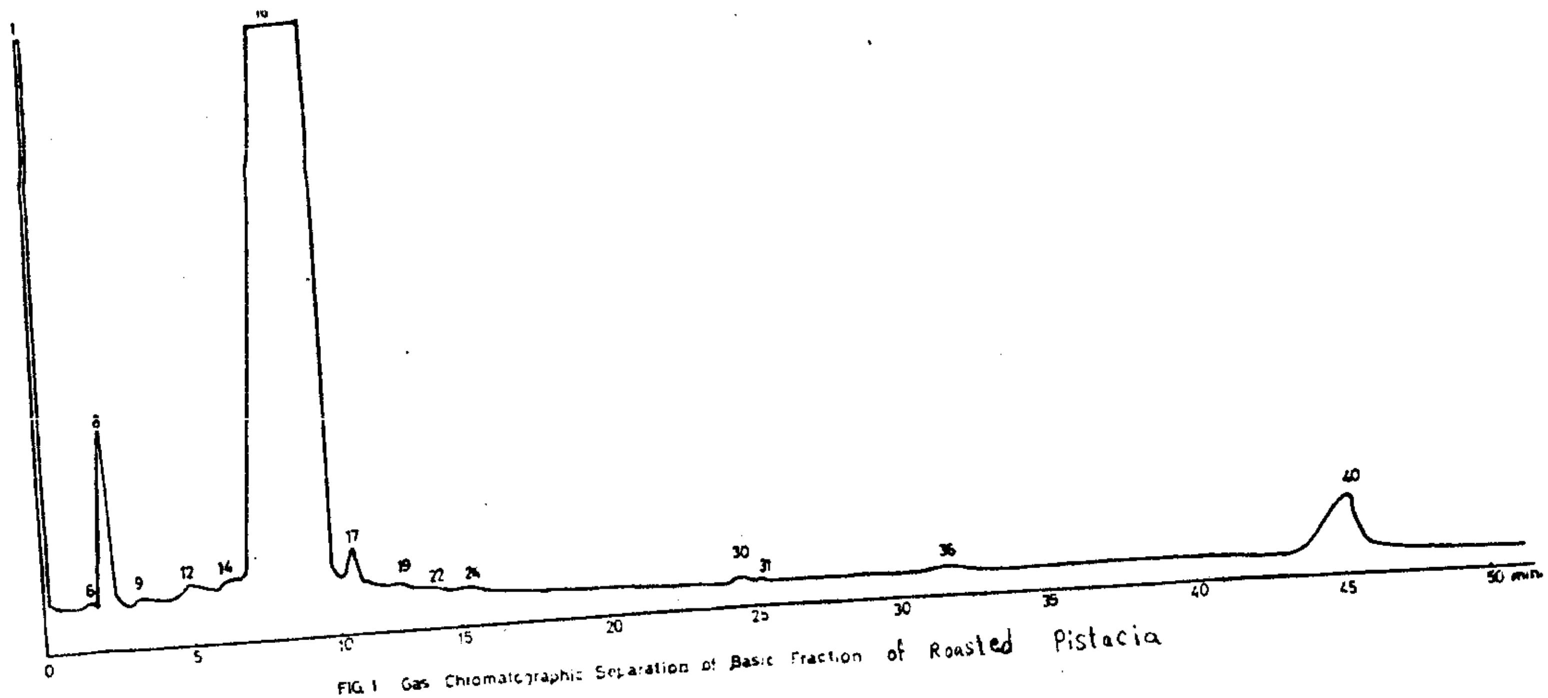


FIG. 1 Gas Chromatographic Separation of Basic Fraction of Roasted Pistacia

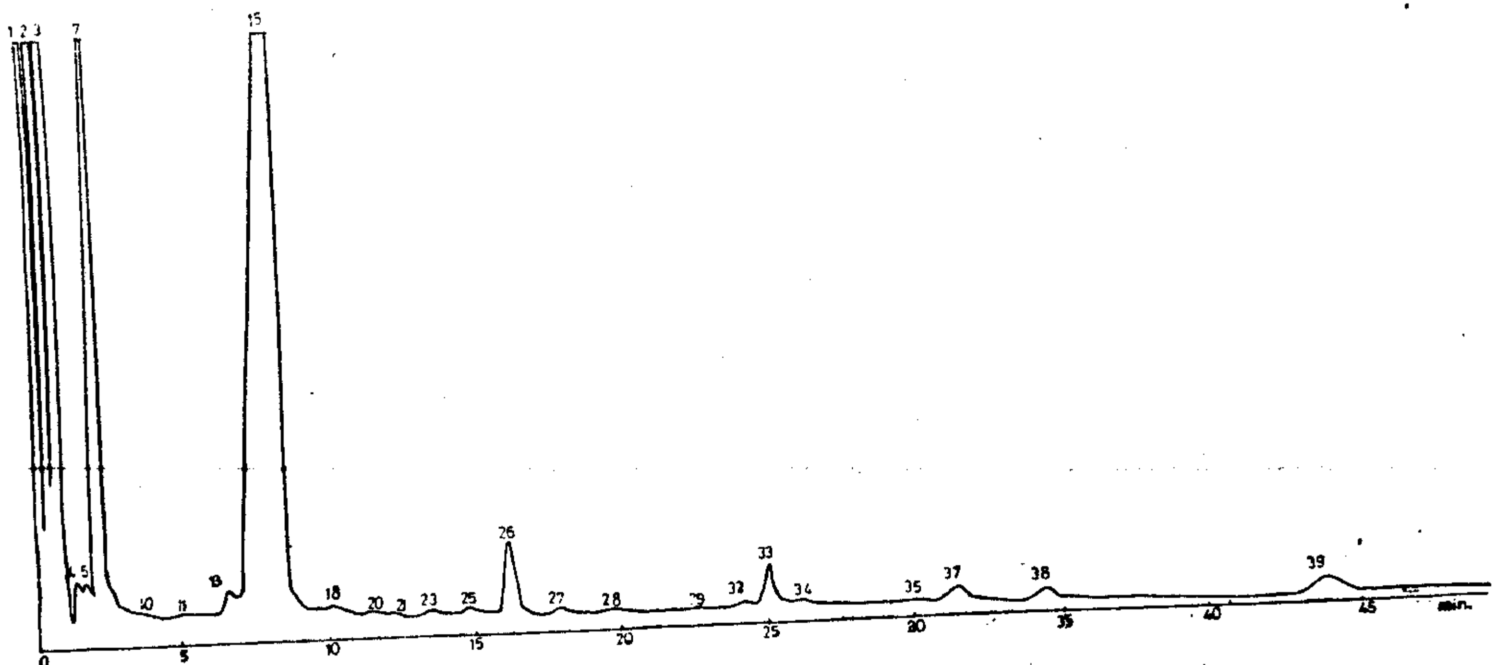


FIG. 2. Gas Chromatographic Separation of Neutral and Acidic Fraction of Roasted Pistacia

