Characterization of lavandin Abrialis, Super, and Grosso by GC-MS

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Lavender oil may be imported into the U.S. free of duty, while lavandin oil is subject to duty and artificial mixtures, which include adulterated oils, are assessed a higher rate of duty.[4] It is necessary, therefore, that an analytical method be available by which these oils may be identified correctly.

Comparative studies of these oils described in the literature usually stress differences in some physicochemical constants and concentrations of a few major components, especially linalool, linalyl acetate, camphor and 1,8-cineole.[2-6] It was believed that for Customs purposes a more detailed characterization was required, and concentration ranges were established for components present to the extent of more than 0.5% in these oils.[7] Glass capillary gas chromatography was found to be a suitable method of analysis, and mass spectrometry of the separated components aided in their identification.

During the course of that work about twenty lavandin oils were used, both reference samples obtained from perfume companies and commercial samples submitted to Customs on importation. All of these samples were labelled lavandin Abrialis. For the past few years, because of the decline of lavandin Abrialis,[8] two other hybrids, Grosso and Super, have also been submitted to this laboratory upon importation. It was necessary to be sure that these newly received lavandin hybrids could also be correctly classified and that the gas chromatographic procedure[7] was adequate for this purpose.

Steltencamp and Casazza analyzed ten samples of lavandin Abrialis and five of lavandin Super and presented averages and ranges for five components, only three of which, linalool, camphor and linalyl acetate, were present to the extent of 0.5% or more on the average in these samples.[9] Martin and Zola also analyzed these two hybrids and presented average concentration values for a large number of components that accounted for over 95% of the composition of the samples.[10] Since no information was given concerning the number of samples analyzed or the concentration ranges encountered for the components of the oils, the data do not provide a sufficient basis for characterizing the oils of interest. Subsequently Zola and Le Vanda presented somewhat different data for these oils and also analyzed three lavandin Grosso samples.[11] Again only average concentrations were listed for the components of the three hybrids, but the authors stated that they can be differentiated on the basis on linalyl acetate, terpineol-4 and trans-ocimene plus octanone-3 concentrations. Recently Bruns presented concentrations ranges and averages for seven components of these three different lavandins and found that they could be distinguished on the basis of 1,8-cineole, camphor and linalyl acetate content.[12] Moutet showed that for lavandin Abrialis and Grosso the concentration ranges differed for linalyl acetate, ocimene, and terpineol-4.[8]

Recently four samples labeled lavandin Abrialis analyzed in this laboratory were found to be adulterated on the basis of a detailed GC analysis. Three of the samples contained inordinately large amounts of limonene and/or pinenes. Adulteration of these oils could not have been recognized if only linalool, linalyl acetate, camphor and 1,8-cineole concentrations had been determined. In addition, nine samples labeled lavender but judged to be mixtures generally contained the expected amount of linalool, but camphor

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and 1,8-cineole concentrations were intermediate between the observed ranges for lavender and lavandin oils. Concentrations of some other components including cis β-ocimene, borneol, and terpineol-4 plus β-caryophyllene were much better indicators of adulteration. Therefore, it seemed advisable that the concentration ranges of all components present to the extent of at least 0.5% in lavandin Super and Grosso be determined to assure that these oils could be correctly identified.

Experimental

The experimental procedure was identical to that previously used.[7] The work was performed with a Perkin-Elmer Model 3920 gas chromatograph equipped with a flame ionization detector and splitting injector providing a split ratio of 30:1. A 33 meter by 0.5 mm i.d. Scott glass capillary column containing Carbowax 20M stationary phase was operated for 4 minutes at an initial temperature of 60°C and was then programmed at 2°C/min to 200°C where it was held for 32 minutes to complete an experiment. The injector was maintained at 225°C and the detector at 250°C. Flow rates used were 19 ml/min for the helium carrier gas (as specified by the column manufacturer) and the flame of the detector was maintained with 40 ml/min hydrogen and 550 ml/min air. Quantitative determination of the eluted components was achieved with a Hewlett-Packard Model 3352B Laboratory Data System.

