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ABSTRACT

For verification of the purity and originality of Turkish Rose Oi standard methods of analysis have been set up and applied on pure samples. These samples were taken from each of three succesive years production of seven major Rose Oil production factories in Turkey operating on steam distillation basis.

Using these laboratory methods, minimum and maximum limits on physical and chemical constants and gas chromatographic results have been determined.

These datas were used for the preparation of the National Standard for the Turkish Rose Oil, Comprising specifications and methods of analysis.

In Turkey scientific studies on Turkish Rose Oil were started by Prof. Dr. Ali Rıza Gürgen [1].

The production of pink rose flowers (Rosa Damascena Mill) reaches to 2500 tons per year [2], which is used for industrial purposes. Nearly 80 % out of this crop is consumed for the production of rose oil by steam distillation and the rest is subjected to hexane extraction for the production of the concrete of rose.

Rose oil producing centers of Turkey are the cities of Isparta and Burdur and their surroundings, which are situated at the south - west part of the country. The altitude of this area is in average 1000 meters from the sea level [3]. The contribution of several lakes, located in this part of the country is so that the atmosphere is more humid than would be expected at this altitude. During the month of June, which is the season of rose harvesting and rose oil production in Turkey, at 7 o' clock in the morning, relative humidity measurements have been taken 45 % to 55 % at several rose plantations.

The aim of this research work was as follows:

1) To investigate the problems of the rose oil industry in Turkey and possibly to help them for the best way of processing,

2) To make a survey of the quality on the original samples taken from each of the factories from the point of view of:

a) Physical and chemical charasteristics,

b) Gas chromatographic and infrared spectrophotometric analysis.

3) Collecting and preparing necessary data for setting up a National Standard for steam distilled Turkish rose oil, including specifications and standard methods of analysis.

As mentioned above rose flower harvesting season and parallel to these activities, rose oil production time in Turkey starts each year towards the end of May and ends at the end of June. The exact time of starting of the campaign depends on the rate of rainfall during this season. During wet seasons the campaign starts earlier.

Each morning starting at 3 o' clock people begin to pickup flowers and try to bring their daily crop before 8 A.M. to the rose oil production factories. These plants try to process this crop on the same day, so that the flowers do not deteriorate or become fermented. Some factories have cool storage rooms which enable them to store the rose flowers more than one day. Each year the yield of rose oil depends to some extend on the amount of rainfall; it is statistically known that the yield varies between 0,033 % and 0,025 % of the processed rose flowers. During seasons with high rainfall the yield of rose oil is higher compared with the dry seasons.

Parallel to these observations, the problem to be solved was to find out how the weather conditions during the harvesting season affect the physical and chemical constants and the chemical composition of the processed rose oil.

During the years 1967 (good rainfall), 1968 (low rainfall) and 1969 (good rainfall) original pure rose oil samples have been taken from 7 different major rose oil production plants and analysed in the laboratories.

At the end of this research work, there were serious evidences to believe that the composition and the quality of the rose oil do not vary to large extend with the meteorological conditions but vary with the rose flower storage conditions and steam distillation procedures at each factory. Softness of the water to be used in the kettles, temperature of the steam and time of distillation were carefuly observed and these subjects were discussed with the manufacturers with necessary suggestions.

We started our laboratory studies with the primary aim of establishing standard methods of analysis [4]. These activities continued until we could realise correlation between the results of physical and chemical determinations and gas chromatographic [5] results. In connection with this, we were successful to determine on the same sample, the amount of total free alcohols (calculated as citronellol) and the amount of total esters (calculated as citronellylacetate) with identical results within very small limits of tolerances, by both methods as mentioned above.

