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STUDIES ON TURKISH ROSE CONCRETE, ABSOLUTE, AND HYDROSOL

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The production of rose absolute from fresh flowers of the cultivated Rosa damascena Miller *was realized using traditional and modern techniques, such as molecular distillation, extraction with liquified gases, etc. Headspace trapping and SPME techniques were employed in the sampling of volatile constituents in the concrete, absolute, and hydrosol, for analysis by GC/MS.*

Key words: *Rosa damascena* Miller, rose oil, rose concrete, rose water.

Rose concrete is obtained by solvent extraction of fresh rose flowers of the cultivated *Rosa damascena* Miller followed by removal of the solvent *in vacuum*. Concrete represents the true fragrance of rose flowers. It is a semisolid mass with a waxy look.

Industrial production of rose concrete is as follows: 600–750 kg of rose flowers are charged into 3000 L extraction vessels equipped with stirrers. The vessel is filled with *n*-hexane up to the halfway mark and the extraction takes place for 20 min at 60–65°C. After removal of the extract, extraction is repeated with a second charge of *n*-hexane.

The extracts are combined in the evaporator to recover *n*-hexane at 60–65°C. Traces of *n*-hexane in the resulting extract are removed in a vacuum evaporator and the rose concrete is filled into 5 L storage tins while hot, where it solidifies on cooling. Approximately 375–400 kg of rose flowers yield 1 kg of concrete [1–3].

In Bulgaria, rose flowers are extracted with petroleum ether and rose concrete is obtained after removal of the solvent. Absolute is produced by dissolving the concrete in hot ethanol. It is then cooled to 0°C to precipitate waxes and filtered at the same temperature, vacuum evaporation of ethanol under nitrogen yields the rose absolute [4]. The yield of concrete is reported to be 0.22–0.25% (1 kg from 400 kg of flowers) in Bulgaria [5]. The yield of rose absolute has been reported as 62–65%, rarely 68% [6]. Another source reported the yield of concrete and absolute as 0.15% and 50%, respectively [7].

Rose absolute is produced by extracting rose concrete with ethyl alcohol. Cooled ethanolic extract (–15/–20°C) is filtered through cooled filters. Removal of ethanol *in vacuum* yields rose absolute [1–3, 7–9].

Phenylethyl alcohol (60–75%) is the main constituent of rose absolute. Since phenylethyl alcohol is soluble in water, its content in rose oil is generally low (1.2–2.2%) [1, 9–12].

The fragrance of rose absolute is described as rich, sweet, rose spicy, and honey [13]. Rose oil and rose concrete are used in perfumery [14].

Industrial Rose oil distillation is described elsewhere [15, 16].

This paper describes various techniques to produce rose absolute from Turkish Rose concrete carried out by us, the physico-chemical and spectral features of the absolutes so produced, and rose water.

Gulbirlik rose concrete (1991) yielded 12% essential oil (A). Oil-free distilate was extracted with diethylether three times and the removal of ether *in vacuum* yielded 10% essential oil (B).

The same concrete (Gulbirlik 1991) yielded 63.6% of absolute using Method-2 (C). GC and GC-MS analysis of the products are seen in Table 1.

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TABLE 1. The Composition of Rose Absolute, %

Main components	A	B	C	D	E	F	G	H	I
Ethanol	0.01	-	0.1	0.02	0.2	1.3	0.6	0.1	1.3
Germacrene D	0.2	0.1	0.1	0.2	1.6	1.9	1.1	0.1	1.1
Heptadecane	0.8	0.02	1.9	0.7	-	-	-	-	-
Citronellol	18.7	3.6	9.7	8.8	10.4	9.6	7.2	8.1	11.9
Nerol	5.7	1.2	2.8	2.0	3.3	4.4	2.9	2.0	2.5
Geraniol	14.0	2.9	7.0	5.2	8.4	10.9	7.4	5.3	6.1
Benzyl alcohol	0.5	1.6	0.7	0.9	0.9	0.6	1.2	1.2	0.8
Phenylethyl alcohol	**44.1**	**86.0**	**46.7**	**63.0**	**54.0**	**49.6**	**61.1**	**65.9**	**53.3**
Nonadecane	2.6	0.2	13.0	3.3	6.5	6.1	4.7	6.8	4.9
Nonadecene	1.0	0.1	5.0	3.8	4.6	5.0	4.9	0.03	3.4
Methyl eugenol	1.4	0.4	0.9	0.8	1.2	0.8	0.8	0.8	1.2
Heneicosane	0.3	-	2.9	0.3	0.5	0.4	0.3	0.3	0.4
Eugenol	2.3	0.7	0.5	1.4	1.6	2.1	1.5	1.1	1.5
Yield, %	12	10	64	60	61	62	59	60	58

