# Composition of the Essential Oil of Lavandin

Robert J. Steltenkamp and William T. Casazza

Forty-eight components of lavandin oil have been isolated through gas chromatographic collection techniques and identified through infrared and mass spectroscopy. Twenty-two of these components had not previously been reported. The percentage composition of these components was estimated through gas chromatographic analysis of the original oil and of the various chromatographic fractions. A comparison of several varieties of lavandin oil and of true lavender oil indicated sizable quantitative differences in linalool, camphor, and linalyl acetate. Many commercial samples of lavandin oil were adulterated with terpenes, 3,5,5-trimethylhexanol, and the corresponding acetate.

avandin oil is an essential oil which is important in the perfumery of a wide variety of household products because of its fresh and herbaceous odor and its availability. This oil is produced commercially in Southern France where it is steam-distilled from the flowers and stalks of the small shrub harvested at full bloom (Guenther, 1949). The lavandin plant (Lavandula hybrida, Reverchon) is a cross between spike lavender (Lavandula latifolia, Villars) and true lavender (Lavandula officinalis, Chaix) (Vinot and Bouscary, 1964). This hybrid furnishes an oil which is harsher and more herbaceous in odor than true lavender. The plant, however, is hardier and more resistant to disease than true lavender. Because of this hardiness and a higher yield of oil per acre, lavandin has become commercially more important than true lavender. In the last ten years, the production of lavandin oil in Southern France has ranged from 500,000 to 950,000 kg. per year, thus comprising one of the world's 10 largest natural perfume oils. As a result of its commercial importance, lavandin has been the subject of several excellent investigations. The reported components are listed (Table I), and those which have only been tentatively assigned are indicated with a question mark. Even though much has been reported on the composition of lavandin, the oil is so complex that many components have remained unidentified. This paper concerns the further characterization of the composition of this oil.

## EXPERIMENTAL

Lavandin Oil. The essential oil was obtained in Southern France in 1965 at various distillation areas. Samples from these areas representing the abrialis variety were combined. Other varieties and commercial samples of *Lavandin abrialis* were also examined.

Colgate-Palmolive Research Center, Piscataway, N.J.

**Gas Chromatographic Columns.** The following columns were employed in this study:

1. 20% Carbowax 20M on Chromosorb P, regular 60to 80-mesh, 3 meters  $\times \frac{1}{4}$ -inch O.D., air = 0.00.

2. 20% Craig Succinate on Chromosorb P, regular 60to 80-mesh, 3 meters  $\times$  <sup>1</sup>/<sub>4</sub>-inch O.D., air = 0.00.

3. 20% Ucon 550 saturated with Tween 20 on Chromosorb W, regular 60- to 80-mesh, 3 meters  $\times 1/4$ -inch O.D., point of injection = 0.00. The substrate was prepared by shaking equal quantities of Ucon 550 and Tween 20 and allowing two layers to form. The top layer, Ucon 550 saturated with the Tween 20, was separated and used as the substrate.

4. 3% Carbowax 20M on Chromosorb G, 60- to 80mesh, nonacid-washed, 6 meters  $\times \frac{1}{s}$ -inch O.D.

**Procedure.** The isolation techniques involved vacuum distillation of the oil into five fractions and a pot residue, and subsequent column chromatography on alumina (A-540, 60- to 200-mesh, 62 cm.  $\times$  2-cm. I.D., Fisher Scientific Co.) into fractions of varying polarity and final isolation by gas chromatography. Fractions were isolated from the gas chromatograph by passing the eluent into a glass U-tube (3-mm. O.D.) immersed in a dry ice bath. Positive identification was accomplished by comparison of GLC elution times and infrared (Beckman IR-12) and/or mass spectra (Consolidated Electrodynamic Corp., Model 21-103 C) with those of authentic samples.

