

Qualitative Analysis of the Most Volatile Neutral Components of Reunion Geranium Oil (*Pelargonium roseum* Bourbon)

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The volatile constituents of geranium oil Bourbon were concentrated and separated by gas-liquid chromatography. Thirty-eight components were identified by comparison of their glc retention times, mass spectra, and infrared spectra with those of

authentic samples, namely nine formates, seven alcohols, seven aldehydes, ten ketones, three hydrocarbons, dimethyl sulfide, and furan. Most of them were not previously reported as constituents of geranium oil.

Over a hundred papers dealing with the chemical composition of geranium oil (*Pelargonium roseum*) have been issued since Gintl (1879) published the results of his investigation on this subject. These papers reported the presence of more than 100 constituents in geranium oils from various sources. Major components of the oil are citronellol, geraniol, linalool, citronellyl formate, geranyl formate, menthone, and isomenthone.

This paper describes the isolation and identification of relatively volatile neutral constituents of geranium oil comprising those compounds which elute from a gas chromatographic column packed with Porapak Q (a nonpolar polymer) before α -pinene. Although this volatile part only represents about 0.3% of the oil, its contribution must be considered particularly important for the typical top note of geranium oil. Only a few workers investigated this part of the oil. Volatile carbonyls and alcohols were reported by Bohnsack (1942), Alder and Schmidt (1961), Peyron (1962a,b), and Wellendorf (1963). Dimethyl sulfide was first identified by Schimmel (1909), and has also been detected by Peyron (1962b). In a recent publication Kami *et al.* (1969) described the chromatographic analysis of volatiles collected from escaping vapors during steam distillation of certain crops of *Pelargonium roseum* Bourbon.

Initially we attempted to identify the volatile components by headspace gas chromatography on columns of different polarity. Difficulties were encountered due to the complexity of the headspace samples. Separation of the volatile fraction from the oil by stripping with helium (according to Nelson and Hoff, 1968) proved unsatisfactory. The collection of an amount of concentrate sufficient for analysis by coupled gas chromatography-mass spectrometry and other spectral techniques required (ir, etc.) appeared to be very time-consuming.

The geranium volatiles could be concentrated more efficiently by using a technique described by Honkanen and Karvonen (1966). Those authors used a low temperature vacuum distillation with carbon dioxide and solvent vapor as carrier gases to isolate volatiles from molten fat. Solid

carbon dioxide mixed with solvent served as a source for the gaseous carrier.

The stripping gases were condensed together with the oil volatiles in a collection flask, cooled in liquid nitrogen. In our experiments it proved to be advantageous to omit the addition of solvent to the solid CO₂, thus avoiding loss of volatiles during evaporation of the solvent. The collected geranium volatiles—still containing undesired terpenes—were further concentrated by spinning band distillation. The whole procedure for the analysis of the volatile part of geranium oil is given schematically in Figure 1.

EXPERIMENTAL

Isolation of the Volatiles from Geranium Oil. The volatile part of geranium oil was concentrated according to the method described by Honkanen and Karvonen (1966). The apparatus used is given in Figure 2.

The reservoir (A) was filled with 300 g of solid carbon dioxide which was evaporated at a pressure of 5 mm of mercury. The gaseous CO₂ was passed at a rate of 100 g of CO₂ per hour through a flask containing 200 ml of geranium oil at a temperature of -20° C. After passage through the oil, the stripping gas, together with the geranium volatiles, was condensed in a liquid nitrogen trap (B). After completion of the distillation the condensed CO₂ was allowed to evaporate at atmospheric pressure. The remaining concentrate of the volatiles of geranium oil (about 5 ml) still contained many high boiling substances.

The most volatile compounds were distilled off in a spinning band distillation apparatus. The distillation was carried out at atmospheric pressure in an inert atmosphere. The head temperature did not exceed 100° C. Three fractions (each about 100 mg) were obtained. Only the first one did not contain any relatively high boiling compounds (*e.g.*, terpenes).

Combination Gas Chromatography-Mass Spectrometry. The fractions obtained by spinning band distillation were analyzed in a combined gas chromatograph-mass spectrometer. The gas chromatograph, a Varian Aerograph Model 1220, was equipped with a 100-m Ucon LB 550X-coated cupronickel capillary of 0.01 in. i.d. and a 1-60 inlet splitter. The column was operated at a temperature of 70° C and a helium flow of 0.9 ml/min.

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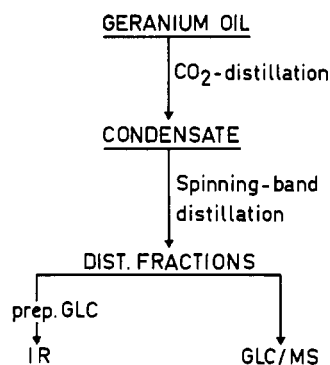


Figure 1. Procedure for the analysis of volatiles from geranium oil

The outlet of the column was admitted directly to the inlet of a single focusing 90° magnetic sector field mass spectrometer (Varian-MAT, CH5, Bremen, Germany). The total ionization current obtained from the ionization chamber working at 20 eV was recorded. The mass spectra were obtained from the material entering the other ionization chamber operating at 70 eV.