TABLE 2. The Composition of Rose Absolute from Ercetin - 1992 Rose Concrete Using Method 3 and 4**, %

Main components	K1 (P1)	K2 (P2)	K3 (P3)	K4 (P4)	K5 (P5)	K6 (P6)
Heptadecane	0.4 (1.0)	0.8 (0.5)	1.1 (0.4)	1.2 (0.6)	1.4 (1.4)	0.9 (0.1)
Citronellol	8.7 (3.1)	7.5 (7.6)	6.9 (8.5)	3.7 (8.9)	1.9 (6.8)	1.0 (6.0)
Nerol	2.0 (0.7)	1.7 (2.0)	1.6 (2.1)	0.8 (2.2)	0.4 (1.6)	0.2 (1.4)
Geraniol	5.0 (2.2)	4.4 (4.7)	4.2 (5.3)	2.2 (5.6)	1.3 (4.1)	0.6 (2.4)
Benzyl alcohol	1.2 (0.2)	0.9 (1.3)	0.7 (1.3)	0.3 (1.2)	0.1 (0.9)	0.02 (2.1)
Phenylethyl alcohol	**65.4 (15.9)**	**55.7 (69.0)**	**46.7 (66.8)**	**22.1 (64.4)**	**8.3 (51.9)**	**3.6 (82.0)**
Nonadecane	**2.1** (16.9)	**6.9** (3.1)	**15.5** (3.1)	**37.6*** (2.7)	**53.4** (17.6)*	**56.9*** (0.2)
Nonadecene	4.4 (3.2)	3.3 (1.7)	3.3 (1.9)	(2.8)	1.2	(0.04)
Eicosane	0.1 (2.1)	0.4 (0.1)	1.0 (0.2)	2.7 (0.2)	4.0 (1.2)	4.9 (0.02)
Heneicosane	0.1 (16.1)	1.1 (0.3)	3.1 (0.5)	8.8 (0.3)	11.9 (5.2)	15.9 (0.1)
Eugenol	1.4 (0.9)	1.3 (1.5)	1.2 (1.4)	0.7 (1.6)	0.4 (1.2)	0.4 (0.5)
Tricosane	Tr. (9.0)	0.2 (0.03)	- (0.01)	1.0 (Tr.)	1.1 (1.0)	1.6 (0.03)
(E,E)-Farneol	(1.5)	(0.2)	(0.1)	(0.4)	(0.3)	(0.01)
Tetracosane	(3.4)	-	-	(0.03)	-	-
Heptacosane	(4.1)	-	-	(0.03)	(0.2)	-
Yield, %	36.4 (12)	23.4 (29)	3.2 (30)	1.0 (24)	0.4	0.3 (1)

*Sum of nonadecane and nonadecene.

**P1: volatiles trapped on the condenser for study I; P2: captured in dry-ice trap for study I; P3: volatiles trapped on the condenser for study II; P4: volatiles trapped on the condenser for study III; P5: volatiles trapped on the condenser for study III (solid); P6: captured in dry-ice trap for study II.

The phenylethyl alcohol content of the first oil (44.1%) and the absolute (46.7%) were found to be lower than the second oil (86.0%). The citronellol content of the first oil (18.7%) was found to be the higher than the second oil (3.6%) and the absolute (9.7%). Likewise, the nerol and geraniol contents of the first oil (5.7% and 14.0%, respectively) were higher than those in the second oil (1.2% and 7.0%, respectively).

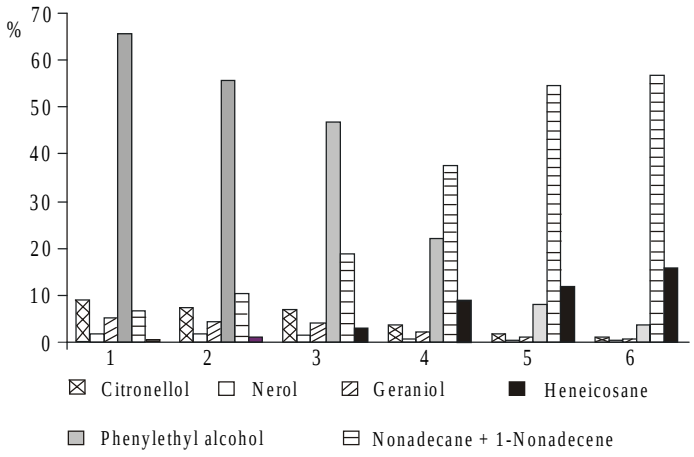

Fig. 1. Graphical distribution of main constituents in absolutes obtained in different stages.

