

Infrared Spectral Composition of Rose Oil From Turkey

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This work presents an approach to analyze the chemical structure of rose oil by means of infrared spectroscopy. It is shown that the main components of the rose essential oil can be ascertained through FTIR-ATR technique and pellets with KBr, using spectral information from the pure standard substances. Spectroscopic analysis is based on the characteristic vibrational frequencies of the standard substances and essential oil. Basically, these techniques define the characteristic bands of rose oil and recognize the main components of essential rose oil by comparing the spectroscopic data of pure standards to that of rose oil. The highest percentages contents of essential oil are chosen to investigate unique wavenumbers. IR data results give valuable information to interpret the key bands of rose essential oil. Main components of rose oil obtained from IR spectroscopy are good agreement with those by GC-MS analysis.

Key Words: Essential oil, Rose, FTIR, ATR, GC-MS.

INTRODUCTION

Isparta is famous for its rose and now its fame spreads all over the world with its position in the world market¹. Until now researches on essential oil of rose were focused on determining components of rose oil by using GC-MS technique^{2,3}, effects of factors on oil quality in advance⁴, different extraction methods⁵⁻⁸, genotype of roses in a restricted region⁹. According to Tucker and Maciarello¹⁰ there are four types of rose used in rose oil production. These are *R. damascena* Mill, *R. gallica* L, *R. mashata* Herrm and *R. centifolia*. In this study, Isparta roses (*R. damascena* Mill) are used. For commercial reasons, quality is indispensable to export firms. Today, Turkey is one of the leading countries in rose production in the world market. In their trade with Europe, it is inevitable for exporting firms to maintain some standards and check by using technology whether the product meets the commercial standards. Rose oil, with its use in perfume sector, has to contain some materials in certain quantities. At this point necessary analyses can be carried out with GC-MS method. However, a structural analysis of rose oil has never been carried out with

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FT-IR spectroscopy method until now. Analyses carried out with vibrational spectroscopy can be used both in quality control and in characterization as infrared spectrum of every element, apart from optical isomers, is different from each other (originality). Consequently, various spectra are obtained in each kind of plant. In this context, present study will characterize Isparta rose oil and show its features. Alternatively, in this work, FTIR-ATR spectroscopic method has been successfully applied to identify the main components of the essential oil of rose. IR spectra present characteristic key bands of each sample.

EXPERIMENTAL

Citronellol [106-22-9], nerol [106-25-2], nonadecane [629-92-5], eugenol [97-53-0], heneicosane [629-94-7], PEA [1517-69-7] and hexane [110-54-3] were purchased from Sigma-Aldrich, Germany and Methyl-eugenol [93-15-2] were supplied by Fluka, Germany and Geraniol [106-24-1] was provided by Acros, USA.

R. damascena Mill. is cultivated in commercial rose gardens located in Isparta, Turkey. Samples were collected from different region of Isparta, at different times. The essential oil produced by industrial steam distillation method. Essential oil diluted in hexane (1:1000). 1 μ L injected to GC-MS. 20 μ L of essential oil is used for FTIR spectroscopic analysis. Major components of essential oil were chosen to examine for FTIR spectroscopy, which are citronellol, nerol, geraniol, eugenol, methyl-eugenol (eugenol methyl ether), 2-phenylethanol, nonadecane and heneicosane.

GC-MS analysis: Samples were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a crosslinked polyethylene glycols CP-Wax 52 CB 50 m \times 0.32 mm ID capillary column with a 0.25 μ m film thickness (Palo Alto, CA, USA). The injector with a split insert was set at 240 $^{\circ}$ C and the oven temperature was programmed at 60 $^{\circ}$ C raised to 220 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/220 $^{\circ}$ C for 0.5 h. Total run time 80 min. Helium was the carrier gas and the flow rate was 2 mL/min. Split ratio, 1/5 mL/min. The GC was directly interfaced to a Shimadzu QP 5050 quadrupole mass spectrometer operated in the electron impact ionization mode at 70 eV with an interface temperature of 250 $^{\circ}$ C. Fragment ions were analyzed over 30-500 m/z mass range in Scan mode. All GC/MS parameters were implemented using Class-5000 software. Mass spectrum analysis was performed in the electron impact ionization (EI) mode and in Scan mode. Mass spectra correlations were done using Wiley, NIST, Tutor library.

FTIR-ATR analysis: 45 $^{\circ}$ ZnSe-ATR equipment was used as well as KBr pellet technique. The IR measurements were performed on a Perkin-Elmer BX FTIR spectrometer in 4000-600 cm^{-1} region. For liquid substances, 20 μ L of samples (the essential oil and standard substances) were placed on the ATR crystal. For solid standards KBr pellet technique is used.

