Gas Chromatographic Analysis on Turkish Rose Oil, Absolute and Concrete

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Rose oil and concrete samples from the Isparta district and rose absolute prepared in our laboratory were analyzed by gas chromatography and results were interpreted. By investigating the analysis results it seemed that it would be possible to offer the standardization of these rose products by increasing the number of samples from different origins in Turkey. It was observed that the qualities of Turkish rose oil, concrete and absolute could compete with Bulgarian and other products which have higher export prices. Moreover, it was more profitable to produce and export rose absolute instead of concrete.

Turkey occupies second place among the countries which grow rose flower and produce rose oil, rose water and concrete coming after Bulgaria.[1] Rose oil, concrete, absolute and rose water being rose complexes are valuable and important base materials of the perfumery industry.

As known, rose oil is a blend of decante oil and water oil which are obtained in two steps by steam distillation. In the first step of steam distillation the oil formed as a separate layer above water is called decante oil or direct oil or first oil. By another steam distillation of residue water, indirect oil (water oil or second oil) is obtained.

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Rose oil represents the sum of specifications of both of them. The last distillation water is rose water.

Rose concentrate is a waxy, semisolid material produced by extraction of rose flower with volatile solvents such as hexane, petroleum ether benzene, and subsequently by evaporation of the solvent in vacuum. Concrete is extracted with alcohol. This second extract is cooled to precipitate the waxes and then filtered. The alcoholic solution is distilled under reduced pressure to remove alcohol and finally the essential oil which is so-called "absolute" is obtained.

Rose oil has been the subject of a number of studies since ancient times. Although the last fifty years most of research has been gathered on production and analysis of Bulgarian rose oil,[2] all the chemicals in rose oil haven't been identified yet. The number of studies on Turkish rose oil do not exceed more than a few. A notable local study belongs to A. Dağcioğlu[3] and there are also some foreign researchers, G. Igolen[4] and J. Garnero, G. Guichard and P. Buil.[5]

Nowadays scientists have been requiring a detailed analysis of the oil including low level constituents. A completed analysis will solve the problems of detection of the presence of possible adulteration[6] and investigation of the role of the trace constituents on the odour and performance of the rose product.[7]

The analysis of rose products may be realized by gas or liquid chromatographic techniques. Our investigations showed that liquid chromatography have been used only in a few studies to separate essential oils and terpenoid compounds,[8] and a sufficient separation has not been obtained. Rose products are constituted from terpene derivatives such as alcohols, aldehydes, ketones, phenols, ethers etc., sesquiterpenes and hydrocarbons. Rose oil which is a steam distillation product does not represent correct proportion of ingredients as they exist in the flower. Because of the heat operation some changes may occur. For that reason rose absolute may represent the more genuine character of rose, e.g., the percentage of phenylethyl alcohol in rose oil is much lower than the absolute due to its solubility in hot water.

Experimental

The origins of rose oil and concrete samples, investigated in this study are:

Oils: Gülbirlik (cooperative) 1980, 1981 products; M. Gürkan (private fabric) 1981, 1982 products, decante oil (1982), and water oil (1982); E. Erçetin (private fabric) 1979, 1980, 1981 products.

Concretes: Gülbirlik 1981 product; M. Gürkan 1980 and 1981 products. Rose absolutes were prepared in our laboratory from Gülbirlik 1981 concrete according to the following procedures.

Procedure I: Concrete sample was treated with ten times sample's weight of high-proof ethyl alcohol by stirring vigorously at room temperature for one week. The mixture containing undissolved stearoptens (high hydrocarbons) was cooled at −34°C for one day and then filtered in vacuum. Extract was distilled at 50°C/10 mm Hg to remove alcohol. The residue is rose absolute I.

Procedure II: The procedure mentioned above was realized with 75% ethyl alcohol. The residue is rose absolute II.