Essential oil distilled from Bulgarian rose concrete was reported to contain 82.2% phenylethyl alcohol in the oxygenated and non-oxygenated fraction [17]. Since previous results have often been cited as oxygenated and non-oxygenated fractions, it is not possible to make a true comparison with our results.

Gulbirlik rose concrete (1991) was dissolved in ethanol using Method-3 to obtain rose absolute using dry ice for cooling. The yield of rose absolute was 61% (E).

This absolute contained a lesser amount of waxes than the absolute obtained by dissolving the concrete at room temperature following the method 2 (C). Phenylethyl alcohol content in E (54.0%) was found higher than C (46.7%). Similar observations were made for citronellol, geraniol, and nerol.

The same technique was applied to rose concrete samples of Konur-1991 (F), Ercetin-1991 (G), Gurkan-1991 (H), Ercetin-1992 (D), and Gulbirlik-1994 (I) to produce absolutes in 58–62% yield.

In all absolute samples, the main constituents were found as follows: phenylethyl alcohol (49.6–65.9%), citronellol (7.2–11.9%), nerol (2.0–4.4%), and geraniol (5.2–10.9%).

Method-3 was applied in 6 stages on Ercetin-1992 rose concrete at –20°C. Filtration was carried out using a filter assembly cooled with dry ice.

1st stage (K1) yielded 36.4% absolute containing phenylethyl alcohol (65.4%), citronellol (8.7%), and geraniol (5.0%).

2nd stage (K2) yielded 23.4% absolute with phenylethyl alcohol (55.7%), citronellol (7.5%), and geraniol (4.4%) as main constituents.

3rd stage (K3) yielded 3.2% absolute with the following main constituents: phenylethyl alcohol (46.7%), citronellol (6.9%), nonadecane (15.5%), and geraniol (4.2%).

4th stage (K4) produced an absolute in 1.0% yield. It contained nonadecane + nonadecene (37.6%) and phenylethyl alcohol (22.1%) as major constituents.

Nonadecane + nonadecene (37.6%) contents increased in 5th (K5) and 6th (K6) stages (54.6% and 56.9%, respectively), while phenylethyl alcohol contents decreased (8.3% and 3.6%, respectively).

Total absolute yield in 6 stages reached 64.7%, while in the first 2 stages it was 59.9%, and together with the 3rd stage, it was 63% (Fig. 1, Table 2).

Method 4 was applied in three separate studies for the production of rose absolute from Ercetin-1992 rose concrete using molecular distillation. Results are given in Table 2.

The yields of volatiles trapped on the condenser were 12.1% for study I, 29.7% for study II, and 24.0% for study III, while those captured in dry-ice trap were 29.1% for study I and 1.3% for study II. No compound was trapped in study III.

Commercially available Essence Absolute de Rose (Pharmachim) (ST1) (Bulgarian) and Absolute de Rose Turque (Givaudan Roure) (ST2) (Turkish) gave the following compositions. Phenylethyl alcohol (59.3 % and 67.5%) was the predominant component followed by citronellol (10.2% and 8.3%), nonadecene (7.1% and 2.8%), geraniol (5.3% and 5.1%), nerol (2.4% and 2.1%), nonadecane (2.4% and 2.0%), and methyl eugenol (1.4% and 0.7%).