RESULTS AND DISCUSSION

Essential oils are complex mixtures of acyclic monoterpene alcohols; geraniol, citronellol and nerol and long-chain hydrocarbons like nonadecane, 1-nonadecene or heneicosane. The results obtained from GC-MS are given in Table-1 which shows percentage weight of the components of rose essential oil.

TABLE-1
CHEMICAL COMPOSITION OF ROSE ESSENTIAL OILS
FROM DIFFERENT REGION OF ISPARTA

Contents	Samples							
	Ratio (%)							
	1	2	3	4	5	6	7	8
Ethanol	0.69	0.74	0.33	-	-	-	-	1.20
Geranyl acetate	0.55	0.73	1.28	2.06	2.01	2.17	2.55	1.20
Citronellol	48.87	48.50	44.38	40.94	40.01	34.78	34.50	46.25
Nerol	4.65	6.01	8.17	7.17	6.79	11.44	10.87	7.74
Geraniol	10.05	13.08	17.86	17.32	16.93	24.61	24.23	17.54
Nonadecane	14.10	13.06	11.62	14.39	15.82	9.56	10.75	11.35
9-nonadecene	3.78	3.39	2.69	3.31	3.49	2.29	2.79	2.51
2-Phenyl ethanol	2.61	2.52	1.41	1.32	1.14	1.05	1.01	1.40
Methyl-Eugenol	2.13	2.68	2.33	2.23	2.28	1.71	1.81	2.19
Heneicosane	6.11	5.27	4.61	5.28	5.78	3.69	4.18	4.25
Eugenol	1.65	1.58	1.23	0.68	0.52	0.45	0.55	1.11
Eicosane	1.20	0.95	0.95	1.06	1.17	0.83	0.89	0.65

% ratio shows weight of contents over total weight of sample.

FT-IR spectra of 8 samples of essential oil are given in Fig. 1. They are almost the same in their characteristic wavenumbers. To identify the main components effects on essential oil, IR spectra of major constituents are given in Fig. 2. Molecular structures of major components are given in Fig. 3.

One of the main constituent of rose oil is citronellol (acyclic monoterpene) and it occurs naturally in many plant oils. In infrared spectroscopy, bands between 4000-3000 cm^{-1} assigned to the OH vibrations¹¹. OH vibrations observed at each monoterpene alcohol at this range. OH stretching vibration band occurs at 3324 cm^{-1} in citronellol, 3341 cm^{-1} in nerol and 3407 cm^{-1} for geraniol. FTIR spectral data of geraniol and citronellol had already been reported¹². In essential oil of rose, OH band is observed at 3332 cm^{-1} . Vibrational bands of standards and essential oil with their assignments are summarized in Table-2. The band at 2728 cm^{-1} of rose oil is the C-H stretching vibration belongs to aldehyde¹³ is observed in the same position of both citronellol and nerol, the result makes the band at 2728 cm^{-1} characteristic band for rose oil. The weak intense band at 1719 cm^{-1} of rose oil can be attributed to saturated C=O stretching vibration¹⁴. The band at 1450 cm^{-1} of rose oil indicated the presence of monoterpene alcohols; due to bands at 1449 cm^{-1} for geraniol, 1445 cm^{-1} for nerol, 1451 cm^{-1} for citronellol. For citronellol standard, there is a