The yields of the two absolutes were approximately 60%. The standard chemicals (from Fluka, Merck, SCM Terpene products) were used as purchased.

The operation conditions of gas chromatography was chosen as shown below:

Apparatus: Shimadzu 5A (F.I.D.)
Column: OV-17 3% on Chromosorb W 100/120 mesh, 3 mm I.D. × 3m
Temperature Programme: 6′ isothermal at 80°C, 80°→ 295°C at 2°C/min heating rate, isothermal at 295°C
Detector Temperature: Injector Temperature: 250°C
Carrier Gas (N_2): 0.35 l/min
Range: 0.16 V
Input Attenuator: 10^2 MΩ
Chart Speed: 2.5 mm/min
Integrator: ITG-4A

The relative percentages of constituents of rose oils investigated in this study are illustrated in Table I and a few examples of chromatograms in Figure 1. In order to observe the effects of decante oil and water oil on the resulting blend oil, the results of analysis of these two oils, 1982 M. Gürkan products, are included.

The results of analysis of concrete samples and chromatograms are shown in Table II and Figure 2. (Hexane, residue extraction solvent, is not included for calculation.)

The Gas Chromatographic analysis results of Rose Absolute I and II prepared from Gülbirlik 1981 concrete are shown in Table III and Chromatograms in Figure 3.

For the purpose of comparison literature values of a Bulgarian oil[5] and a Maroc Rose Absolute* are shown in Table IV.

Results and Discussion

A good separation of rose products has been obtained by OV-17 column.

When we compared the compositions of Turkish and Bulgarian rose oils (Table I and IV), outside of a few exceptions we found a close similarity in composition of these two oils. Small increase was observed in the percentages of citronellol, nerol, neryl acetate, p.C_{17}, ol.C_{17}, p.C_{19}, ol.C_{19}, p.C_{22} while geraniol, neral, eugenol, trans, trans-farnesol decreased.

When the analysis results of decante and water oil were examined (Table I) few considerations

*Unpublished work in progress by F. Buccellato, Alpine Aromatics International, Inc., 1979. F. Buccellato is now with Custom Essence

were taken in account: The expected increments in volatile components and in compounds having no solubility in water (paraffins, olefins, esters) were really observed in decante oil. In the water oil the higher percentages of water-soluble components (citronellol, nerol, geraniol, neral, n-nonanol, geranial, carvone, phenyl-ethyl alcohol) were determined. Hence the individual effect of each oil on the characterisation of the blended rose oil was highly important.