TABLE 3. Compositions of Commercial Bulgarian (ST1) and Turkish Rose Absolutes (ST2)

Main components	ST1	ST2
Phenylethyl alcohol	59.3	67.50
Citronellol	10.2	8.3
Geraniol	5.3	5.1
Nerol	2.4	2.1
Eugenol	-	1.5
Methyl eugenol	1.4	0.7
Nonadecane	2.4	2.0
Nonadecene	7.1	2.8

TABLE 4. The Composition of Phytosol Extracts from Ercetin-1992 Rose Concrete

Main components	T1	T2	T3	T4
Ethanol	-	-	0.04	-
α-Pinene	1.2	0.4	0.2	0.1
Citronellol	6.9	6.1	6.1	6.3
Nerol	1.7	1.4	1.4	1.5
2-Phenylethyl acetate	Tr.	0.3	0.3	0.02
Geraniol	4.1	3.7	3.6	3.8
Benzyl alcohol	1.1	1.0	0.9	0.8
Phenylethyl alcohol	**62.4**	**53.9**	**53.4**	**50.8**
Nonadecane	6.3	8.1	8.0	12.0*
1-Nonadecene	1.3	3.8	2.2	
Methyl eugenol	0.7	0.7	0.7	0.8
Heneicosane	4.7	5.3	5.3	5.4
Eugenol	1.0	1.1	1.1	1.2
Tricosane	2.2	1.9	2.0	2.0
Yield, %	18	1	6	10

T1: extract was obtained after the process time of 10 min in study I; T2: half of the extract was collected in 5 min in study II; T3: the rest was recovered after 1 h in study II; T4: re-extracted with fresh solvent for 3 h in study II.

*Sum of nonadecane and nonadecene.

If compared with the results for ST1 and ST2 given in Table 3, the best result seems to have been obtained with study III (P3). The colorless absolute oil obtained in 30% yield contained phenylethyl alcohol (66.8%), citronellol (8.5%), geraniol (5.3%), nonadecane (3.1%), and nerol (2.1%) as shown in Table 3. These amounts show similarity with those of the commercial Turkish and Bulgarian rose absolutes.

From the concrete left out of study II, an absolute was obtained in 41.5% yield. It contained phenylethyl alcohol (18.4%), nonadecane (7.5%), nonadecene (15.5%), and citronellol (4.7%) as main constituents.

Ercetin-1992 rose concrete was extracted with 1,1,1,2-tetrafluoroethane using a mini extraction unit (Method 5). In study I, whole extract was obtained after a process time of 10 min (T1). In study II, half of the extract was collected in 5 min (T2), and the rest was recovered after 1 h (T3). The mass was re-extracted with fresh solvent for 3 h (T4).Yields were 17.7%, 1.0%, 5.5%, and 10.0%, respectively. Total absolute yield in study II was 16.5%.

The phenylethyl alcohol content gradually decreased from 62.4% (T1) to 50.8% (T4), while nonadecane content showed a gradual rise from 6.3% (T1) to 12.0% (T4). The other important components were citronellol (6.1–6.9%), geraniol (3.6–4.1%), and nerol (1.4–1.7%). Prolonged extraction time, naturally, allows more paraffins to be extracted (Table 4).

TABLE 5. Results of Headspace Analysis of Rose Concrete

Main components	Rose Concrete (Ercetin 1992)	
	active charcoal	Porapak Q
Phenylethyl alcohol	44	47
Citronellol	9	3
Geraniol	3	1
Nerol	2	1
Eugenol	-	0.2
Methyl eugenol	-	0.1
α-Pinene	9	10
Myrcene	5	3
β-Pinene	2	2
Sabinene	1	1

TABLE 6. Results of SPME-Analysis of Rose Concrete

Main components	Rose Concrete (Gulbirlik 1997)		
	rose absolute, %	headspace-SPME, %	
		room temp.	heat applied
Phenylethyl alcohol	50	43	51
Citronellol	18	17	18
Geraniol	6	5	6
Nerol	3	4	3
Eugenol	2	1	2
Methyl eugenol	2	2	2
Nonadecane	5	0.1	0.7
Nonadecene	3	-	-

A similar study was reported from Bulgaria, however, due to lack of quantitative data, a comparison was not possible [18].

The melting point of the Turkish rose concrete was found to be 45°C for the years 1971–1973 and 42°C for 1991. Bulgarian standard is between 41.0–46.5°C [6]. Although rose oil and rose concrete have been produced in commercial scale in Turkey since 1930s, rose absolute production in commercial scale is nonexistent. Our studies have aimed at finding the most efficient way for the production of rose absolute of acceptable quality.

Our results have shown that the best yield of absolute in the shortest process time is obtained by dissolving the concrete in ethanol in an ultrasound bath followed by freezing and cool filtering *in vacuum*. In this technique, rose absolute was obtained in 60% yield. Its composition compared well with commercial rose absolutes.