Lavandin oil (145.4 grams) was fractionated under vacuum in a Todd distillation assembly. The isolation scheme for the oil is shown in Figure 1. Each of the alumina fractions (2A to 6E) were analyzed by GLC and the resolved components were collected from the 1/4-inch O.D. column using approximately 40 µl. of sample. Repeated collections were made on trace components. A droplet was generally sufficient for the infrared analysis, while a vapor or mist was satisfactory for the mass spectral analysis. In several cases, the sample size was sufficient only for a mass spectral analysis. Distillation cut 1 and

Table I. Reported Constituents of Lavandin Oil								
Compound	Reference	Compound	Reference					
Hydrocarbons		Linalyl butyrate	(Sfiras and Vanderstreek, 1943)					
$\alpha$ -Pinene	(Naves, 1945a)	Terpinyl acetate (?)	(Sfiras and Vanderstreek, 1943)					
Camphene	(Naves and Angla, 1941; Naves,	Geranyl acetate (?)	(Sfiras and Vanderstreek, 1943)					
-	1945a)	Bornyl acetate (?)	(Calvarano, 1964)					
$\beta$ -Pinene	(Calvarano, 1964)	$(-)$ -Lavandulyl- $(+)$ - $\alpha$ -	(Teisseire, 1954)					
Limonene	(Naves, 1945a)	methylbutanoate						
Ocimene	(Naves, 1945a; Sfiras and Van-	(-)-Lavandulyl caproate	(Teisseire, 1954)					
	derstreek, 1943)	Lavandulyl benzoate	(Teisseire, 1954)					
Alloocimene (?)	(Naves, 1945a)	Epoxy linalyl acetate	(Naves, 1945b)					
$\beta$ -Myrcene	(Calvarano, 1964)							
3-Carene (?)	(Calvarano, 1964)	KETONES						
$\gamma$ -Terpinene	(Calvarano, 1964)	Diacetyl	(Igolen, 1944)					
Sabinene	(Calvarano, 1964)	Diisopropyl ketone	(Stadler, 1960)					
Bisabolene	(Igolen, 1944)	(-)-Nopinone	(Stadler, 1960)					
A		(–)-Cryptone	(Stadler, 1960)					
ALCOHOLS	(Stadler, 10(0))	$(\pm)$ -Carvone	(Stadler, 1960)					
2-Methyl-3-buten-2-ol	(Stadler, 1960)	Methyl heptadienone	(Stadler, 1960)					
1-Hexanol	(Benezet and Igolen, 1943)	Methyl heptenone (?)	(Stadler, 1960)					
1-Octanol	(Igolen, 1944)	( – )-Sabinaketone ( ?)	(Stadler, 1960)					
3-Octanol	(Igolen, 1944)	3-Octanone	(Sfiras and Vanderstreek, 1943					
1-Octen-3-ol	(Sfiras and Vanderstreek, 1943)		Igolen, 1944)					
(-)-Linalool	(Naves, 1945a; Sfiras and Van- derstreek, 1943; Igolen, 1944)	(+)-Camphor	(Ripert, 1937; Naves and Angla 1941; Naves, 1945a)					
(+)-Borneol	(Naves and Angla, 1941; Naves,							
	1945a; Sfiras and Vander-	ALDEHYDES	(7 1 1010)					
	streek, 1943; Naves, 1959)	1-Hexanal	(Igolen, 1944)					
Geraniol	(Sfiras and Vanderstreek, 1943;	1-Octanal	(Igolen, 1944)					
	Igolen, 1944)	Furfural	(Igolen, 1944)					
$(-)-\alpha$ -Terpineol	(Naves, 1945a)	Cuminaldehyde	(Igolen, 1944)					
(-)-Lavandulol	(Naves, 1945a)	(-)-Phellandral	(Stadler, 1960)					
Nerol	(Naves, 1945a)	PHENOLS						
(-)-Perillyl alcohol	(Naves, 1945a)		(Igolen, 1944)					
Linalool oxide	(Naves, 1945b)	Eugenol	(Igoleli, 1944)					
Terpinen-4-ol	(Sfiras and Vanderstreek, 1943)	Lactones						
Esters		Coumarin	(Igolen, 1944)					
<i>n</i> -Hexyl acetate	(Igolen, 1944)	Coumarin	(igoleii, i)++)					
<i>n</i> -Hexyl butyrate	(Peyron and Benezet, 1966)	Oxides						
(+)-n-Octyl acetate	(Igolen, 1944)	Cineole	(Sfiras and Vanderstreek, 1943					
	(Sfiras and Vanderstreek, 1943)	Cilicole	Igolen, 1944)					
1-Octen-3-yl acetate		Acids	igoleli, 1944)					
1-Octen-3-yl butyrate	(Sfiras and Vanderstreek, 1943)	Acetic	(Igolen, 1944)					
Linalyl formate	(Sfiras and Vanderstreek, 1943)	Butyric	(Igolen, 1944)					
Linalyl acetate	(Sfiras and Vanderstreek, 1943;		(Igolen, 1944) (Igolen, 1944)					
	Naves, 1945a; Igolen, 1944)	Caproic	(1801CII, 1744)					