Table I. The Gas Chromatographic Analysis of Rose Oils

Compounds	Relative Percentage								
	Gülbirlik 1980	Gülbirlik 1981	E.Erçetin 1979	E.Erçetin 1980	E.Erçetin 1981	N.Gürkan 1981	N.Gürkan 1982	N.Gürkan 1982 decante oil	N.Gürkan 1982 water oil
Ethanol	0.78	0.31	0.001	-	-	0.05	0.01	0.006	0.001
Acetic Acid	-	0.001	0.003	0.12	0.14	-	0.003	0.001	-
[illegible]-hexenol	0.27	0.11	0.02	0.05	0.02	0.005	0.002	0.005	0.015
α-pinene,n-hexanol	0.58	0.58	0.53	0.49	0.98	0.89	1.16	3.12	0.28
Camphene	0.01	0.02	0.005	0.017	0.008	0.004	-	-	-
Myrcene,β-pinene	0.092 0.016	0.10 0.02	0.33	0.28	0.54	0.55	0.24 0.24	2.20	0.28
.....	-	-	-	0.001	0.003	0.004	0.003	0.02	0.01
Limonene	0.026	0.014	0.03	0.044	0.014	0.014	0.013	0.04	0.017
Benzaldehyde,6-methyl-5-heptenone	0.042	0.035	0.056	0.077	0.048	0.032	0.03	0.10	0.017
.....	-	0.007	0.003	0.008	0.018	0.02	0.026	0.04	0.02
n-octanol	0.01	0.016	0.02	0.02	0.02	0.026	0.02	0.005	0.015
Linalool cis-rose oxide and nonanal	0.67 0.06	1.32	2.68	3.14	2.19	1.36	1.00	0.42	0.6 0.04
trans-rose oxide	0.10	0.08	0.04	0.08	0.05	0.06	0.05	0.03	0.10
l-menthone,n-nonanol	0.15		0.06	0.10	0.08	0.04		0.07	0.06
.....	-	2.25	1.23	0.38	1.14	-	2.14	0.06	0.31
Phenylethyl alcohol, decanal	1.15			0.32		1.64		0.14	0.45
Terpinene-1-ol-4	0.04		0.07	0.31	0.07	0.02		0.03	0.05
Citronellol,nerol	56.69	56.71	53.15	56.26	48.16	48.01	48.00	28.07	61.97
Geraniol,neral	8.02	8.16	8.43	10.09	14.72	14.46	8.38	2.54	11.42
Geranial,carvone	0.68	0.61	0.34	0.45	0.47	0.43	0.55	0.10	0.44
.....	0.30	0.10	0.05	0.04	0.08	0.07	0.03	0.11	0.04
Citronellyl acetate	0.37	0.49	0.44	0.58	0.64	0.70	0.52	1.05	0.32
Neryl acetate	0.44	0.38	0.50	0.71	0.46	0.45	0.54	1.21	0.31
Cinnamaldehyde,p.C_{15}	0.33	0.40	0.30	0.29	0.32	0.29	0.34	0.76	0.23
Geranyl acetate	0.16	0.32	0.31	0.37	1.00	1.80	0.55	0.68	0.52
.....	0.05	0.04	0.10	0.18	0.03	0.006	0.06	0.11	0.03
.....	-	-	-	0.002	0.003	0.12	0.10	0.01	0.18
β-damascone,...	0.25	0.52	0.60	0.51	0.61	0.30	0.78	1.64	0.20
.....	0.22	0.21	0.20	0.33	0.25	0.18	0.23	0.44	0.13
Methyl eugenol,p.C_{16}	2.81	2.39	2.35	2.67	1.64	1.76	1.70	0.49	2.05
β-ionone	0.05	0.05	0.03	0.16	0.03	0.036	0.06	0.08	0.02
.....	0.02	0.02	0.06	0.07	0.05	0.06	0.034	0.05	0.006
p.C_{17}+ol.C_{17}	2.29	2.38	2.53	2.14	2.20	2.47	3.11	5.40	1.99
.....	0.02	0.02	-	0.002	-	0.003	-	-	-
.....	0.002	-	-	0.004	-	0.01	0.007	0.005	0.005
.....	-	-	0.05	0.004	0.046	-	-	-	-
p.C_{18}+ol.C_{18}	0.39	0.40	0.46	0.36	0.42	0.42	0.47	0.74	0.30
Farnesol (mix.)	0.04	0.054	0.08	0.074	0.07	0.074	0.073	0.09	0.004
trans,trans-farnesol	0.2	0.3	0.31	0.28	0.45	0.5	0.43	0.42	0.02
p.C_{19}+ol.C_{19}	15.17	15.22	16.67	12.49	15.34	16.14	19.26	34.55	13.04
.....	-	0.003	0.003	0.003	0.005	0.001	0.003	0.005	-
p.C_{20}+ol.C_{20}	1.16	1.07	1.08	0.92	1.10	1.12	1.38	2.31	0.73
.....	0.002	0.001	0.001	0.004	0.002	0.001	0.001	0.001	0.002
p.C_{21}+ol.C_{21}	4.72	4.49	5.11	4.00	4.81	5.06	5.94	9.78	3.08
.....	-	-	0.005	0.003	0.002	-	-	-	-