The mass spectra and retention volumes of the geranium volatiles were compared with those of authentic reference materials examined under identical conditions.

Preparative Gas Chromatography. The spinning band distillation fractions were separated with a F&M Model 810 gas chromatograph equipped with two flame ionization detectors and a 6 to 1 effluent splitter to permit collection. The distillates were first chromatographed on a 2 m × 1/8 in. o.d. stainless steel column packed with Porapak Q. The temperature was programmed from 100–200° C at a rate of 2° C/min with a helium carrier gas flow of 40 ml/min.

Unresolved components were rechromatographed on a 4 m × 1/8 in. o.d. column packed with 20% Carbowax 400 on 60–80 mesh Embacel support at a temperature of 50° C and a helium flow rate of 30 ml/min. In some cases a 2 m × 1/8 in. o.d. column packed with 25% tricyanoethoxypropane on 60–80 mesh Embacel support at a temperature of 40° C and a helium flow rate of 40 ml/min was utilized.

The components were collected in U-shaped glass capillaries with an internal diameter of 0.03 in., cooled with liquid nitrogen. After the collection of an individual component the trap was immediately sealed at both ends in order to prevent loss by evaporation. The trapping efficiency of the traps was tested with ether, methyl formate, and acetone. Almost quantitative recoveries were achieved.

Infrared Spectra. The sealed U-shaped traps were first immersed in liquid nitrogen in order to condense the individual volatile components completely. After a few minutes the trap was cooled with a solid carbon dioxide-

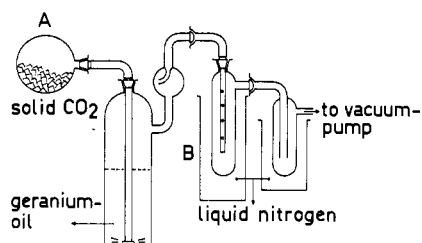


Figure 2. Apparatus used for the distillation of geranium oil with carbon dioxide. (A) reservoir filled with solid CO₂; (B) liquid nitrogen trap for condensing the CO₂ + the geranium volatiles

2-propanol mixture, maintained at -80° C. Subsequently the trap was unsealed at both ends and rinsed with 2 μl of carbon disulfide. This solution was transferred into an ultramicro cavity cell with a path length of 0.5 mm and compensated against pure carbon disulfide.

The spectra were recorded on a Perkin-Elmer Model 137 Infracord fitted with a 4 × beam condenser and a beam attenuator.

RESULTS AND DISCUSSION

In Figure 3 the degree of concentration of the volatiles of geranium oil Bourbon is clearly demonstrated. It shows the first part of the gas chromatograms of the original oil and of the CO₂ distillate and the gas chromatogram of the first fraction of the spinning band distillation obtained under identical gas chromatographic conditions on Porapak Q. In the stripping procedure a better yield of concentrate was obtained without the addition of solvent to the solid carbon dioxide in the reservoir (see Figure 2). We found that losses occurred during careful evaporation of solvents even with a low boiling one like ethyl chloride. Also, introduction of impurities from the solvent was avoided in this way. The solid carbon dioxide used did not contain any volatile contaminations.

Table I. Volatiles Identified in Geranium Oil

Compound	Method of identification			Previously reported by ^a
	glc	ms	ir	
1,3-Pentadiene	+	+		
Isoprene	+	+		
Toluene	+	+	+	
Furan	+	+		
Methanol	+			3
Ethanol	+	+	+	2, 3, 4, 5, 7,
2-Propanol	+	+	+	
2-Methyl-1-propanol			+	
2-Methyl-1-butanol	+		+	
3-Methyl-1-butanol	+		+	2, 4, 5
2-Methyl-3-buten-2-ol	+	+		
Ethanal	+	+		1, 3, 4
2-Methyl-1-propanal	+	+	+	3
2-Methyl-1-butanal	+	+	+	
3-Methyl-1-butanal	+	+	+	1, 3, 4
<i>trans</i> -2-Methyl-2-butenal	+	+	+	
3-Methyl-2-butenal		+	+	
2-Furaldehyde	+	+	+	4
Acetone	+	+	+	1, 3
2-Butanone	+	+	+	
2-Pentanone	+		+	
3-Methyl-2-butanone		+	+	
2-Hexanone	+		+	
4-Methyl-2-pentanone		+	+	
2-Methyl-3-pentanone		+	+	
4-Methyl-3-penten-2-one	+		+	
2-Methylcyclopentanone	+		+	
3-Methylcyclopentanone	+	+	+	
Methyl formate	+	+	+	3
Ethyl formate	+	+	+	
Propyl formate	+		+	
Isopropyl formate	+	+	+	
<i>n</i> -Butyl formate	+	+	+	
2-Methylpropyl formate	+	+	+	
2-Methylbutyl formate	+	+	+	
3-Methylbutyl formate	+	+	+	
<i>n</i> -Hexyl formate	+		+	
Dimethyl sulfide	+	+	+	3, 5, 6

^a (1) Alder *et al.* (1961); (2) Bohnsack (1942); (3) Kami *et al.* (1969); (4) Peyron (1962a); (5) Peyron (1962b); (6) Schimmel (1909); (7) Wellendorf (1963).