Molecular distillation produced a colorless absolute in 29% yield. Although its composition is similar to commercial absolutes, the low yield and high operational cost preclude its commercial use.

Forty-eight compounds were previously reported from Turkish rose absolute; here we report the occurrence of 94 compounds.

The results clearly show that there is no significant qualitative and quantitative difference between the Turkish and Bulgarian rose absolutes.

Closed-loop stripping headspace analysis of the concrete using active charcoal and Porapak Q as adsorbents gave slightly different results. Phenylethyl alcohol and citronellol were characterized as main constituents, however, unlike the absolute, monoterpene hydrocarbons such as α-pinene and myrcene were also detected in significant amounts, as shown in Table 5.

TABLE 7. Composition of Rose Water, %

Main components	Rose water			
	hexane extraction	headspace-SPME	immersion-SPME	immersion-SPME*
Phenylethyl alcohol	50	3	4	10
Citronellol	13	34	31	45
Geraniol	13	21	22	11
Nerol	5	10	11	5
Eugenol	5	3	5	5
Methyl eugenol	4	13	13	16
Nonadecane	0.24	2	1	-
Nonadecene	0.05	0.5	0.3	-

*Undiluted rose water.

The detection of unusual constituents that are not present in rose absolute, such as α-pinene, β-caryophyllene, and other hydrocarbons, and inconsistencies in the use of different adsorbents do not qualify this method as an efficient and reliable technique for analysis.

However, headspace-SPME of the rose concrete with or without heating the concrete showed highly comparable results with rose absolute, as shown in Table 6. These results clearly show that headspace-SPME can be the preferred method of analysis for rose concrete. The composition of the heated sample is quite comparable with that of rose absolute. Another advantage of the headspace SPME was the insignificant adsorption of paraffins; while conventional sampling technique requires a tedious, messy, and time consuming procedure, sampling with headspace-SPME can be completed in 15 min and the analyte is ready for direct analysis by GC or GC/MS [19–21].

The conventional sampling technique for the analysis of rose water is liquid-liquid extraction with *n*-hexane. It yields an oil in which phenylethyl alcohol (50%) is the main constituent. However, different results were obtained with immersion and headspace-SPME of the same rose water. Citronellol, geraniol, nerol, and methy eugenol were characterized as main constituents. These results are reminiscent of the composition of Turkish rose oil (Table 7). SPME can be efficiently used both for headspace and immersion sampling. Due to the simplicity of operation and reliability, SPME may be expected soon to replace conventional sampling techniques [19–21].

EXPERIMENTAL

Rose concretes = 1991, 1994, and 1997 Crops of Gulbirlik, 1991 and 1992 Crops of Ercetin, 1991 Crops of Konurlar, and 1991 Crops of Gurkan

Commercial rose absolutes = Absolute de Rose Turque (Givaudan-Roure). Essence Absolute de Rose (Pharmachim). Rose water = Rose Water of Gulbirlik

Simple Distillation (Method 1). Rose concrete (Gulbirlik-1991) was mixed with water and distilled for 3 h using a simple distillation setup.

Extraction (Method 2). Concrete was dissolved in ethanol and left to stand overnight in a deep freezer (–20°C) and filtered through blackband filter paper under vacuum. The concrete that remained on the filter paper was redissolved in ethanol, left to stand overnight in a deep freezer, and evaporated *in vacuum* using a rotary evaporator to yield the absolute.

Extraction Using Ultrasonic Bath (Method 3). Concrete + ethanol mixture was dissolved using an ultrasonic bath. The mixture was left to stand overnight in a deep freezer. It was filtered using a black band filter paper *in vacuum.*

Molecular Distillation (Method 4). A short-path distillation apparatus was utilized to obtain absolute from rose concrete applying the following parameters:

	I	II	III
Feed vessel surface temperature (°C)	80	80	80
Condenser temperature (°C)	30	10	8
Evaporator surface temperature (°C)	100	115	115
Vacuum (mbar)	20	20	20
Roller-wiper speed (rpm)	200	200	300
Feed quantity (drop/min)	5	20	10

Liquefied Gas Extraction (Method 5). Rose concrete was dissolved by heating and extracted with liquefied 1,1,1,2-tetrafluoroethane gas in a pressurized vessel. A hand-held extraction unit was utilized. Depressuring the collecting flask yielded rose absolute. Two different experiments were carried out.

1 – The entire extract was transferred to the collecting flask to obtain the absolute.