Table I continues

Table I continued

Compounds	Relative Percentage								
	Gülbirlik 1980	Gülbirlik 1981	E.Erçetin 1979	E.Erçetin 1980	E.Erçetin 1981	M.Gürkan 1981	M.Gürkan 1982	M.Gürkan 1982 decante oil	M.Gürkan 1982 water oil
.....	-	0.002	-	0.018	-	—	-	-	-
p.C_{22}	0.17	0.16	0.21	0.24	0.31	0.32	0.20	0.27	0.05
.....	0.003	-	-	0.002	0.01	0.002	-	-	-
.....	-	0.003	0.005	-	-	0.007	0.006	0.005	0.006
p.C_{23}	0.88	0.77	1.05	0.82	0.87	1.01	1.15	2.06	0.525
.....	0.005	0.005	0.006	0.024	0.017	-	-	-	-
.....	0.05	0.04	0.05	0.05	0.07	0.06	0.06	0.04	0.003
.....	0.006	0.005	0.01	-	0.017	-	0.008	0.007	-
.....	0.001	0.002	0.003	-	0.006	-	-	-	-
.....	0.13	0.15	0.28	0.22	0.22	0.21	0.25	0.45	0.07
.....	-	0.0003	-	-	0.0006	-	-	-	-
.....	0.05	0.014	0.04	0.002	0.04	-	-	-	-
.....	0.003	0.003	-	0.001	-	-	-	-	-
.....	0.09	0.09	-	0.01	0.005	0.17	0.27	0.47	0.01
.....	0.03	0.0014	-	0,001	0.001	-	-	-	-
.....	0.01	0.006	-	0.004	-	-	-	-	-
.....	0.01	0.007.	-	-	-	-	-	-	-
.....	0.1	0.1	-	-	-	0.19	0.1	-	-