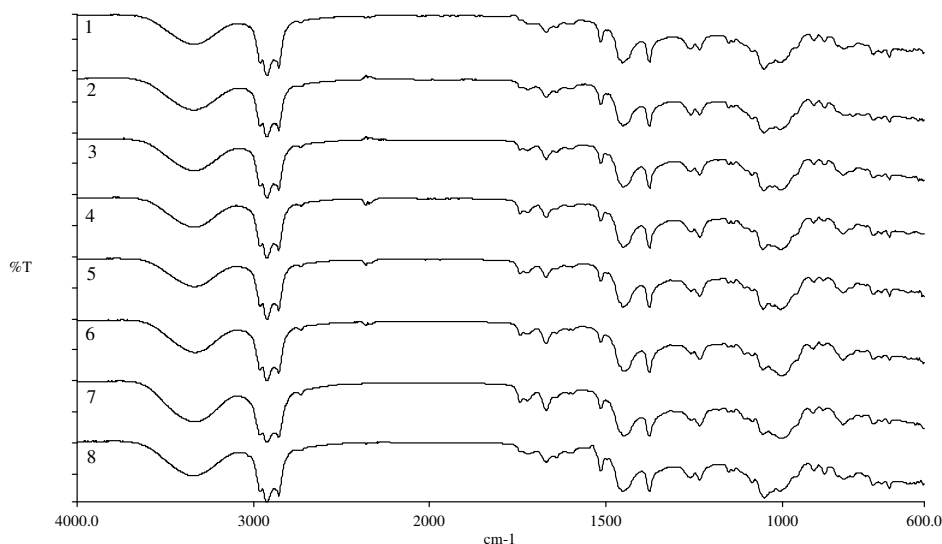


Fig. 1. FT-IR spectra of essential oil from different region of Isparta

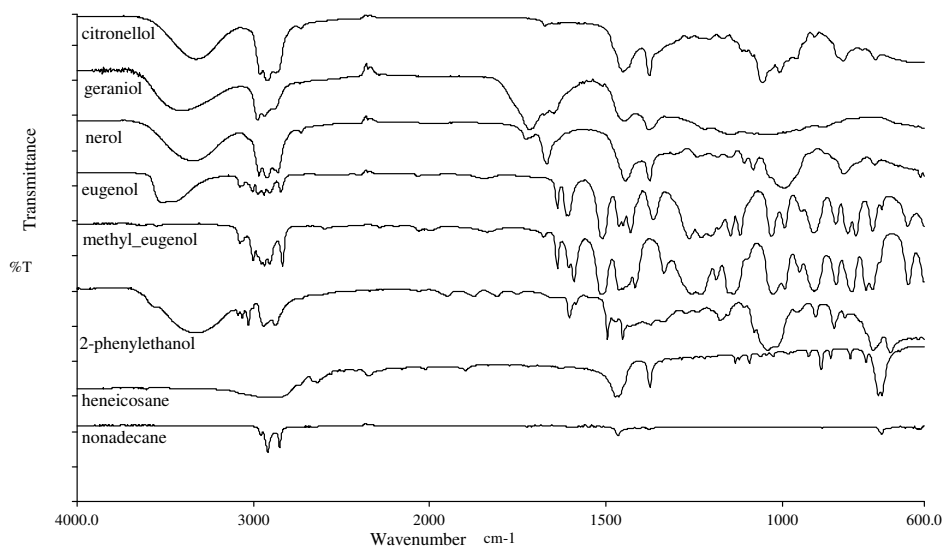


Fig. 2. IR spectra of standards

characteristic band at 1376 cm^{-1} which was assigned to C-O-H deformation band by Baranska¹⁵. The same band observed at 1376 cm^{-1} for nerol and 1377 cm^{-1} for geraniol. The band which is observed at 1376 cm^{-1} of rose oil can probably be the trace of monoterpene. The methylene rocking vibration appears¹⁶ at 720 cm^{-1} for rose oil. This band occurs in long-chain hydrocarbons at 719 cm^{-1} for nonadecane, 720 cm^{-1} for 1-nonadecene and 724 cm^{-1} for heneicosane. The band at 720 cm^{-1} for rose oil can be assigned to availability of long-chain molecules. There is no such a

band near 698 cm^{-1} in other standards except 2-phenyl ethanol, for this reason, the middle intense band at 698 cm^{-1} of rose oil may probably attributed to trace of 2-phenyl ethanol, due to 696 cm^{-1} band at 2-phenyl ethanol standard. One of most intense band at 698 cm^{-1} indicated mono-substituted phenyl bond.