Most major components could be identified by mass spectrometry with a Hitachi-Perkin-Elmer Model RMU-6L, single focus low resolution instrument, which was coupled to the gas chromatograph with a jet separator. The operating parameters for the spectrometer were: ionization voltage 70 eV, source temperature 200°C, interface 250°C, target current 50 ua and accelerating voltage 3200 V.

To characterize the three hybrids, reference samples obtained from perfume companies were used as well as samples from importations submitted for Customs examination. To aid in the mass spectrometric identification of the separated components, samples of these compounds were obtained from various perfume companies and laboratory supply houses and their spectra were recorded. Published compilations of spectral data were also used.[13-15]

For each oil and reference compound 0.2 ul sample was injected directly into the gas chromatograph. Retention times of the eluted peaks were measured relative to that of linalool=1. Peak areas were recorded for components present to the extent of 0.1% or more.

Results and discussion

Lavandin Abrialis, Super, and Grosso were found to contain the same major components. The general features of the chromatograms were, therefore, the same and a typical chromatogram for a lavandin Abrialis oil is shown in figure 1. About fifteen compounds which were present in one or more of these hybrids to the

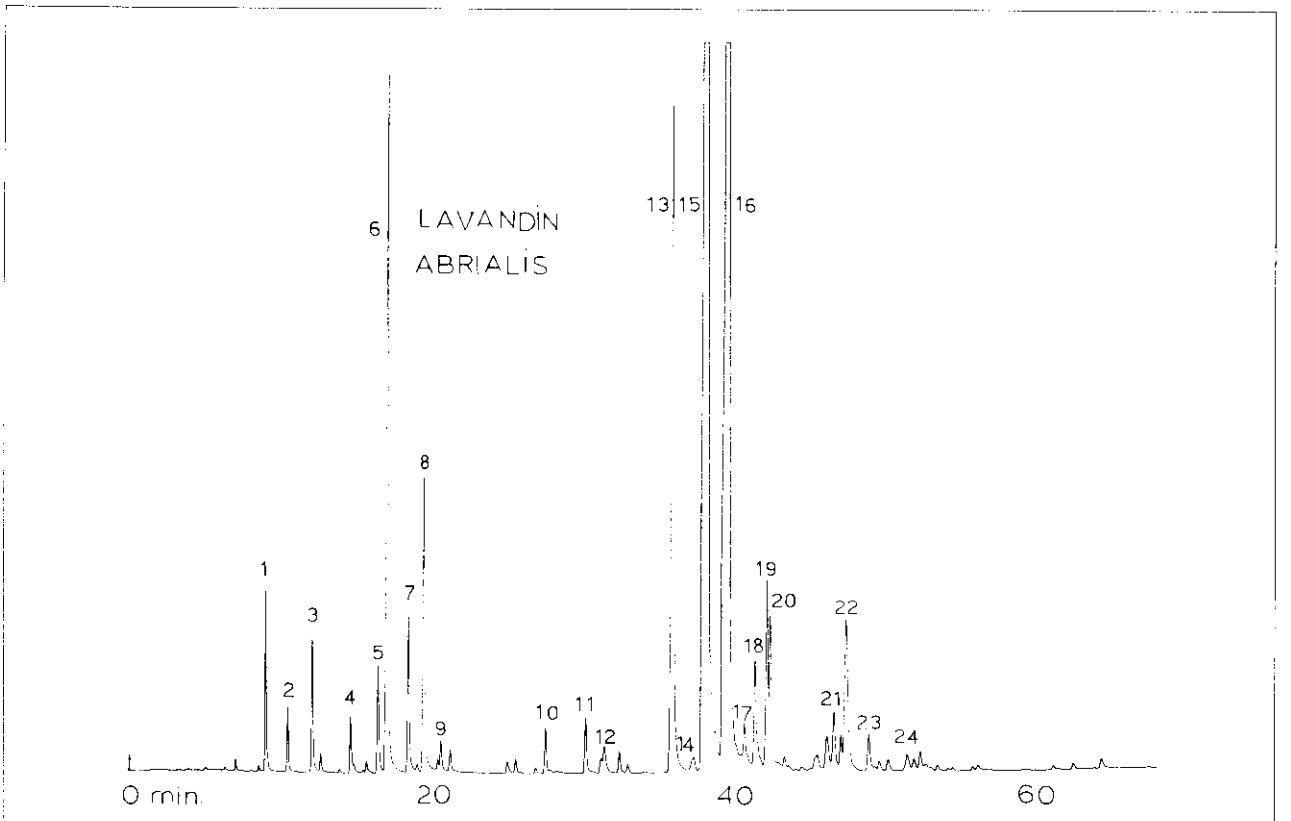

Figure 1. Chromatogram of lavandin Abrialis. (The peak numbers correspond to those of Table 1.)