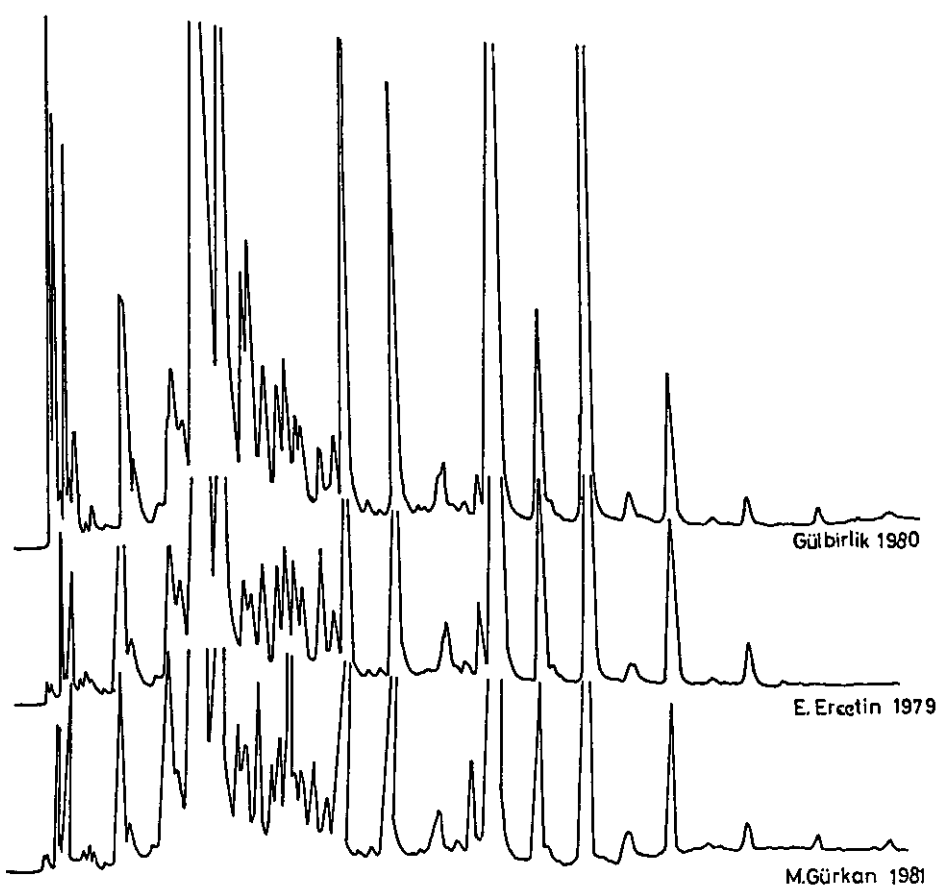

Fig. 1 Three Typical Examples of Chromatograms of Oils

Table II. The Gas Chromatographic Analysis of Rose Concretes

Compounds	Relative Percentage: Gülbirlik 1981	M.Gürkan 1980	M.Gürkan 1982
α-pinene,n-hexanol	0.136	-	0.07
Myrcene,β-pinene	0.08	-	0.02
Linalool,cis-rose oxide,nonanal,trans-rose oxide	0.39	0.04	0.08
Phenylethyl alcohol,nonanal	29.67	28.33	28.06
Citronellol,nerol	5.61	5.72	5.91
Geraniol,neral	1.55	1.62	1.10
Geranial,carvone	0.10	0.06	0.06
Citronellyl acetate	0.007	0.03	0.002
Neryl acetate	0.05	0.05	0.03
Cinnamaldehyde,p.C_{15}	0.04	0.07	0.05
Geranyl acetate	0.04	0.11	0.05
..... .	0.12	0.22	0.002
β-damascone,....	0.006	-	0.0004
.....	0.02	0.03	0.02
Methyl eugenol,p.C_{16}	0.86	0.43	0.32
.....	0.01	0.01	0.005
p.C_{17},el.C_{17}	1.24	0.69	0.87
.....	0.003	0.008	0.001
p.C_{18},el.C_{18}	0.10	0.12	0.13
.....	0.002	0.004	0.001
Farnesol(mix.)	0.008	0.014	0.01
trans,trans-farnesol	0.09	0.11	0.09
p.C_{19},el.C_{19}	6.43	7.11	8.96
.....	0.001	-	-
p.C_{20},el.C_{20}	0.79	0.81	0.90
p.C_{21},el.C_{21}	4.85	5.25	5.56
.....	0.002	0.003	0.001
p.C_{22}	0.38	0.35	0.36
.....	0.02	0.02	0.02
p.C_{23}	3.72	3.80	3.53
.....	0.0005	0.007	0.001
.....	0.66	0.70	0.56
.....	0.06	0.09	0.07
.....	2.78	2.98	2.66
.....	0.10	0.14	0.14
.....	0.82	0.84	0.84
.....	0.29	0.46	0.40
.....	6.99	6.85	7.05
.....	0.04	0.10	0.08
.....	1.19	0.87	1.09
.....	0.48	0.61	0.63
.....	0.03	—	-
.....	5.09	5.36	5.27
.....	1.11	1.12	1.05
.....	0.27 / 5.55	7.56	6.80
.....	0.08	0.03	0.06
.....	0.12	0.17	0.17
.....	1.34	1.35	1.22
.....	0.26	0.69	0.39

Table II continues on page 12

Table II continued

Compounds	Relative Percentage: Gülbirlik 1981	M.Gürkan 1980	M.Gürkan 1982
.....	1.66	2.08	1.85
.....	0.30	0.40	0.27
.....	2.43	2.69	2.31
.....	1.88	1.43	1.03
.....	5.53	4.95	4.01
.....	3.52	2.42	3.45
.....	0.25	0.33	0.24
.....	0.03	0.06	0.04
.....	0.07		0.06
.....	-	0.18	-