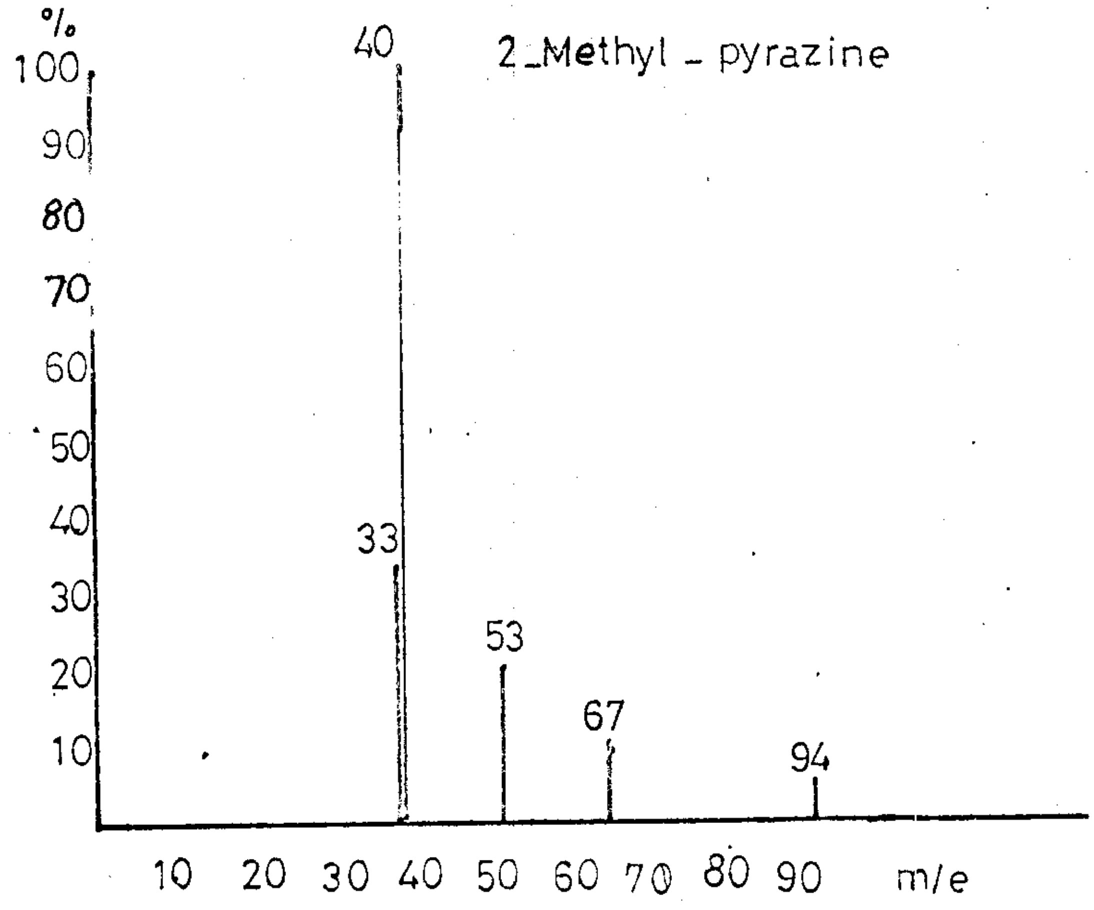


FIG. 10 .Mass Spectrum of Peak 8.

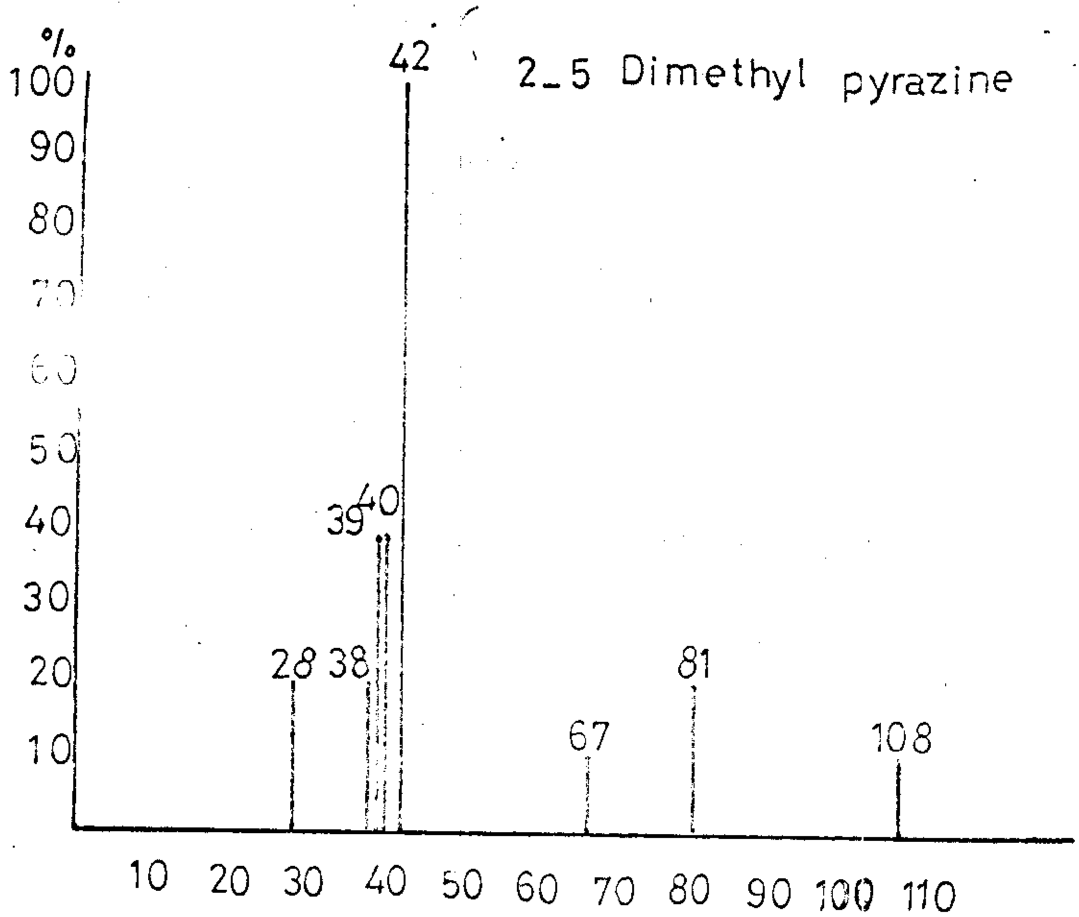


FIG. 11 .Mass Spectrum of Peak 16.

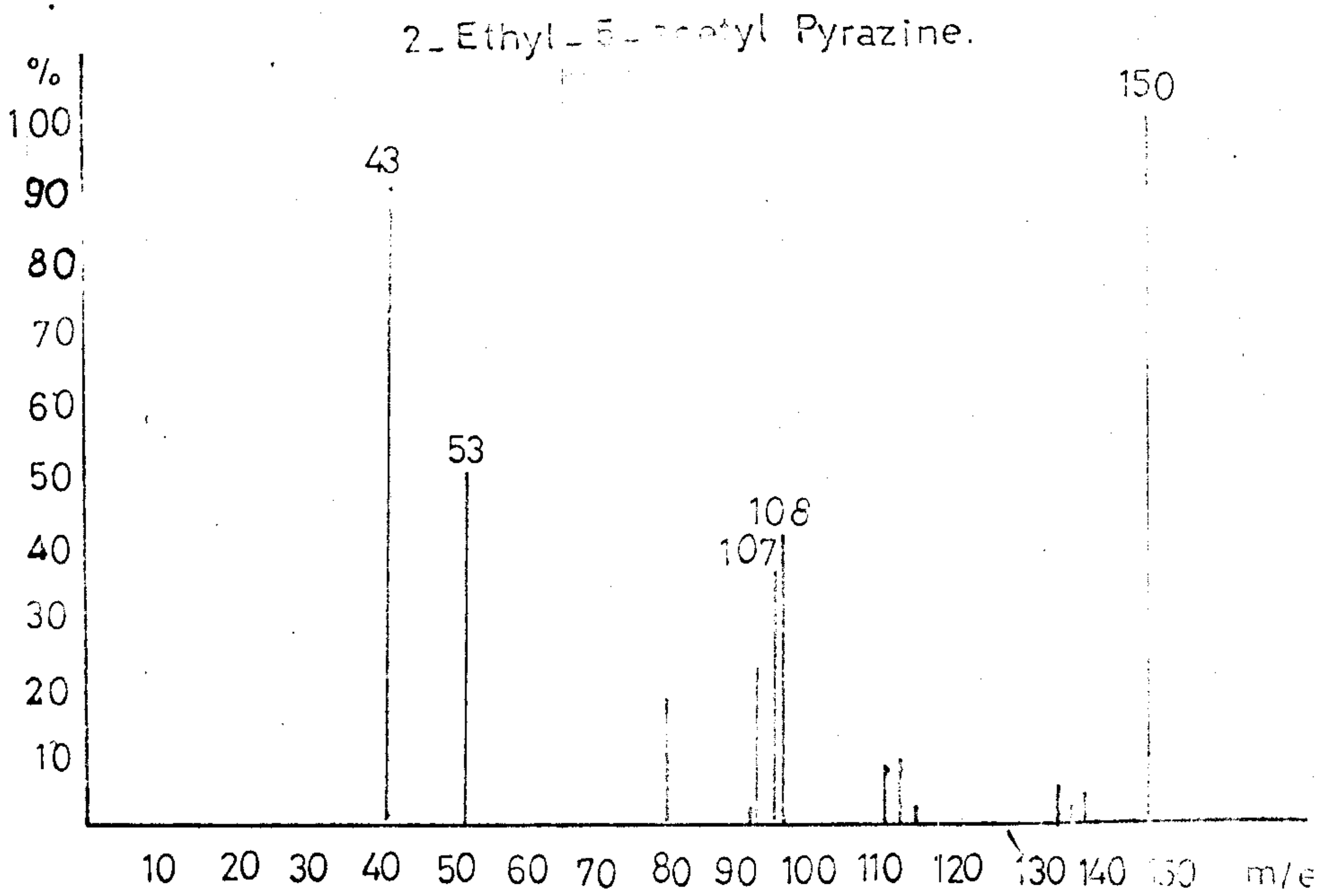


FIG. 12 .Mass Spectrum of Peak 40.