extent of at least 0.7%. The concentrations of these components fell into fairly narrow ranges, which were often characteristic of the hybrid. There were about a dozen additional components at concentrations of 0.1-0.6% common to these oils. Because of the sample to sample concentration variation only a few of these minor components were useful for oil identification. Table 1 shows concentration ranges for each hybrid and averages for the important components. These compounds account for 97% on the average of the composition of these oils. These data were obtained with twenty-six samples of lavandin Abrialis, ten of Super and nine of Grosso. Only ten component concentrations have been excluded, because these fell outside the ranges shown by more than 30%. In addition to all these data, only one sample exhibited one additional peak corresponding to a concentration greater than 1.0%. Peak identification is provided in Table 1 for those components that could be analyzed by mass spectrometry.

The chromatographic separation of terpineol-4 and β-caryophyllene was accomplished in only about two thirds of the samples analyzed. Since the terpineol-4, but not the β-caryophyllene concentrations appeared to be useful for characterizing the hybrids, in Table 1 are given terpineol-4 data for those samples for which it was obtained, as well as combined terpineol-4 plus β-caryophyllene results for all samples. For only 40% of the samples were α-terpineol and borneol separated. Since both of these compounds appeared to be

Table 1. % Concentrations of Important Components of Lavandin Oils

Peak[a]	Rel. Ret. Time	Abrialis Av.	Abrialis Range	Super Av.	Super Range	Grosso Av.	Grosso Range	Identity
1	0.22	0.8	0.5-1.3	0.4	0.2-0.5	0.6	0.5-0.7	α-pinene
2	0.26	0.5	0.4-0.7	0.3	0.0-0.4	0.3	0.3-0.4	camphene
3	0.29	0.6	0.3-1.0	0.2	0.0-0.6	0.4	0.4-0.5	β-pinene
4	0.36	0.5	0.3-0.6	0.5	0.2-0.5	0.5	0.4-0.7	myrcene
5	0.40	1.0	0.6-1.3	0.9	0.7-1.1	0.8	0.6-1.1	limonene
6	0.42	7.4	5.2-9.4	3.6	3.7-4.2	5.2	4.2-5.9	1,8-cineole
7	0.45	1.5	0.9-2.3	1.3	1.1-1.7	0.9	0.7-1.0	cis β-ocimene
8	0.48	2.7	1.4-4.2	1.6	0.8-2.2	0.4	0.2-0.7	trans β-ocimene
9	0.52	0.2	0.0-0.4	0.6	0.5-0.7	0.2	0.1-0.4	p-cymene
10	0.70	0.4	0.2-0.7	0.4	0.2-0.5	0.4	0.3-0.4	
11	0.78	0.4	0.2-0.6	0.6	0.5-0.8	0.2	0.0-0.4	
12	0.82	0.4	0.0-0.7	0.2	0.0-0.6	0.2	0.0-0.5	
13	0.92	8.7	7.9-9.7	5.6	4.9-6.9	6.9	6.3-7.6	camphor
14	0.97	0.3	0.0-0.6	0.2	0.0-0.5	0.1	0.0-0.1	
15	1.00	34	30-38	31	27-34	30	27-32	linalool
16	1.04	28	19-33	42	40-47	35	30-37	linalyl acetate
17	1.07	0.8	0.4-1.6	0.3	0.0-0.5	0.9	0.6-1.5	
18	1.09[b]	1.2	0.4-1.8	0.6	0.4-1.0	3.3	2.7-3.9	terpineol-4
19	1.09-1.11	3.2	2.3-4.2	2.6	1.7-2.3	4.9	4.2-5.4	terpineol-4 plus β-caryophyllene
20	1.13	1.6	1.0-2.4	1.5	1.4-1.6	2.6	2.2-3.0	lavandulyl acetate
21	1.23	0.7	0.0-1.2	0.7	0.0-1.2	0.8	0.2-1.5	lavandulol
22	1.25-1.26	3.2	2.6-4.0	2.4	2.1-3.2	3.0	1.9-4.1	α-terpineol plus borneol
23	1.29	0.3	0.0-0.6	0.4	0.0-0.8	1.1	0.7-1.4	
24	1.34	0.2	0.0-0.3	0.2	0.0-0.4	0.5	0.3-0.7	