Table III. The Gas Chromatographic Analysis of Rose Absolute

Compounds	Relative Percentage: Absolute I	Absolute II	Compounds	Relative Percentage: Absolute I	Absolute II
Ethanol	3.63	-	.....	0.02	0.007
Acetic acid	-	0.001	p.C_{22}	0.07	0.15
β,γ-hexenol	-	0.006	.....	0.03	0.25
α-pinene,n-hexanol	0.004	0.005	.....	0.03	
Camphene	0.002	-	p.C_{23}	0.04	0.25
Myrcene,β-pinene	0,003	-	.....	0.007	
Limonene	0.0004	-	.....	0.005	-
n-octanol	0.02	0.001	.....	0.15	0.16
Linalool,nonanal,cis-rose Oxide	0.07		.....	0.015	
trans-rose oxide	0.24	0.28	.....	0.08	0.007
l-menthone,n-nonanol	0.002		.....	0.002	-
....,phenylethyl alcohol,decanal,terpinene-1-ol-4	37.73	78.79	.....	0.13	0.04
Citronellol,nerol	7.31	14.04	.....	0.2	0.02
Geraniol,neral	2.66	4.21	.....	0.35	0.002
Geraniol,carvone	0.04	0.01	.....	0.134	0.04
.....	0.07	0.05	.....	0.40	0.05
Citronellyl acetate	0.08	0.01	.....	0.45	0.006
Neryl acetate,cinnamaldehyde,p.C_{15}	0.17	0.06	.....	0.26	
Geranyl acetate	0.12	0.15	.....	0.006	-
.....	0.55	0.12	.....	0.03	-
β-damascone,...	0.01		.....	0.67	0.08
.....	0.04	0.006	.....	0.33	0.03
Methyl eugenol,p.C_{16}	0.48	0.89	.....	0.68	0.08
β-ionone	0.002	-	.....	0.28	0.05
....	0.03	0.02	.....	0.04	
p.C_{17},el.C_{17}	0.34	0.05	.....	0.10	0.47
.....	0.01	0.01	.....	0.32	
p.C_{18},el.C_{18}	0.08	0.03	.....	0.15	
....	0.01	0.006	.....	4.67	2.41
Farnesol (mix.)	0.03	0.01	.....	3.41	0.04
trans,trans-farnesol	0.20	0.20	.....	9.74	1.17
p.C_{19},el.C_{19}	2.15	0.05	.....	5.71	0.18
.....	0.001	0.003	.....	7.79	1.62
p.C_{20},el.C_{20}	0.15	0.021	.....	2.72	0.005
p.C_{21},el.C_{21}	0.21	0.05	.....	3.34	0.002
.....	0.01	0.03			