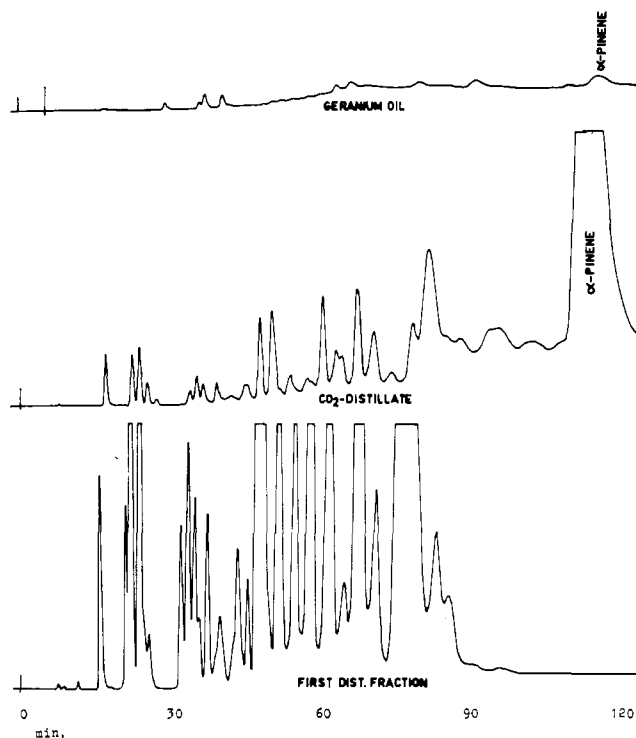


Figure 3. Gas chromatograms showing concentration of the volatiles of geranium oil. Top: Geranium oil Bourbon up to and including α -pinene. Middle: CO_2 distillate up to and including α -pinene. Bottom: First fraction obtained by spinning band distillation of the CO_2 distillate

It was desirable to eliminate the monoterpene hydrocarbons from the concentrate because they interfere with the analysis of the volatiles on polar column packings. This could be achieved by means of spinning band distillation. As can be seen in Figure 3, the first distillation fraction does not contain α -pinene, which is one of the first eluting terpenic compounds.

Identification on the basis of glc-ms alone was not possible in all cases. Infrared spectra provided complementary information.

The compounds identified in this study are listed in Table

I; 38 volatile components have been identified of which 28 have not previously been reported to be present in geranium oil. Except methanol every constituent has been identified by at least one spectrometric method. Acetone and dimethyl sulfide represent rather large percentages of the volatile fraction. It is noteworthy that no other esters except formates have been found. Kami *et al.* (1969) reported the presence of methyl formate in steam volatiles. Its presence could be confirmed. In addition, eight other low boiling formates were found. Another feature of the geranium oil is the large number of volatile carbonyl compounds present. Of these, three aldehydes and nine ketones were identified for the first time. Seven lower alcohols were detected. Methanol, ethanol, and 3-methyl-1-butanol were reported before.

The volatile fraction contains three hydrocarbons. Their appearance in geranium oil was not known previously. With infrared analysis several furans could be classified. At present, only evidence could be obtained for the presence of furan and 2-furaldehyde. Further work is in progress to provide additional structural proof for the other furan derivatives. Only 2-furaldehyde has previously been identified in geranium oil from Morocco (Peyron, 1962a).

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LITERATURE CITED

- Alder, E., Schmidt, W., *Militzer Ber.* 121 (1961).
 Bohnsack, H., *Ber.* 75B, 502 (1942).
 Gintl, W., *Jahresber. Chemie* 941 (1879).
 Honkanen, E., Karvonen, P., *Acta Chem. Scand.* 20, 2626 (1966).
 Kami, T., Otaishi, S., Hayashi, S., Matsuura, T., *Agr. Biol. Chem.* 33, 502 (1969).
 Nelson, P. E., Hoff, J. E., *Food Technol.* 22, 1395 (1968).
 Peyron, L., *Compt. Rend.* 255, 2981 (1962a).
 Peyron, L., *Parfum. Cosmet. Savons* 5, 270 (1962b).
 Schimmel *Ber.* 50 (April 1909).
 Wellendorf, M., *Dan. Tidsskr. Farm.* 37, 145 (1963).

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