[a]Peak numbers are the same as in Figure 1

[b]Data for 20 samples of lavandin Abrialis, 4 of lavandin Super and 8 of lavandin Grosso

present in similar amounts in all types of lavandins, only the sum of the concentrations of these components is shown in Table 1. For those samples for which a separation was achieved, α-terpineol contributed less than 20% to the area under the peaks of the two components.

There were about a dozen distinguishing features which aided in the identification of the hybrids. Identification of a particular sample is most reliable if it is based on all of these components, rather than only one or a few of them. Lavandin Super samples contained much less of the three early eluting hydrocarbons, α-pinene, camphene, and β-pinene, than Grosso and Abrialis: 0.6% compared to 1.4 and 1.7% respectively on the average. No lavandin Super sample contained as much of these components as any of the other lavandin samples analyzed. Lavandin Super samples were also found to contain less 1,8-cineole than any of the other samples. On average, they contained 3.6% compared to 5.2% for Grosso and 7.4% for Abrialis. Only two of the twenty-six Abrialis samples contained less than 6%, while no other hybrids contained that much.

Lavandin Grosso samples has less cis β-ocimene and also trans β-ocimene than the other hybrids, while Abrialis samples contained the most of these components. Only two of the twenty-six samples contained less than 2% trans β-ocimene, while only one of the Super and none of the Grosso samples had that much.

Lavandin Super samples contained more p-cymene than any of the others. On average, this hybrid also exhibited more of the component with RRT=0.78 than any of the other oils. Only three Abrialis samples contained as much as any of the Super samples of the latter component. On the other hand, lavandin Super contained less camphor on the average than any of the other hybrids. All Super samples had a lower camphor content than any Abrialis sample. Only one Super sample contained more than 6.0% camphor, while all other hybrids analyzed contained more than that.

The most abundant component of all lavandin Super and Grosso samples was linalyl acetate, while all but two of the twenty-six lavandin Abrialis samples tested contained more linalool than linalyl acetate. All lavandin Super samples contained more linalyl acetate than any of the other samples. The lavandin Abrialis oils contained the least of this component on average, and in all but two samples less was found than in any lavandin Grosso sample.

Lavandin Super samples showed the lowest amounts of the component with RRT=1.07. They contained less than all lavandin Grosso, and less than all but four Abrialis samples.

Adequate separation of terpineol-4 and β-caryophyllene was achieved for twenty Abrialis, four Super and eight Grosso samples. It was observed that the Grosso samples contained more terpineol-4 than any of the others. This hybrid also contained more lavandulyl acetate than the other oils on average. All Grosso samples contained more lavandulyl acetate than any Super and all but two Abrialis samples investigated. Finally, the component with RRT=1.29 also was present in larger amounts in lavandin Grosso than in the other oils. None of the Abrialis and only two of the Super samples contained as much of this compound as any of the Grosso samples.