These methods of analysis have been published in the TURKISH NATIONAL STANDARD No. 1040 in 1971. Minimum and maximum limits of physical and chemical chracteristics as determined on the genuine turkish rose oil samples are listed in Table No. 1 below:

TABLE No. 1

	Specifications	minimum	maximum
1.	Specific gravity, 25°C/25°C	0,844	0,863
2.	Refractive Index, nD25	1,4520	1,4630
3.	Optical Rotation, 25°C	(—3,3°)	(—5,9°)
4.	Congealing Point °C	16,4°C	22,5°C
5.	Acid number, mgKOH/g	1,00	3,82
6.	Ester number, mgKOH/g	8,4	17,3
7.	Stearoptene %	12,0	23,0
8.	Total alcohols %	68,2	83,1

For gas chromatographic analysis we have used a (F and M Scientific Gas Chromatograph Model 720, with 1609 Attachement) which combines:

Katharometer and Flame Ionization Detector facilities.

Columns packed by 10 % carbowax 20 M on 60–80 mesh chromosorb W and by 10 % silicone gum rubber (methyl) GE SE – 30 on the same support were found to be adequate for our purposes. After our first trials, to analyse the rose oil samples on the gas chromatograph, we found out that it would be much advantageous to seperate at first, the adorous components, which are originally called the elaeoptene [6], consisting of oxygenated derivatives of terpenes, from the waxy components.

For that purpose [7] we used a 50 ml analytical burette, filled with 20 grams of 60–200 mesh silica gel, after wetting the silica gel phase with petroleum ether (b.p 30–40°C) we could separate the non odorous parts of the diluted rose oil sample in petroleum ether, which run through the silica gel phase without being held and could be weighed in a beaker after the evaporation of the petroleum ether in a vacuum dessicator.

After trial of several low boiling point solvents, we found out that diethyl ether is the best solvent for regaining of the elaeoptene from the silica gel filled burette. By washing successively 6 times with 20 ml portions of diethyl ether, elaeoptene is collected in a beaker, after diethyl ether evaporates in a vacuum dessicator.

On the gas chromatograms, identification of the peaks of the components could be done by addition of pure authentic substances [8], by comparing relative retention times and by verification of particular absorbences on the infrared spectrograms [9].

Samples of the elaeoptene have been subjected to saponification and then analysed again on the gas chromatograph. Observations were made that here the particular peaks of the esthers did not appear on the chromatograms.

After determination of the response factors [10] of the components, quantitative calculations have been done. Minimum and maximum limits of the components of the elaeptene and of the

stearoptene of the Turkish Rose Oil, determined on pure samples taken from successive 3 years production of various rose oil factories in Turkey are listed in Table No. 2 and Table No. 3.

TABLE No. 2

Compoments of the Rose Oil without stearoptene	% minimum		% maximum
Ethylalcohol	0,2	—	0,9
Nonylaldehyde	0,6	—	2,0
Citronellal	0,4	—	1,2
Linalol	1,1	—	3,1
Citronellylacetate	1,3	—	1,9
Citral	1,6	—	2,0
Geranylacetate	1,5	—	2,2
Citronellol	36,5	—	54,6
Nerol	4,6	—	10,2
Geraniol	7,8	—	23,5
Phenylethylalcohol	1,2	—	1,9
Eugenolmethylether	1,2	—	3,3
Eugenol	0	—	0,8
Farnesol	0,2	—	1,6
Others	0,6	—	1,3

Typical gas chromatograms indicating the identified peaks of the components of the Rose Oil without stearoptene and the components of the stearoptene of the Rose Oil are shown on Figure No. 1 and Figure No. 2.