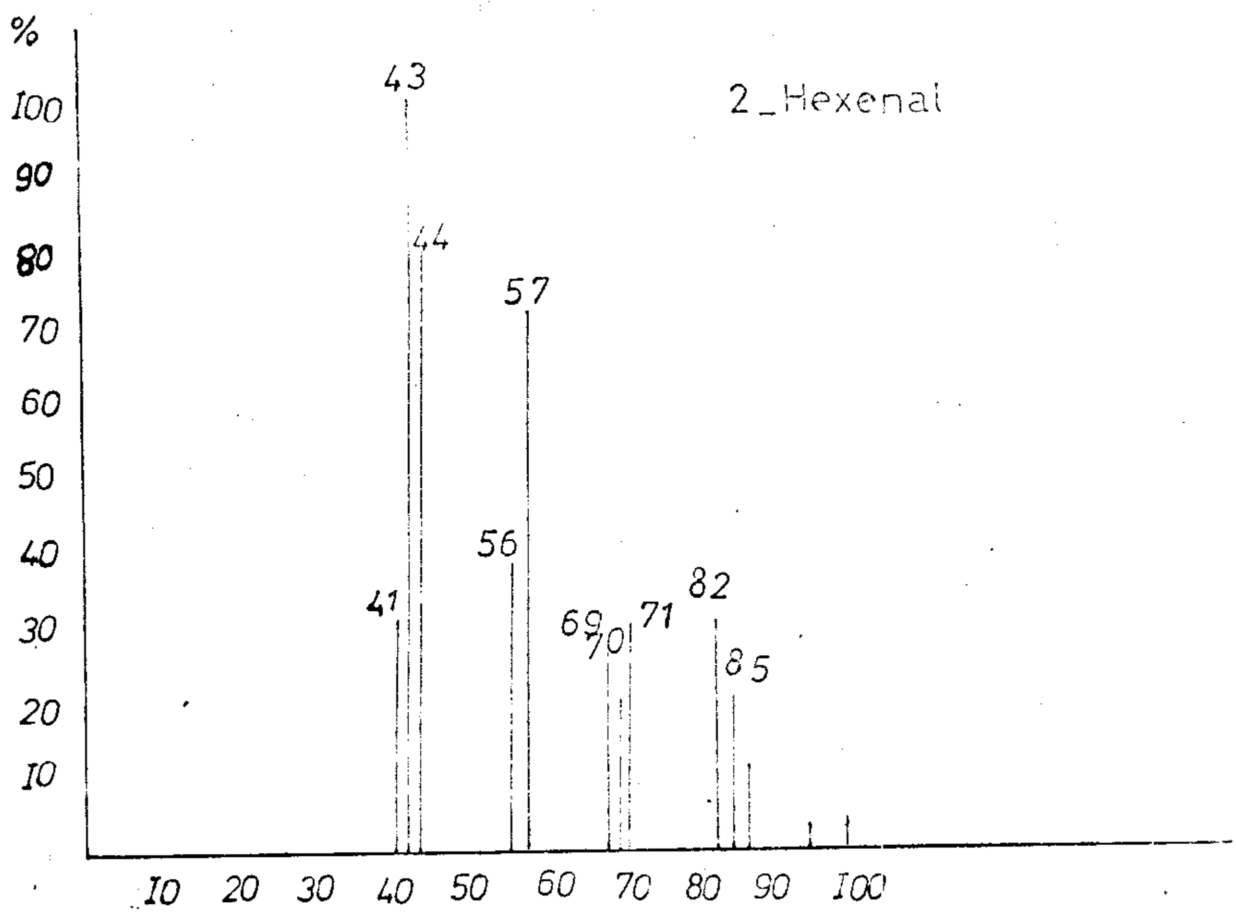


FIG. 13 . Mass Spectrum of Peak 3 .

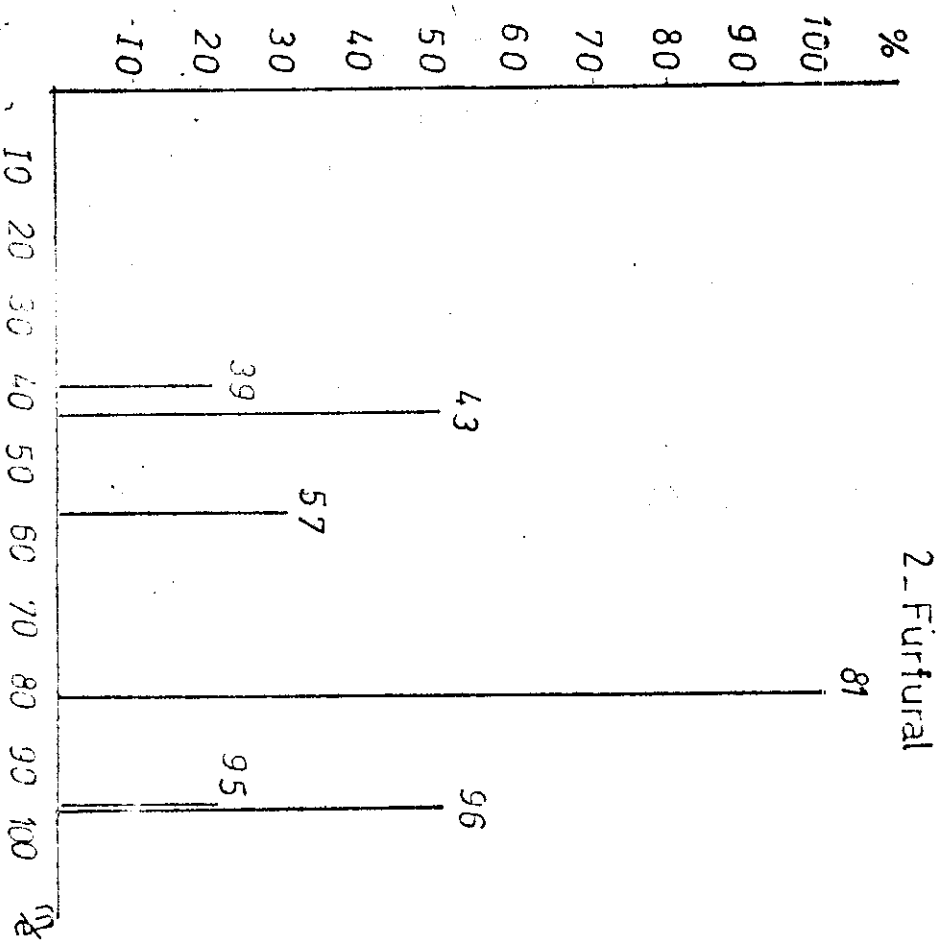
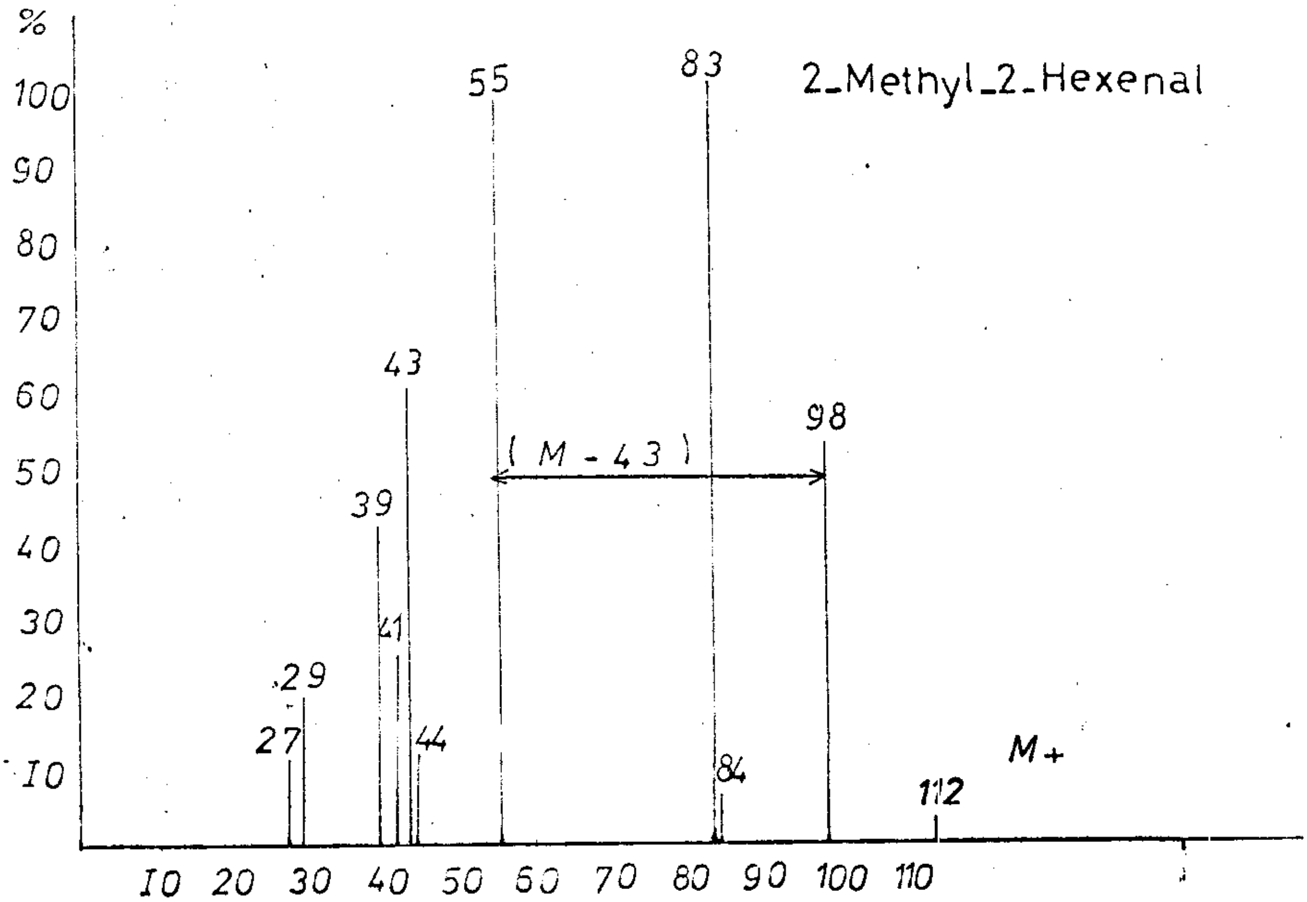


FIG. 14. Mass Spectrum of Peak 15.