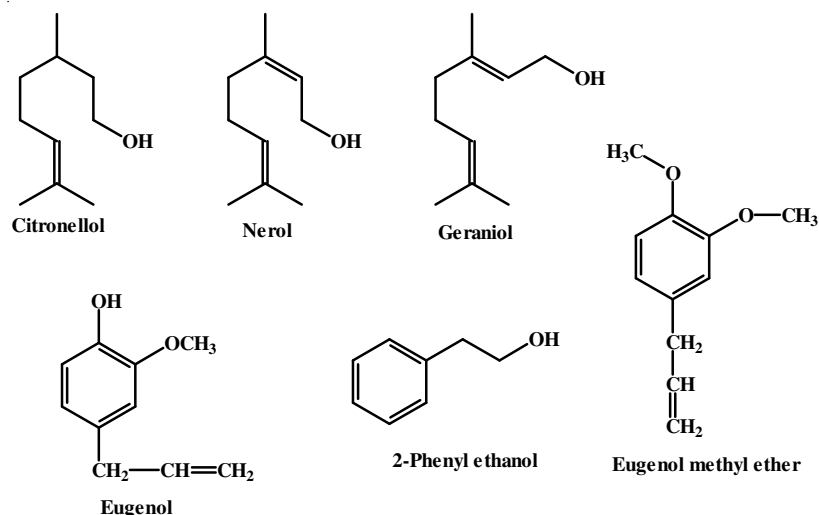


Fig. 3. Molecular structures of main substances detected in rose oils

TABLE-2
IR FREQUENCIES OF STANDARD SUBSTANCES AND
ROSE OIL AND THEIR ASSIGNMENTS

Citronellol	Nerol	Geraniol	Nona decane	Heneicosane	Methyl- eugenol	2- Phenyl ethanol	Eugenol	Rose oil	Assing- ment
3324	3341	3407	—	—	—	3325	3513	3332	$\nu(\text{OH})$
2961	2965	2973	2955	2958	2951		2974	2959	$\nu_{\text{as}}(\text{CH}_3)$
2914	2914	2934	2916	2919	2934	2941	2937	2922	$\nu_{\text{as}}(\text{CH}_2)$
2856	2857	2879	2848	2848	2832	2873	2841	2853	$\nu_{\text{s}}(\text{CH}_2)$
2728	2728							2728	$\nu_{\text{s}}(\text{C-H})$
	1726	1717	1725			1748		1741	$\nu(\text{C=O})$
								1719	$\nu(\text{C=O})$
1672	1667	1675			1677			1668	$\nu(\text{C=O})$
1451	1445	1449					1450	1452	$\delta_{\text{as}}(\text{CH}_3)$
1376	1376	1377						1376	$\delta(\text{C-O-H})$
1266					1257		1264	1261	$\delta(\text{C-C-O})$
	1240				1232		1230	1234	$\nu(\text{C=O})$
738	739	738						743	$\pi(\text{C-H})$
			719	724				721	$\rho_r(\text{CH}_2)$
						696		698	

where as = asymmetric, s = symmetric, ν = stretching, δ = in plane bending or deformation, ρ_r = rocking, π = out-of-plane bending) vibrations, respectively.

Both complementary spectroscopy techniques described in this study have the potential to replace existing standard procedures presently applied for quality control purposes. In particular, both methods can be used in the flavour, fragrance and pharmaceutical industries to perform fast quality checks of incoming raw materials and to continuously control distillation. Vibrational spectroscopy has proven to be a fast and reliable approach that is easy to learn and that requires minimal sample preparation and only small amounts of essential oils. For quality control purposes some new techniques, FTIR spectra present characteristic key bands of individual standards of rose oil and due to unique results of IR, it is suitable to recognize compounds of essential oil. Characterization of essential oil of roses from Isparta region by FTIR spectroscopy is an alternative way defining compounds.

REFERENCES

1. Y.S. Agaoglu, *Biotechnol. Biotechnol. Eq.*, **14**, 16 (2000).
2. K.G.D. Babu, B. Singh, V.P. Joshi and V. Singh, *Flav. Frag. J.*, **17**, 136 (2002).
3. M.Z. Özel and F. Gögüs, *Anal. Chim. Acta*, **566**, 172 (2006).
4. H. Baydar and N.G. Baydar, *Ind. Crop. Prod.*, **21**, 251 (2005).
5. M.H. Eikani, F. Golmohammad, S. Rowshanzamir and M. Mirza, *Flav. Fragr. J.*, **20**, 555 (2005).
6. M. Verma, B.B. Borse, G. Sulochanamma and B. Raghavan, *Flav. Frag. J.*, **20**, 122 (2005).
7. L. Jirovetz, G. Buchbauer, A. Stoyanova, A. Balinova, Z. Guangjiun and Ma. Xihan, *Flav. Frag. J.*, **20**, 7 (2005).
8. M.Z. Özel and A.A. Clifford, *Flav. Frag. J.*, **19**, 354 (2004).
9. S. Ercisli, *Genet. Resour. Crop Ev.*, **52**, 787 (2005).
10. A.O. Tucker and M. Maciarello, *Flavors and Fragrances: A World Perspective*, Elsevier, Amsterdam (1988).
11. N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, London (1964).
12. T. Chatterjee and D.K. Bhattacharyya, *J. Am. Oil Chem. Soc.*, **75**, 651 (1998).
13. R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley, New York (1991).
14. L.J. Bellamy, *Infrared Spectra of Complex Molecules*, Chapman & Hall, New York (1975).
15. M. Baranska, H. Schulz, S. Reitzenstein, U. Uhlemann, M.A. Strehle, H. Krüger, R. Quilitzsch, W. Foley and J. Popp, *Biopolymers*, **78**, 237 (2005).
16. B. Smith, *Infrared Spectral Interpretation, A Systematic Approach*. CRC Press, New York (1999).