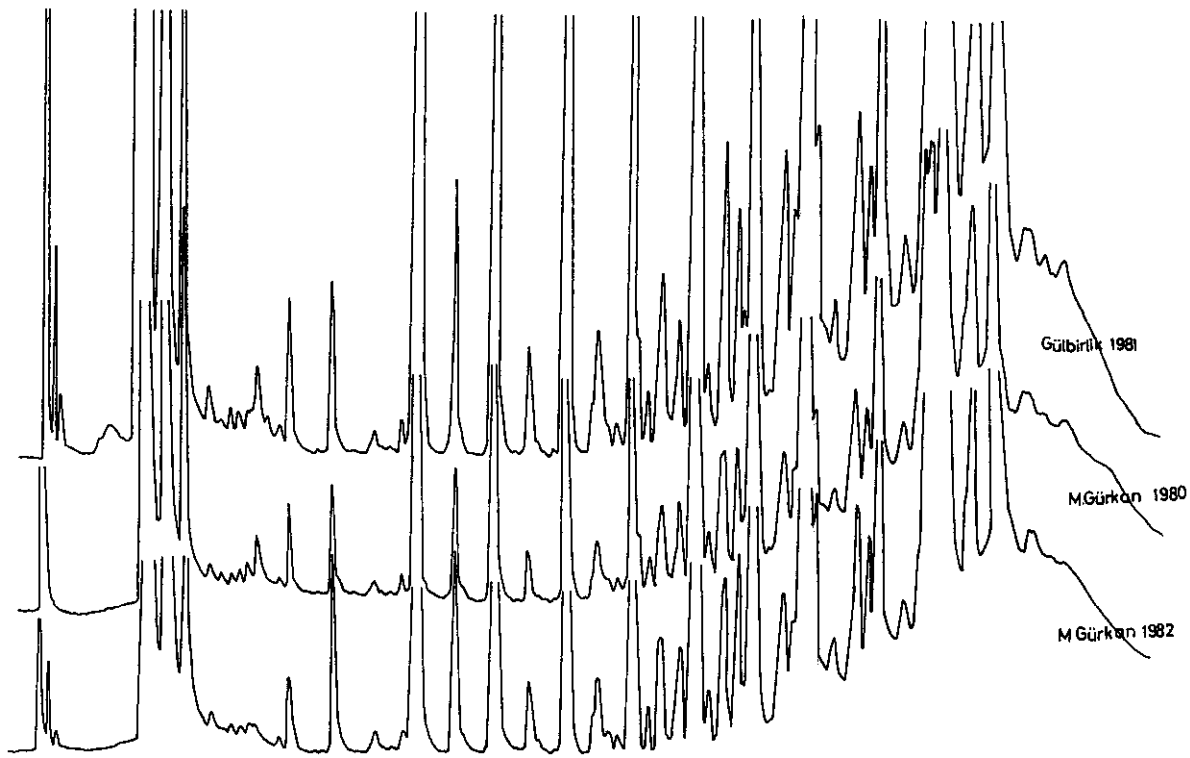

Fig.II The Chromatograms of Concretes

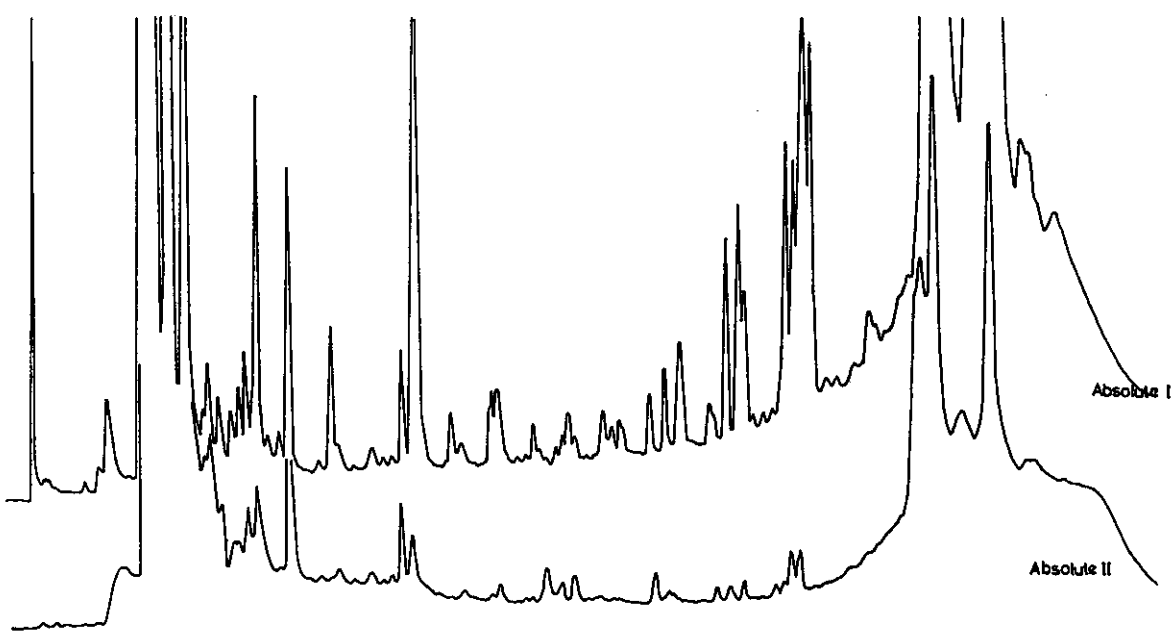

Fig.III The Chromatograms of Absolutes

Table IV. The Gas Chromatographic Analysis of a Bulgarian Oil and a Maroc Absolute