Mass Spectrum Of Peak 7



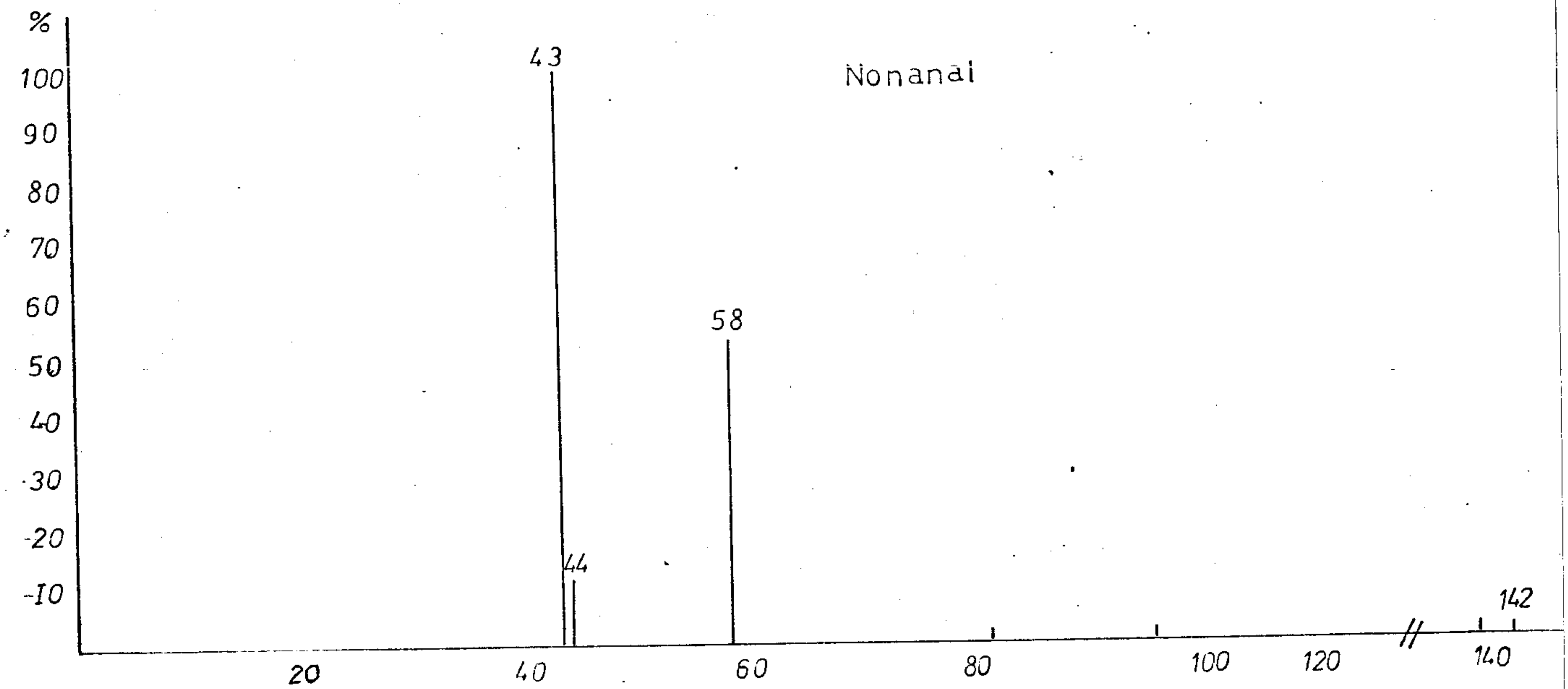


FIG 15. Mass Spectrum of Peak 18.

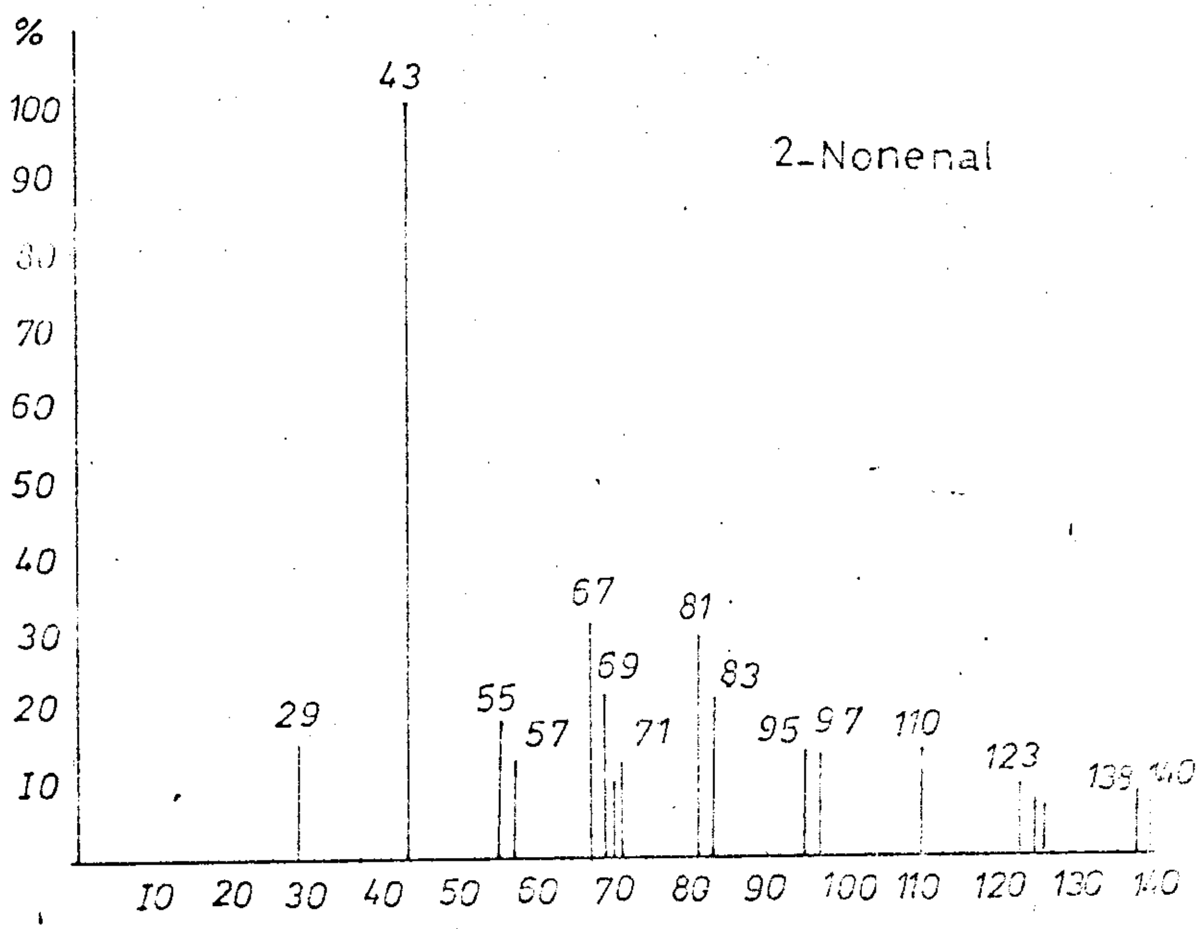


FIG. **16** . Mass Spectrum of Peak 38.

Aroma of Chufa :

The gas chromatogram of neutral-acidic and basic fractions on polar column are shown in Fig. (18) and those of nonpolar column are shown in Fig.(19). The compounds eluted from G.L.C. analysis and their concentrations are shown in Table (13). Identificantion of these components was done by matching their retention times with those of the authentic samples on both polar and nonpolar columns. Also comparison was done by the retention time of the identified compounds of roasted pistacia (Fig. 9 Table 10) .