2 – Half of the extract was removed after 5 min and the extraction was continued for one hour. After removal of the extract, marc was extracted with the same solvent for 3 hours more. Thus, three absolutes were obtained.

Headspace (Method 6). Materials: Active charcoal and Porapak Q were purchased from Supelco. Process time: 24 h, solvent for desorption was carbon disulfide for active charcoal and *n*-hexane for Porapak Q.

Solid Phase Micro Extraction (SPME, Method 7). SPME Fiber: polydimethylsiloxane (PDMS) 100 mm film.

GC and GC/MS Conditions. The oils were analyzed by capillary GC and GC/MS using a Shimadzu GC-9A coupled with CR4A integrator, and Hewlett-Packard GC-MSD system.

GC. The GC analysis was carried out using a Shimadzu GC-9A coupled with CR4A integrator. Thermon 600T fused silica capillary column (50 m × 0.25 mm) was used. Carrier gas was nitrogen. Oven temperature was kept at 70°C for 10 min and programmed to 180°C at a rate of 2°C/min, and then kept constant at 180°C for 30 min and programmed to 220°C at a rate of 4°C/min, and then kept constant at 220°C for 45 min. Injector and detector (FID) temperatures were 250°C.

GC/MS. The GC/MS analysis was carried out with a Hewlett-Packard GC-MSD system. Innowax FSC column (60 m × 0.25 mm, 0.25 mm film thickness) was used with helium as a carrier gas. GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and then kept constant at 220°C for 10 min C. Split flow was adjusted at 50 mL/min. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was from *m/z* 35 to 425. Library search was carried out using the Wiley GC/MS Library and BASER Library of Essential Oil Constituents.

REFERENCES

1. M. Kurkcuoglu, MSc Dissertation, Anadolu University, Eskisehir (1988).
2. M. Kurkcuoglu, PhD Dissertation, Anadolu University, Eskisehir (1995).
3. Anon, *Gulculuk, Gulbirlik*, Isparta, 1987.
4. B. Stoianova-Ivanova, P. Hadjieva, K. Ubrik, and A. Tzutzulova, *Rivista Ital.*, **56**, 665 (1974).
5. J. Garnero and P. Robertet, *Parfums, Cosmetiques, Aromes*, **47**, 31 (1982).
6. J. Garnero, G. Guichard, and P. Buil, *Parfums, Cosmetiques, Aromes*, (8), 33 (1976).
7. G. S. Ranade, *Indian Perfumer*, **24**, 49 (1980).
8. B. Lawrence, *Perfum. Flav.*, **16**, 43 (1991).
9. H. Ahterdjiev, *Oleum Rosae, Farmakognozia, Meditsina i Fizkultura*, Sofya (1979), p. 294.
10. K. Bauer and D. Garbe, *Common Fragrance and Flavour Materials*, VCH, Darmstadt (1985).
11. T. Baytop, *Turkiye′ de Bitkiler ile Tedavi*, Ist. Univ. Yay., Istanbul 1984, No. 3255.
12. O. Anac, *Perfum. Flav.*, **5**, 29 (1980).
13. T. Baytop, Turkiye′nin Tibbi ve Zehirli Bitkileri, Ist. Univ. Yay., Istanbul (1963), No. 1039.
14. E. Gunther, *The Essential Oils*, Krieger, Florida (1975), pp. 1, 50.
15. K. H. C. Baser, *Perfum. Flav.*, **17**, 45 (1992).
16. K. H. C. Baser, M. Kurkcuoglu, and Z. Konur, *The Production and Properties of Turkish Rose Oil*, International Conference on Essential Oils for Perfumery & Flavours, Antalya, Turkey, 26–30 May (1990).
17. Y. Ohno and S. Tanaka, *Agric. Biol. Chem.*, 41, 399 (1977).

18. P. F. Wilde and P. G. McClary, *Perfum. Flav*., **19**, 25 (1994).
19. K. H. C. Baser and M. Kurkcuoglu, *SPME and Headspace Assay Development: Application to Rose Products*, IFEAT Conference, London, UK, 8–12 November (1998).
20. J. Pawliszyn, *Solid Phase Microextraction. Theory and Practice*, Wiley-VCH (New York), 1997.
21. B. D. Mookherjee, S. M. Patel, R. W. Trenkle, and R. A. Wilson, *Perfum. Flav*., **23**, 1 (1998).