Acknowledgements

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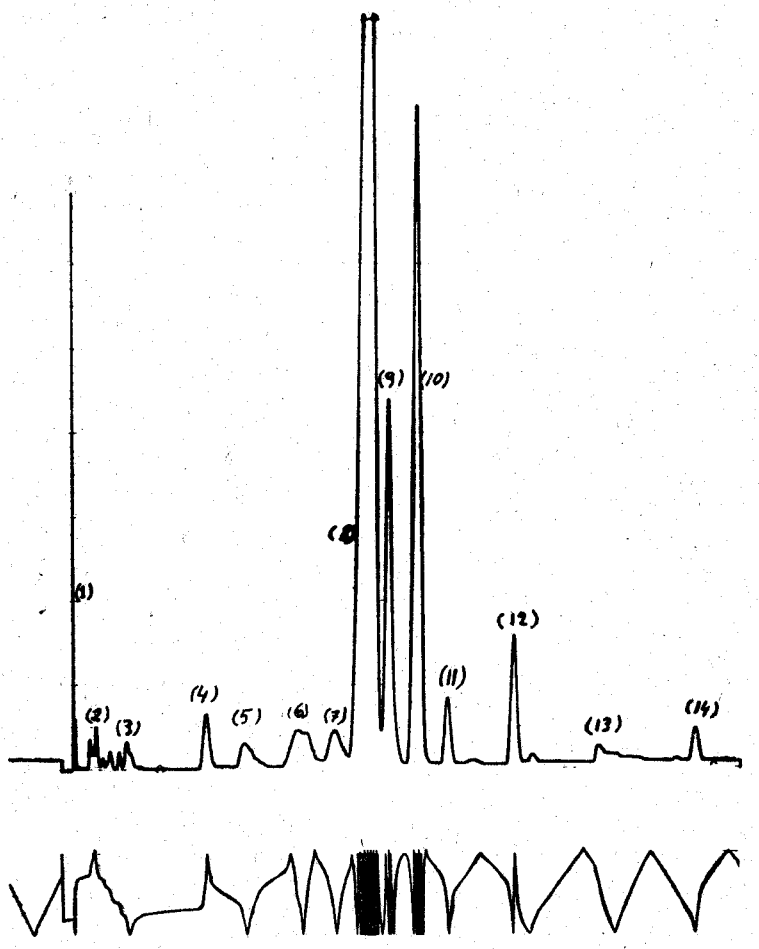
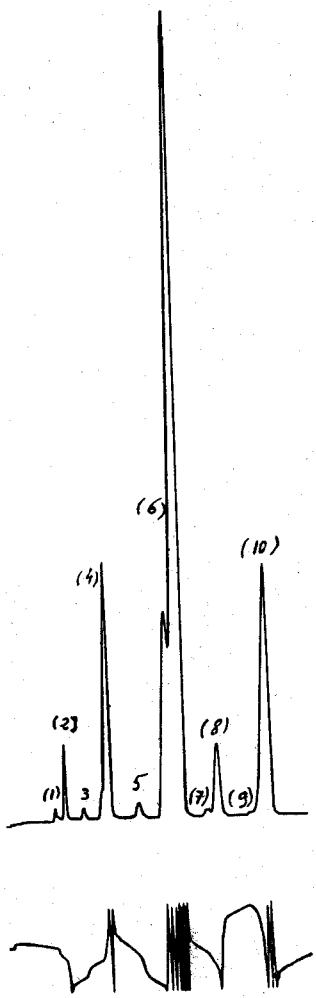
his assistance in the completion of this study. Great appreciation goes to Mr. Faruk A. Sünter, President of the Turkish Standards Institution for his encouragement and support of this project.

TABLE No. 3

Components of the stearoptene of the Rose Oil	% minimum		% maximum
Tetradecane ($C_{14}H_{30}$)	0	—	0,1
Pentadecane ($C_{15}H_{32}$)	0,2	—	0,6
Hexadecane ($C_{16}H_{34}$)	0	—	0,1
Heptadecane ($C_{17}H_{36}$)	1	—	1,7
Octadecane ($C_{18}H_{38}$)	0,1	—	0,2
Nonadecane ($C_{19}H_{40}$)	8,4	—	12,2
Eicosane ($C_{20}H_{42}$)	0,1	—	0,2
Heneicosane ($C_{21}H_{44}$)	0,3	—	0,6
Docasane ($C_{22}H_{46}$)	0	—	0,2
Tricosane ($C_{23}H_{48}$)	1,7	—	4,1
Others	0	—	0,1



1) Ethylalcohol; 2) Nonylaldehyde; 3) Citronellal; 4) Linalool; 5) Citronellylacetate; 6) Citral; 7) Geranylacetate; 8) Citronellol; 9) Nerol; 10) Geraniol; 11) Phenylethylalcohol; 12) Eugenolmethylether; 13) Eugenol; 14) Farnesol.