Neutral -acidic fraction:

Neutral -acidic fraction has sweet-oily aroma. Some aliphatic aldehydes, aromatic aldehydes , heterocyclic ketones were identified.

The peaks were identified as follows :
Peak 2 : 2-methyl butanal ; peak 4 : 3-methyl butanal ; peak 6 : n-propanal ; peak 8 : 2-hexanal ; peak 10: acetic acid ; peak 11: octanal ; peak 14: 2-furfural; peak 16 : 2-acetyl furan, benzaldehyde ; peak 18 : 5- methyl furfural ; peak 20 : benzyl alcohol; peak 24: 2- furfuryl alcohol and peak 28: trans-2, trans-4 decadienal.

From Table (13) it can be seen that components show higher concentration as represented by peak area 45.409 and 37.953 for 2-furfural and trans 2 , trans 4- decadienal, respectively.

Those two major components may be respensible for the sweet-oily flavour of the neutral-acidic fraction. Propanal, 2-hexanal, and octanal are believed to be developed from lipid oxidation (78) .

Similar findings were also reported by Waldrt Yamani (79,80) , in roasted peanuts, whole nuts, almond, and pistacia but with different concentrations.

Basic fraction:

The basic fraction has nutty and pop-corn like flavour. Five pyrazine components and two pyrrole derivatives were identified by matching their retention time with those of authentic samples on polar and nonpolar columns. Also comparison was done with the retention time of the identified components of roasted pistacia. The identified compounds were as follows;

Peak 3: 2- methylpyrazine ; peak 5 : 2-ethyl pyrazine ; peak 12 : 2,6-dimethyl pyrazine ; peak 15: 2,5-dimethyl pyrazine ; peak 17 : pyrrole ; peak 23: 2-pentyl pyrrole.

From Table (13) , it can be seen that 2,5-dimethyl pyrazine is present in very high concentration (79.335 %) and other pyrazines are present in relatively equal amounts.Pyrrole and 2-pentyl pyrrole are present in relatively high concentration than the other pyrazines (2.427 % and 4.248 respectively).

These compounds were identified in the flavour of many other food stuff as previously mentioned.

Fatty acid analysis :

The G.L.C. analysis of fatty acids of chufa lipid before and after roasting is shown in Table (14,15) from the data obtained , it is obvious that there is no significant change in the fatty acid composition of chufa oil before and after roasting and that there are other synergetic compounds in lipid which may be considered responsible for producing chufa aroma.

Table (13)

Identified components and their Composition in Basic and Neutral-Acidic Fractions from Roasted *Cyperus Esculentus* (Chufa Tubers)

Peak No.	Reference to Fig.(12)peak composition (peak area%) Basic F.	Acidic-Neutral F.	Identified compound
1	-	-	Ether
2	-	5.693	2-Methyl butanal
3	1.109	-	2-Methyl pyrazine
4	-	0.996	3-Methyl butanal
5	0.416	-	2-Ethyl pyrazine
6	-	0.960	n-propanal
7	0.404	-	-
8	-	5.782	2-Hexenal
9	0.647	-	-
10	-	1.708	Acetic acid
11	-	0.427	Octanal
12	0.601	-	2,6-Dimethyl pyrazine
13	2.774	-	-
14	-	45.409	2-Furfural
15	79.335	-	2,5-Dimethyl pyrazine
16	-	trace	2-Acetyl furan, Benzaldehyde
17	2.427	-	Pyrrole
18	-	1.067	5-Methyl furfural
19	2.630	-	-
20	-	trace	Benzyl alcohol
21	trace	-	-
22	trace	-	-
23	4.248	-	2-Pentyl pyrrole
24	-	trace	2-Furfuryl alcohol
25	2.630	-	-
26	2.774	-	-
27	trece	-	-
28	-	37.953	Trans-2,trans-4-decadienal

Table (14)

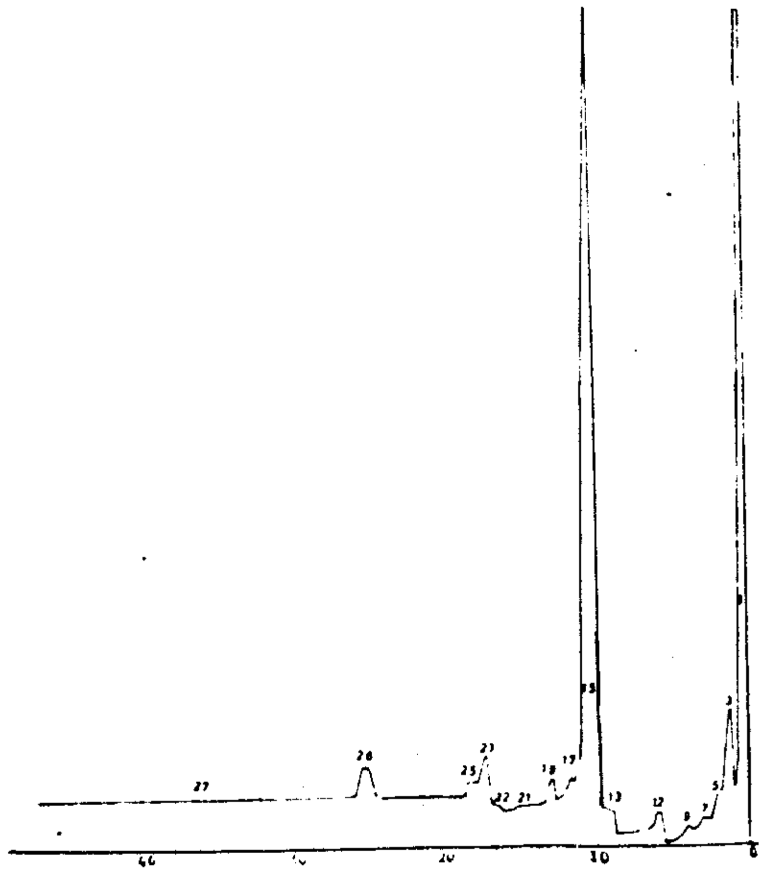
Fatty acid content of unroasted chufa lipid

Peak No.	Peak area	Peak %	Compounds
1	5.25	20.60	Palmitic acid
2	0.72	2.8	Stearic acid
3	15.89	62.40	Oleic acid
4	3.60	14.20	Linoleic acid

Table (15)

Fatty acid content of roasted chufa lipid

Peak No.	Peak area	Peak %	Compounds
1	2.97	18.6	Palmitic acid
2	0.30	1.9	Stearic acid
3	10.59	66.35	Oleic acid
4	2.1	13.15	Linoleic acid