Tables 2, 3, and 4 list the percent concentrations of

Table 3. Composition of Lavandin Abrialis Oils

Sample	Relative Retention Time														
	0.92	0.96	0.97	0.98	0.99	1.00	1.03	1.07	1.09	1.11	1.15	1.25	1.27	1.29	Sum
1	1.3	2.5	9.5	9.2	5.7	8.7	39.8	26.9	6.9	1.1	1.7	1.5	0.6	1.1	91.8
2	0.4	0.9	9.3	1.5	9.3	8.0	2.7	5.9	6.8	1.3	2.0	2.0	0.6	1.0	0.0	95.9
3	0.9	2.0	5.8	1.0	1.0	7.9	38.8	23.1	1.3	1.7	2.3	2.5	0.3	2.4	0.0	95.6
4	0.7	1.1	5.0	0.9	1.2	8.1	32.1	27.7	1.6	1.7	1.9	2.4	0.4	1.5	0.0	92.9
5	0.8	0.9	7.6	1.3	1.3	9.0	27.9	25.3	1.9	0.8	2.3	1.4	1.8	2.4	0.0	97.6
6	1.6	1.9	9.4	1.5	2.8	9.4	9.7	18.6	9.4	2.2		1.0	0.7	1.4	0.0	98.8
7	1.3	1.6	7.4	2.1	2.8	8.5	9.1	27.3	7.5	2.2		1.4	1.1	1.6	0.0	95.1
8	1.8	2.3	6.8	1.8	2.7	8.4	11.2	20.9	6.4	2.0		1.4	1.3	2.0	0.5	98.9
9	1.8	1.7	7.5	1.7	3.2	9.7	31.2	28.8	6.9	0.7	2.7	1.4	0.8	2.8	0.5	96.4
10	1.3	0.9	4.7	1.4	0.7	8.7	27.3	27.5	0.7	1.4	1.8	1.6	0.8	2.0	0.5	91.8
11	0.7	1.0	7.3	1.7	4.7	8.9	14.1	27.6	6.7	1.2	1.9	1.3	1.0	2.7	0.5	92.8
12	0.3	0.8	8.6	1.8	2.9	8.7	23.9	26.5	0.6	0.2	2.6	1.0	1.0	2.8	0.4	93.3
13	0.7	1.1	8.6	1.5	2.7	8.9	23.3	25.3	0.5	1.8	2.1	1.1	1.3	3.1	0.5	92.9
14	0.8	0.7	6.3	1.6	2.9	8.1	28.5	27.0	1.0	1.4	1.8	1.6	0.7	2.4	0.0	98.4

components present to the extent of at least 0.7% on the average in one of the hybrids for all samples tested of lavandin Super and Grosso and representative samples (fourteen of twenty-six) of lavandin Abrialis. These peaks account for 90.8-96.4%, average 93.6%, of the composition of the twenty-six lavandin Abrialis oils analyzed. The concentration data for these samples, all from France, are very similar to those for the lavandin Abrialis samples previously analyzed.[7] For components present to the extent of at least 1%, the average concentrations reported in Table 1 are well within 10% of those previously examined, except for the combined peak obtained for α-terpineol and borneol. Two of the samples are suspected of being adulterated. Sample 1 contained an inordinately large amount of limonene, 2.5%. In forty-three other lavandin Abrialis samples the highest limonene concentration found was 1.4%, and the average for all the samples was 1.1%. This sample also contained unusually large amounts of the component with RRT=1.29. Sample 6 of Table 2 contained excessive quantities of cis β-ocimene and α-terpineol plus borneol. The cis β-ocimene content of 3.5% is 2½ times the average amount found in other samples and about 50% greater than the largest concentration observed.

Nine of the ten lavandin Super samples originated in France. The data given in Table 3 account for 91.2-97.3%, average 94.3%, of the sample composition. Sample 6 was imported from Argentina and showed no distinguishing features. The most unusual sample was number 8 which contained relatively large quantities of α-and β-pinene, 0.9% and 0.6% respectively, compared to average concentrations 0.4% and 0.2% for this hybrid.

All lavandin Grosso samples came from France. Percent concentrations for the components listed in