1) Tetradecane; 2) Pentadecane; 3) Hexadecane; 4) Heptadecane; 5) Octadecane; 6) Nonadecane; 7) Eicosane; 8) Heneicosane; 9) Docasane; 10) Tricosane.

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Ö Z E T

Türkiye'nin GÖLLER BÖLGESİ adı verilen Isparta ve Burdur havalisinde yılda 2,5 milyon kilonun üzerinde (Rosa Damascena Mill) nevinden pembe gül çiçeği yetiştirilmekte ve bunun ortalama % 80'i gülyağı ve kalanı gül konkreti üretilmesinde kullanılmaktadır. Gülyağı üretme mevsimi, Mayısın ikinci yarısı ile Haziran sonu arasına rastlamaktadır. Bu devre yağışlı geçerse gülyağı verimi artmaktadır. Mevsimine ve üretim prosesine bağlı olarak 3000 kg ilâ 4000 kg gül çiçeğinden 1 kg gül yağı elde edilmektedir.

Göller bölgesinde halen 7 gülyağı fabrikası çalışır durumdadır, bunlarda endirekt ısıtma ve buhar destilasyonu ile gülyağı elde edilmektedir. 1967; 1968 ve 1969 yıllarında her 7 fabrikadan orijinal gülyağı numuneleri alınarak üzerlerinde fiziksel ve kimyasal tayinler ile gas kromatografik ve infrared spektrofotometrik metodlarla kimyasal bünye araştırması yapılmıştır. Ayrıca her yıl fabrikaların yetkilileri ile yapılan temaslarda, gülyağı üretimindeki buhar sıcaklığı ve destilasyon süresinin sınırlandırılması ile, gülçiçeğinin fermentasyonunun önlenmesi gibi konulara temas edilerek, Türkiye'deki gülyağı ürününün belirli spesifikasyonlara uygun olarak elde edilmesinin imkânları araştırılmıştır. Araştırma süremiz içinde, gerek kurak, gerekse yağışlı geçen gülyağı kampanya devreleri olmuştur. Bunlara göre fiziksel ve kimyasal sabitlerde elde edilen minimum ve maksimum değerler aşağıdaki (Tablo No. 1 de) gösterilmiştir.

Gas Kromatografik analizlerde: F and M Scientific Model 720 with 1609 Flame Ionization Attachement, cihazı kullanılmıştır.

Gülyağı polar bünyede olan güzel koku veren ve özellikle elaeopten adı verilen terpen alkolleri, esterleri, aldehitleri ve benzerleri ile non-polar bünyede olan vaks nevinden stearoptenden meydana gelmektedir. Buna göre gas kromatografi çalışmalarımız,

bu iki neviden komponentler silikagel kolonu ile birbirinden ayrıldıktan sonra, polar ve non-polar komponentlerin analizinde kullanılan ayrı ayrı gaz kromatografi kolonları yardımı ile sonuçlandırılmıştır.

Silikagel kolonu olarak, 50 ml'lik büret ile 60–200 mesh'lik silikagelden istifade edilmiştir. Stearoptenlerin saf olarak elde edilmesinde 30–40°C petrol eteri ve elaeoptenlerin geri kazanılmasında dietileter olumlu sonuç vermiştir. Gaz Kromatografi analizlerinde, elaeoptenlerin ayrılmasında "3/16" OD, 6 ft % 10 carbowax 20 M, on 60–80 mesh chromosorb W kolonu kullanılmış ve 90/220°C, 5°C/dakika programlı ısıtma ile çalışmıştır. Stearoptenlerin ayrılmasında "3/16" OD, 6 ft, % 10 silicone gum rubber (methyl) GE SE - 30 on 60–80 mesh chromasorb W" kolonu kullanılmış ve 200/230°C 5°C/dakika programlı ısıtma ile çalışmıştır. Buna göre gas kromatografik analizlerde elde edilen minimum ve maksimum değerler aşağıdaki (Tablo No. 2 ve Tablo No. 3) de gösterilmiştir.

Gaz kromatografik analiz sonucunda, gülyağının başlıca komponentinin evvelce kabul edildiği gibi Jeraniol olmayıp, Sitronellol olduğu tesbit edilmiştir.

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