Gas Chromatogram of Acidic Fraction of Roasted Chufa on Polar Column

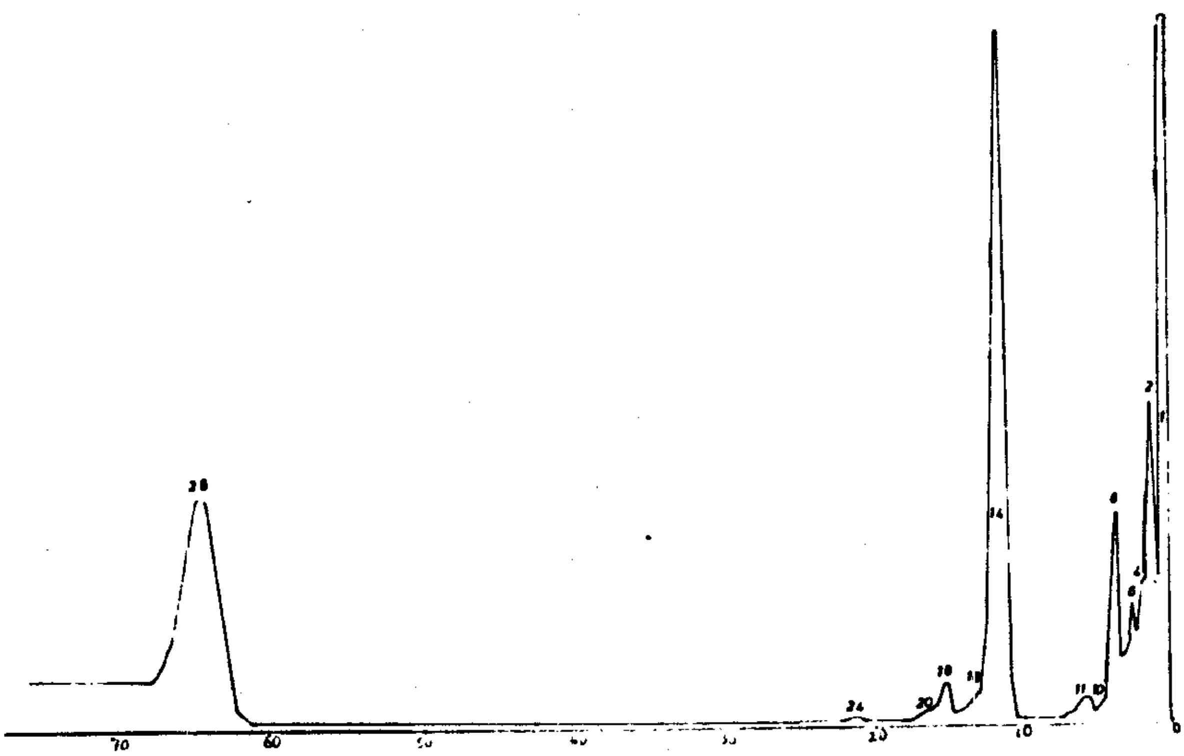
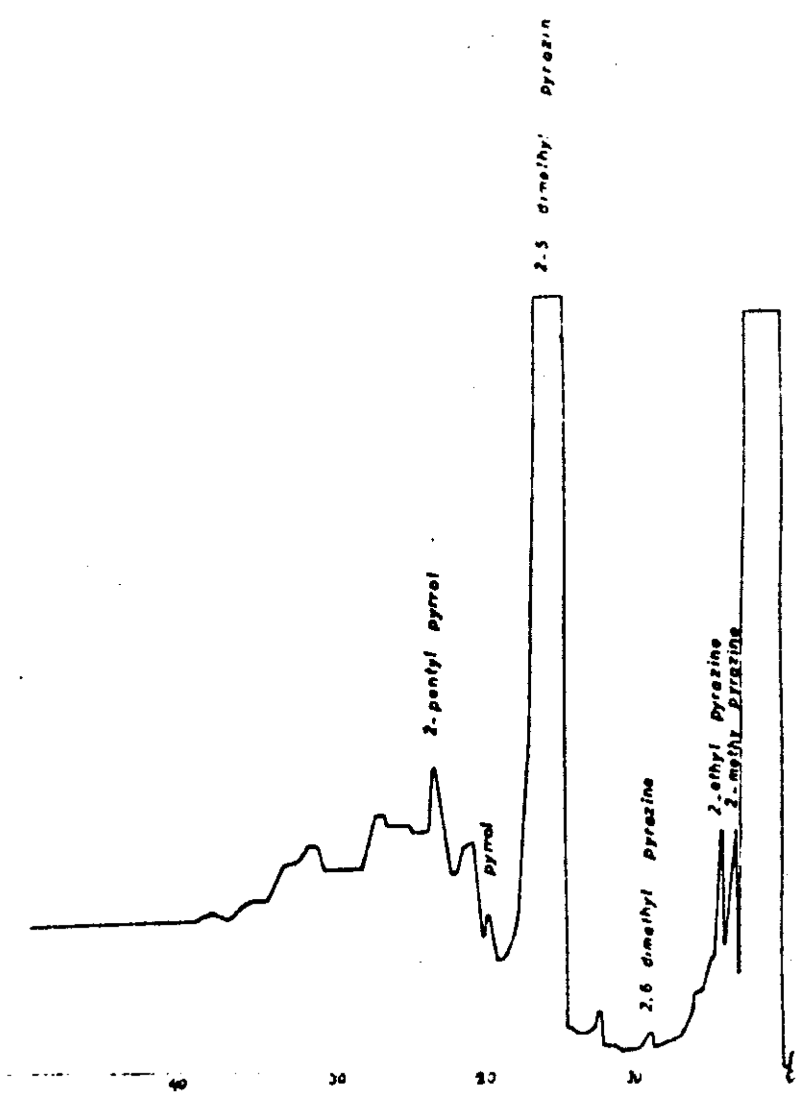


FIG 18 Gas Chromatogram of Neutral-Acidic Fraction of Roasted Chufa on Polar Column



Gas Chromatogram of Basic Fraction of Roasted Chufa on Non-polar Column

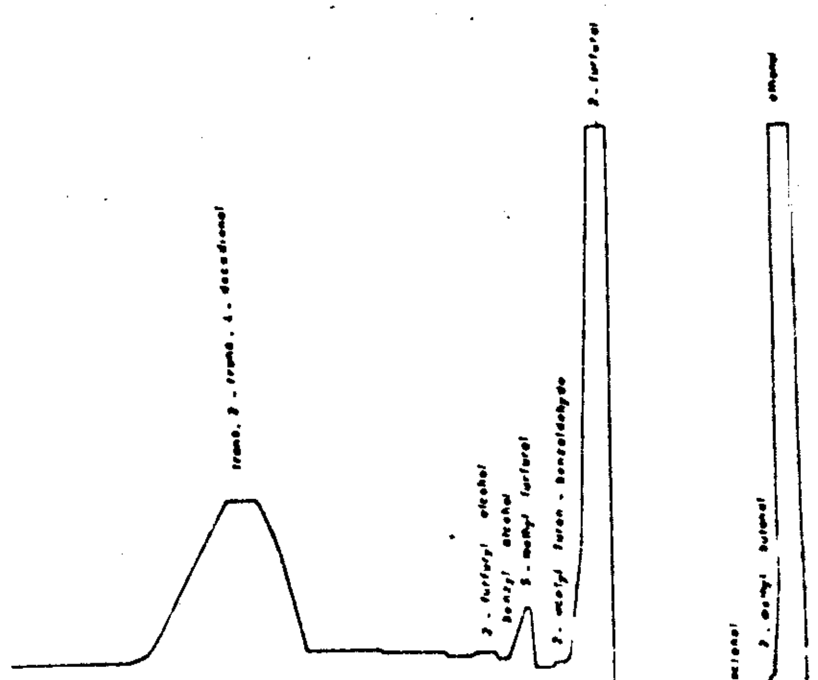


FIG.11 Gas Chromatogram of Neutral-Acidic Fraction of Roasted Chufa on Non-polar Column

General Discussion of the two Aroma Concentrates

Little has been published concerning the flavour components of roasted nuts.

Heating process iniates the condensation of amino acids and reducing sugars, -Maillard reaction - which produces important organoleptic products .

In each food stuff, characteristic aroma and flavour constituents arose on heating and were assumed to be formed , at least in part, via Maillard reaction.

The use of modern analytical techniques.Particularly the coupled gas liquid chromatography-mass spectrometery have revealed the complexity of such heat processed foods.

In the present investigation , a general look to the four chromatograms Fig.(20 , 21) (neutral-acidic and basic fractions of roasted pistacia and chufa.) shows similar components with different concentrations.

Neutral-acidic fractions:

2-Hexenal and 2- furfural are exhibited in higher quantities 14.20% and 53.30 % , respectively, in roasted pistacia, viz 5.78% and 45.409 % for roasted chufa. On the other hand acetic acid , 2-acetyl furan, 5-methyl furfural , furfuryl alcohol and trans 2 , trans 4 , decadienal are produced in relatively small quantities in both fractions.

However, some components e.g (2-methyl butanal, 3-methyl butanal, propanal , octanal , benzaldehyde and benzyl alcohol are present in relatively small concentration in roasted chufa while they are not detected in roasted pistacia.

On the contrary, compounds such as 2-methyl-2-hexenal, nonanal and 2-nonenal are recorded only in roasted pistacia.

Basic fractions:

2-Methyl pyrazine and 2,6-dimethyl pyrazine are present in low concentration in both roasted pistacia and chufa. While 2-pentyl pyrrole is present in relatively high concentration 4.248% in roasted chufa viz 0.07 % in roasted pistacia. On the other hand, 2-acetyl pyrazine is present in roasted chufa while it is absent in roasted pistacia.

Concerning the characteristic compounds for both fractions, 2,5-dimethyl pyrazine and 2-ethyl-5-acetyl pyrazine are present in high cencentration 92.91% and 2.5 % , respictively in roasted pistacia, while only 2,5-dimethyl pyrazine (79.335%) is present in roasted chufa.

The above results and observation recorded during this investigation are in good agreement with those reported by other workers, working on other nuts.