Table 3. % Composition of Lavandin Super Oils

Sample	Relative Retention Time														Sum
	0.22	0.40	0.42	0.45	0.48	0.93	1.00	1.04	1.07	1.09	1.11	1.13	1.23	1.26	1.29	
1	0.5	1.1	3.7	1.1	1.6	6.0	34.2	42.1	0.0	2.1		1.4	0.7	2.5	0.3	97.3
2	0.4	0.9	3.7	1.2	1.9	5.7	29.4	45.2	0.5	2.0		1.5	0.8	2.3	0.4	95.9
3	0.4	0.8	3.7	1.2	1.9	5.3	30.4	43.5	0.0	0.4	1.3	1.8	0.3	2.2	0.0	94.2
4	0.2	0.7	2.7	1.7	1.2	4.9	26.9	46.7	0.0	1.8		1.7	1.2	2.2	0.8	92.7
5	0.3	0.7	3.3	1.1	1.0	5.3	31.4	44.7	0.0	2.3		1.5	1.0	2.2	0.5	95.3
6	0.3	0.7	3.0	1.5	1.6	5.5	32.2	41.6	0.4	2.1		1.6	1.2	2.6	0.6	94.9
7	0.4	1.1	4.2	0.0	0.8	6.9	31.9	40.3	0.4	0.7		1.4	0.5	2.6	0.0	91.2
8	0.9	0.8	4.2	1.2	1.4	5.9	32.6	40.0	0.0	1.0	1.3	1.6	0.0	2.1	0.8	93.9
9	0.5	1.0	3.7	1.1	1.9	5.6	33.3	40.2	0.5	0.5	1.6	1.4	0.8	2.2	0.3	94.7
10	0.3	0.9	4.0	1.3	2.2	5.3	31.3	40.4	0.3	0.4	1.5	1.5	0.9	2.3	0.5	93.1

Table 4. % Composition of Lavandin Grosso Oils

Sample	Relative Retention Time														Sum
	0.22	0.40	0.42	0.45	0.48	0.93	1.00	1.04	1.07	1.09	1.11	1.13	1.23	1.26	1.29	
1	0.7	0.7	4.5	0.9	0.3	6.3	30.5	36.2	0.9	4.7		2.2	1.5	2.8	0.7	92.9
2	0.5	1.6	5.6	1.0	0.7	7.6	31.0	31.8	1.2	1.5	2.7	2.4	1.4	3.9	1.0	93.9
3	0.7	1.1	4.3	0.7	0.3	7.0	29.0	37.2	1.5	3.2	1.8	2.5	0.2	1.9	1.4	92.8
4	0.6	0.6	5.9	0.9	0.4	6.8	29.9	36.1		3.7	1.6	2.7	0.2	2.5	1.4	93.3
5	0.2	0.8	5.0	0.9	0.3	7.1	31.6	36.3		3.4	1.5	2.5	0.2	2.6	1.2	93.6
6	0.5	0.6	5.6	0.8	0.5	7.0	31.3	34.1		3.9	1.5	2.8	0.3	2.9	1.3	93.1
7	0.6	0.7	5.7	0.9	0.6	6.9	30.3	34.3	0.7	3.3	1.9	2.4	1.4	2.5	0.7	92.9
8	0.6	0.6	5.5	0.9	0.2	6.7	29.5	33.9	0.6	2.8	1.6	3.0	1.4	3.1	0.8	91.2
9	0.6	0.6	4.7	0.8	0.3	6.9	27.8	37.2	0.7	2.7	1.5	2.8	0.6	4.1	0.0	91.3

Table 4 represent 91.2-93.9%, average 92.8%, of the composition of the nine samples studied. Sample 2 differed somewhat from the others in that it contained somewhat more limonene, 1.6%, than all except one of the other lavandin oils analyzed. This sample also contained 2.1% of a component with RRT=1.41, while all other samples contained less than 1% of that compound.

Detailed quantitative GC analysis has previously served well in distinguishing between lavandin Abrialis and lavender oils.[7] Lavender oils contain larger amounts of linalyl acetate, terpineol-4 plus β-caryophyllene, cis β-ocimene, and the unidentified component with RRT=0.70. Lavandin Abrialis contains more 1,8-cineole and camphor.

Since lavandin Super and Grosso contain more linalyl acetate than Abrialis the former hybrids will be more difficult to distinguish from lavender oil on the basis of this component. On the other hand, lavandin Super and Grosso can be distinguished more easily from lavender oil on the basis of cis β-ocimene and the component with RRT=0.70. On the basis of terpineol-4 plus β-caryophyllene it will not be possible to distinguish between lavender oil and lavandin Grosso, but it will be easier to distinguish between lavender and lavandin Super. Camphor and 1,8-cineole concentrations will still aid in the identification of these oils. Trans β-ocimene concentrations should facilitate identification of lavandin Grosso and the component with RRT=1.07 in the identification of lavandin Super. Therefore, each of these oils should be readily identifiable on the basis of this quantitative GC-MS procedure.

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