Compounds	Relative Percentage	
	Bulgarian oil	Maroc absolute
Ethanol	1.43	0.38
Pentanal	0.07	-
3-hexenal	0.26	-
α-pinene	0.73	-
camphene,heptanal	0.14	0.01
β-pinene	0.03	0.03
myrcene,hexanol	0.50	-
heptanol	0.02	-
hexyl acetate	0.01	-
methyl heptenone	0.04	-
octanal	0.05	-
Benzaldehyde	0.10	-
octanol	0.07	-
linalool	2.18	0.40
cis-rose oxide,nonanal	0.43	-
trans-rose oxide	0.17	-
nonanol	0.09	-
phenylethyl alcohol,decanal, terpinene-4-ol	1.45	74.06
citronellol	33.40	8.77
nerol	5.90	2.52
geraniol,neral	18.47	5.18
geranial,carvone	0.72	-
citronellyl acetate	0.53	0.23
neryl acetate	0.06	0.10
cinnamaldehyde,p.C_{15}	0.21	-
Geranyl acetate	1.60	0.38
eugenol,trans-β-damascenone	1.20	0.89
methyl eugenol,p.C_{16}	2.37	-
p.C_{17},ol.C_{17}	1.90	-
p.C_{18},ol.C_{18}	0.30	-
trans,trans-farnesol	0.87	1.30
p.C_{19},ol.C_{19}	14.41	2.73
p.C_{20},ol.C_{20}	1.07	-
p.C_{21},ol.C_{21}	4.28	1.75
p.C_{22}	0.10	-
p.C_{23}	0.90	-
p.C_{24}	0.04	-
p.C_{25}	0.07	-

The investigated concrete samples gave similar results (Table II). In the concrete samples the sum of percentages of paraffin C_{23} and higher hydrocarbons were found as 42.29% (1981 Gülbirlik), 48.74% (1980 M. Gürkan), 47.30% (1982 M. Gürkan). If one assumed that the function of higher hydrocarbons on the odour was negligible Gülbirlik concrete seemed to be of the best quality among the analyzed concretes.

As mentioned in experimental section, the yield of absolute from Gülbirlik 1981 concrete was approximately 60%. This value was in agreement with the chromatographic results.

As can be seen the percentages of Rose Absolute I and II differ drastically according to the purities of alcohol used in preparation. The percentages of phenylethyl alcohol, citronellol + nerol, geraniol + neral were 37.73, 7.31, 2.66% in Abs. I while 72.72, 14.04, 4.21 in Abs. II respectively.

On the other hand p.C_{17} + ol.C_{17}, P.C_{19} + ol.C_{19}, p.C_{20} + ol.C_{20}, p.C_{21} + ol.C_{21} and higher hydrocarbons occupied higher percentages in Abs.I. As a result, alcohol having water may be advised for production of rose absolute instead of pure alcohol.

To determine the qualities of rose absolute and rose oil the compositions of rose absolute II (from Gülbirlik 1981) and rose oil (from Gülbirlik 1981) were compared. As the sum of percentages of phenylethyl alcohol, citronellol + nerol, geraniol + neral was approximately 91% in Abs.II, the percentages of the trace of valuable ingredients couldn't be determined although they were present in the absolute. This value was 67.73% for rose oil. The sum of hydrocarbons was 8.077% in Abs.II and 27.31 in rose oil. Based on these results rose absolute showed higher quality than rose oil.

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