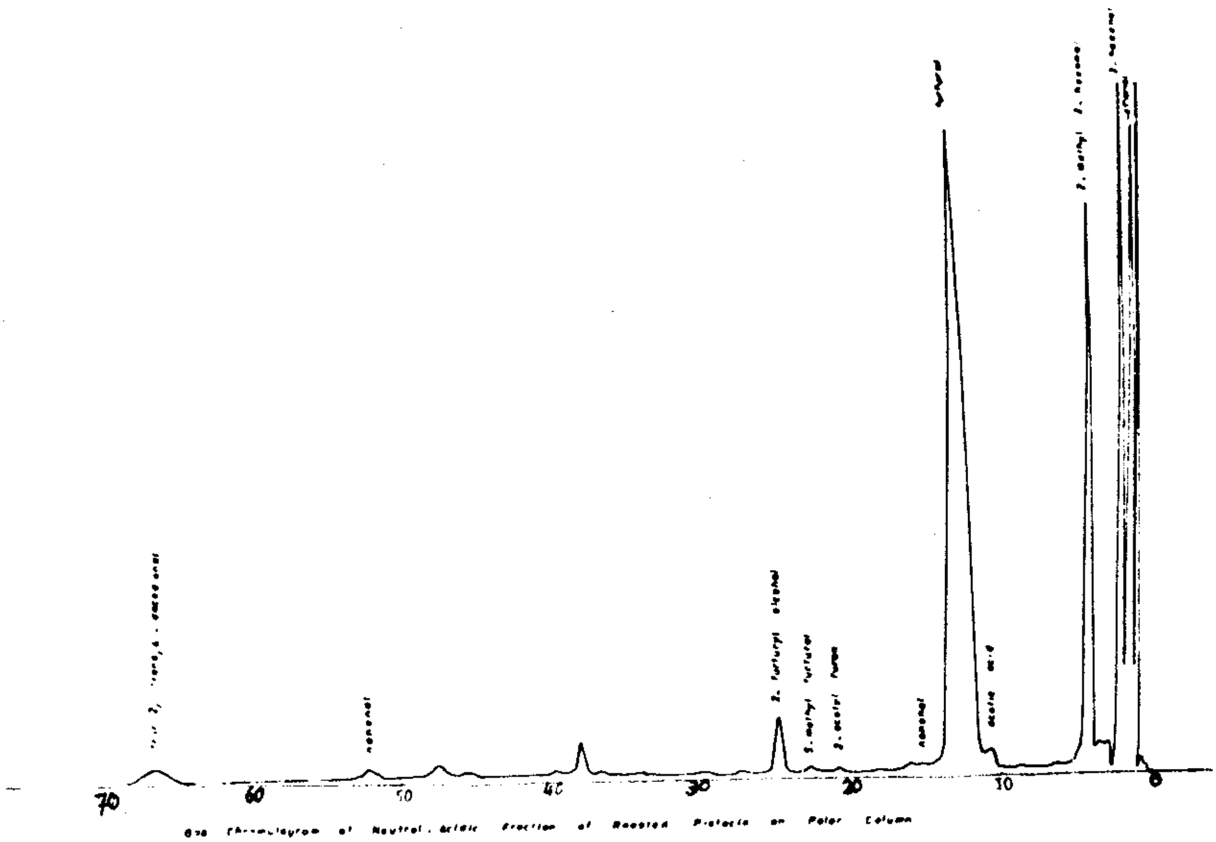
From the above data set out in the two sections, the following conclusions could be derived :

-The aroma of nuts are developed during roasting at 180°C.

-Both Maillard reaction and strecker degradation are involved in the process of aroma formation.

- The different aroma constituents are developed from the reaction of reduced sugars and amino acids of the nuts.
- Basic fraction has nutty flavour and among its components 2,5-dimethyl pyrazine and 2-ethyl-5-acetyl pyrazine are seemed to be the characteristic components of roasted pistacia while 2,5-dimethyl pyrazine is considered only the characteristic component of roasted chufa.

- The lipid fraction proved to have no significant role in aroma formation in both pistacia and chufa.



Gas Chromatogram of Neutral - Acidic Fraction of Roasted Pistacia on Polar Column

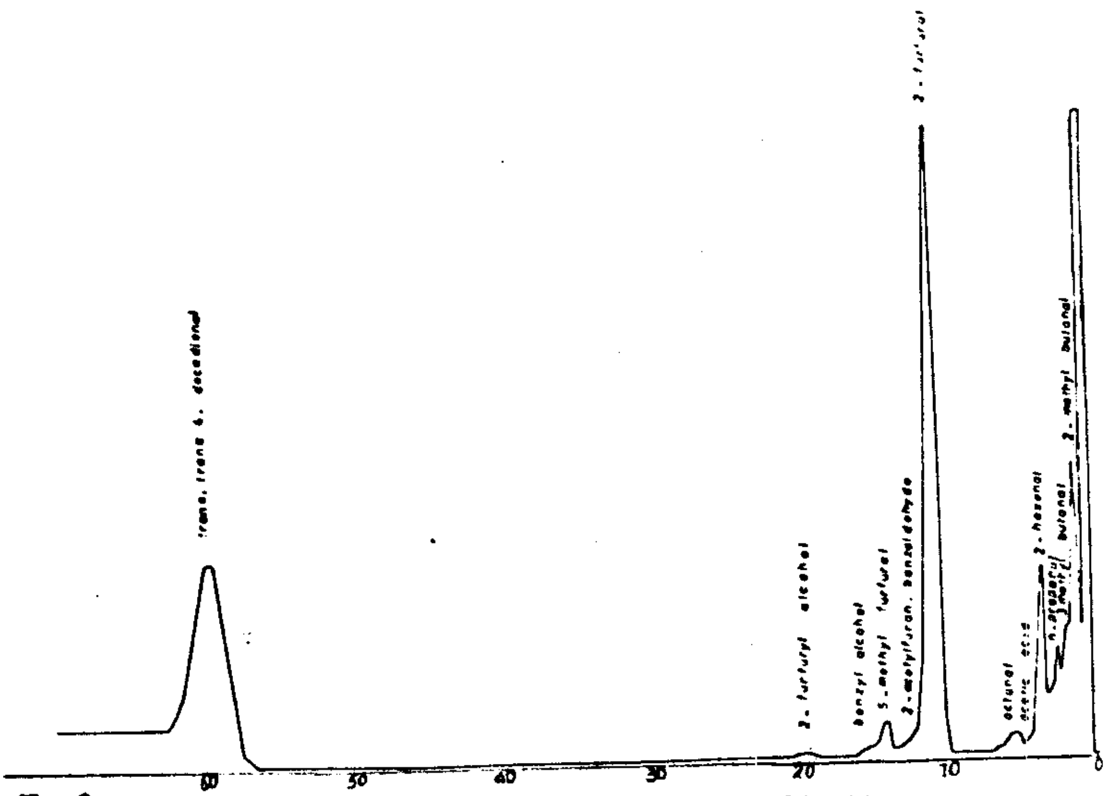
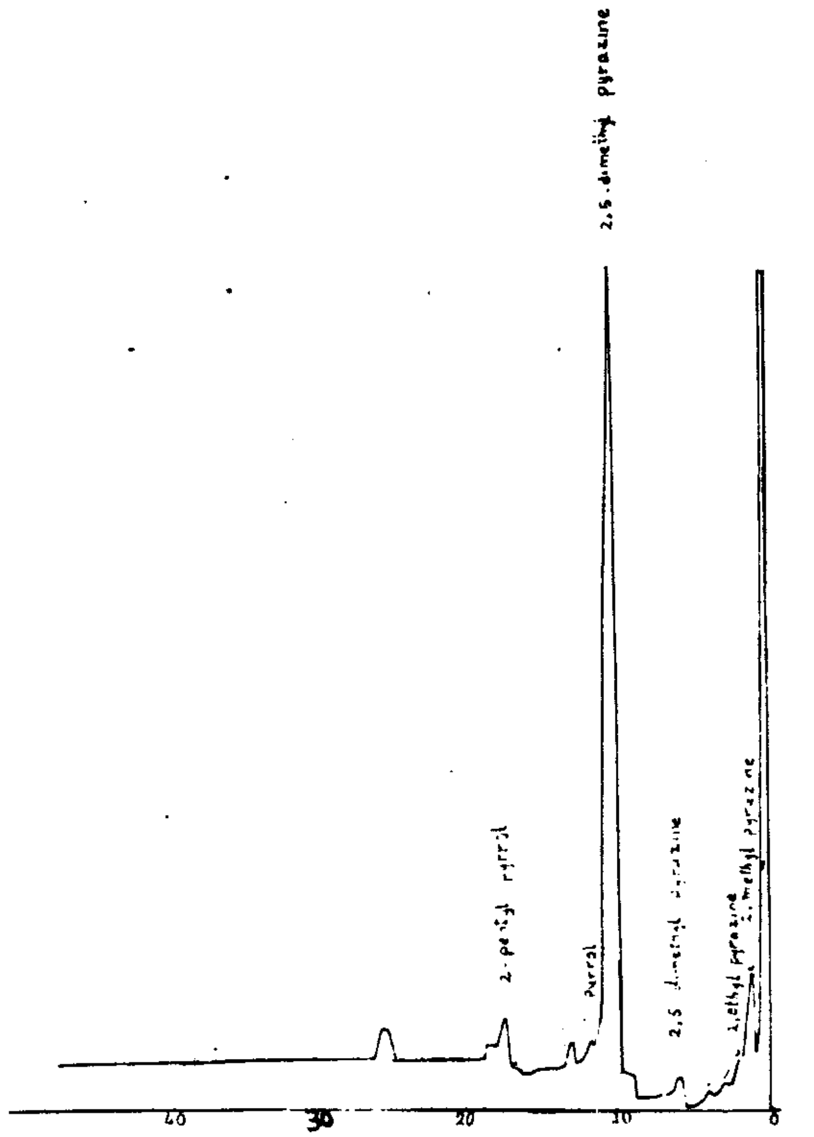


FIG 20 Gas Chromatogram of Neutral - Acidic Fraction of Roasted Chufa on Polar Column



Gas Chromatogram of Basic Fraction of Roasted Chufa on Polar Column

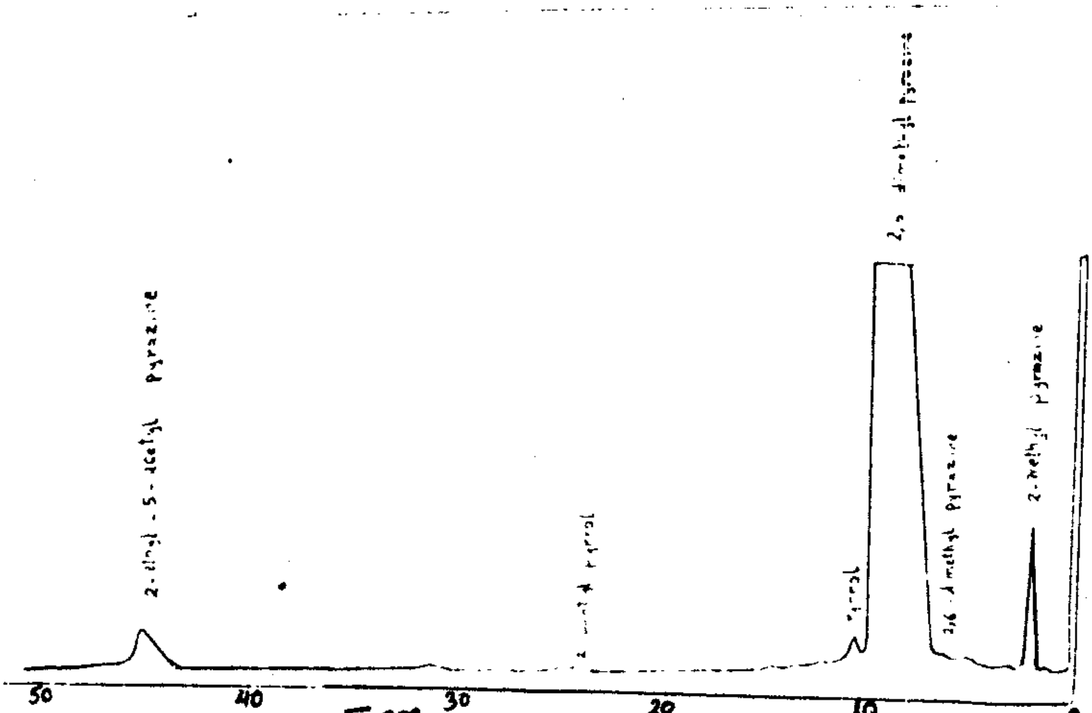


FIG21 [illegible] of Basic Fraction of Roasted [illegible] on polar column

General Conclusion

The marketing trend of food products has changed substantially over the last several years. Food companies are catering to the accepted principle of "less work for mother". This has led to the growth of "convenience" and "instant" foods, resulting in a greater selection and variety for consumer.

Because many of these products are being processed in plants far away from final consumption, the requirements for processing, distribution and storage have resulted in the need for increased stability and larger shelf-life. This has led to the use of specified food ingredients and additives including emulsifiers and aroma concentrates.

In order to counter increased labour and ingredient cost, food processors have increased their research and development efforts which has resulted in the use of improved equipment and additives.

Based on the above mentioned facts, edible emulsifiers and aroma concentrates hold great promise as future additives.

In part I of the present work, the production of partial glycerides as edible emulsifier was investigated using the available raw materials, with varying experimental conditions.

Part II deals with the isolation of aroma concentrates from edible nuts and subsequent quantiation of their components.

From the several experiments carried out to prepare the partial glycerides, it is concluded that the optimum conditions for the preparation of the partial palmitic acid glycerides were six hours reaction time at 180°C using 0.5 % of a mixed catalyst (zinc oxide and butyl amine). At these conditions, the maximum yield of monopalmitin together with a suitable amount of dipalmitin (42.2 and 44.1 % respectively) were obtained.

In case of oleic acid partial glycerides , the optimal conditions, the temperature was higher than that of palmitic glycerides, In this case it is concluded that a temperature of 200°C is needed for a time reaction of six hours with 0.5 % mixed catalyst to obtain the highest amount of both mono- and diolein (35.5 and 58.5 % , respectively).

It is believed that the above mentioned fatty acid glyceride esters prepared in such a simple way, could be produced in any particular factory wheneær needed. The ethoxylated mono-and digly cerides are permitted as food emulsifiers especially in bakery products. Thus it was advisable to investigate the prepared samples of patrial glycerides for ethoxy- lation. The results indicated that ethoxylation greaty increase the emulsification power particularly for the samples containing mono-and diolein glycerides.

Regarding the preparation and identification of two aroma concentrates, the adopted methods used, roasting followed by carbon dioxide distillation method, were convenient for the collection of the characteristic aroma concentrates . To acheive proper identification of the components, the concentrates were fractionated to neutral-acidic and basic fraction. The particular fractions were analysed using gas liquid chromatography on polar and non-polar columns, besides gas liquid -mass spectrometery. In pistacia aroma, 18 components were identified compared to 19 components in case of chufa concentrate.

It is concluded that the substituted pyrazines in the basic fraction namely, 2,5-dimethyl pyrazine and 2-ethyl-5-acetyl pyrazine, are responsible for the nutty flavour of roasted pistacia reaching a value of 92.91 and 2.5 % , respectively.

However, it is believed that the sweet oily aroma is due to the presence of a large number of fatty aldehydes in addition to four furan derivatives, in the neutral-acidic fraction of the roasted pistacia. In the aroma of roasted chufa, it was found that 2,5-dimethyl pyrazine (79.335% , basic fraction) is considered the key component characteristic to the aroma.

Concerning the neutral-acidic fraction, a large number of fatty aldehydes together with furan derivatives are present in concentrations different from those of roasted pistacia.

Amongst these components, 2-furfural is predoment reaching a value of 45.709 % .
It is reported that these compounds participate in the sweet oily aroma.

It is finally concluded that, depending on the intended use, suitable amounts of additives composed from a combination of edible partial glyceride emulsifier and flavour concentrate desired for a particular purpose might be considered essential for certain products. Such additives would be widely accepted as having bifunctional action of improving the texture and imparting the desired particular flavour to the manfactured product.

Summary

This thesis comprises two parts :

Part (1): Partial glycerides as edible emulsifiers.

This part comprises an introduction, a review of literature, an experimental part followed by the results and discussion.

The introduction indicates the utilization of fatty acid glyceryl esters in various purposes.

The review of literature covers the preparation, estimation and utilization of fatty acid mono-, diglycerides and their ethoxylated derivatives .

The experimental part includes the methods of preparation and estimation of the above compounds. The results and discussion are representation of the data obtained for the preparation of mono-and diglycerides under certain conditions. Variations in types of catalysts, time and temperature of reaction were explained. Emulsification power of both ethoxylated and nonethoxylated mono-and diglycerides was discussed.

Part (II) Flavour concentrates from chufa tubers and pistacia nuts.

This part comprises an introduction which gives a short account on flavour of food which is mainly composed of taste and odour.

The rview of literature systematises the attempts of many authors in studying Maillard reaction (browning reaction) and some model systems which lead to the aroma produced during roasting of nuts.

The experimental part includes some information about the materials utilized in the studies. The different experimental procedures and techniques adopted are also explained. These include the preparation of the aroma concentrate, its fractionation, analysis by gas liquid chromatography and identification by couple gas liquid -mass spectrometery. Besides, the fatty acid composition of the lipid fraction is determined. The results of all above studies are illustrated by 6 Tables and 15 Graphs.

In case of pistacia, it was shown that the basic fraction is mainly responsible for the typical characteristic multy aroma.

The neutral-acidic fraction has sweet-oily aroma. The lipid fraction of pistacia seems not essential for producing the paticular nutty aroma .

On the other hand, for chufa, it was shown that also the basic fraction seemed to be responsible for the aroma of chufa. However the lipid fraction seemed to be not responsible for producing its aroma.

The results of the present studies led to the conclusion that the aroma of roasted nuts are developed from the reaction of reduced sugar with amino acids. Also 2,5-dimethyl pyrazine and 2-ethyl-5-acetyl pyrazine seemed to be the characteristic components of roasted pistacia while 2,5-dimethyl pyrazine is considered only the characteristic component of roasted chufa.