## **Distillation Cuts**

# **Alumina Fractions**

Distriction Cuts		
<ol> <li>Up to 72° C./37 mm. (volatiles)</li> <li>72°/37 mm. to 87°/6.0 mm., 13 grams</li> </ol>	2A—Terpenes (pentane) 2B—Cineole (pentane) 2C—3-Octanone (pentane) 2D—Volatile oxygenated compounds (diethyl ether)	
3.287°/6.0 mm. to 69°/5.0 mm., 15 grams	3A—Cineole + esters (pentane)3B—Camphor (pentane)3C—Linalool (pentane-ether)3D—Oxygenated compounds (ether-chloroform)Figure 1. Isolation schemfor lavandin oil	ıe
4. 69°/5.0 mm. to 69°/4.5 mm., 43 grams	4A—Esters (pentane) 4B—Camphor (pentane) 4C—Linalool (diethyl ether) 4D—Oxygenated compounds (diethyl ether)	
5. 69°/4.5 mm. to 64/1.0 mm., 48 grams	5A—Linalyl acetate (pentane-ether)5B—Linalool (pentane-ether)5C—Terpenic alcohols (ether)5D—Terpenic alcohols (ether-methanol)	
	$\begin{bmatrix} 6A - Sesquiterpenes (pentane) & \longrightarrow & (1) redistilled \\ (2) rechromatographed & \begin{bmatrix} 6A - 1A \\ 6A - 1B \\ 6A - 1C \\ 6A - 1D \end{bmatrix}$	
6. Residue, above 64°/1.0 mm., 16 grams	6B—Esters (pentane) 6C—Esters (pentane) 6D—Caryophyllene oxide (pentane) 6E—Oxygenated sesquiterpenes (chloroform)	

sesquiterpene fraction 6A were reisolated from larger samples of lavandin to examine the trace components in these fractions. Optical rotations were determined in carbon tetrachloride when sample size permitted.

#### **RESULTS AND DISCUSSION**

The components which have been isolated and identified in this study are listed in Table II. The percentages were estimated through the gas chromatographic analysis of the original oil and of the various chromatographic fractions. The fraction from which the component was isolated (Figure 1) is indicated along with the column and temperature employed. Identification was made by the method indicated by comparison with either the reported standard or with an authentic sample isolated from the indicated essential oil. Synthetic esters were prepared by the reaction of the corresponding alcohol with the appropriate acid chloride in the presence of N,N-dimethylaniline.

The volatile components which were present in trace quantities and for which only a tentative identification was possible are listed. These trace volatiles which were insufficiently pure for positive identification were tentatively assigned through their mass spectra.

A vapor phase chromatogram of the original oil is shown in Figure 2 and the compounds that have been identified are listed in Table III along with their retention times for several column conditions. This chromatogram shows that many components still remain unidentified. The majority of these appear to be components of lower volatility and probably represent the oxygenated sesquiterpenes. The reported constituents which were not found are apparently present in small quantities. In this study, 48 components are reported, many of which have not previously been positively identified. Isocaryophyllene oxide, for which an authentic sample or reported spectrum was not available, was tentatively identified by analysis of its infrared and mass spectra. The mass spectrum has a fragmentation pattern very similar to that of the caryophyllene oxide, while the infrared spectrum was consistent

with this structure (  $C = CH_2$  at 3057; 1622; 882 cm.<sup>-1</sup>; *gem*-dimethyl at 1373; 1360 cm.<sup>-1</sup>).

Several other trace components were isolated, but because of insufficient sample for complete analytical data, they could not be identified. Some of these include an aldehyde with a terminal methylene ( $\bigcirc$ C=CH<sub>2</sub> at 3073; 1634; 887 cm.<sup>-1</sup>; ---CHO at 2700; 1736 cm.<sup>-1</sup>), a compound of molecular weight 194 (C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>) which appears to be a butyldimethoxybenzene (aromatic at 3044; 1503; 863; 812 cm.<sup>-1</sup>; =-C--O at 1209 cm.<sup>-1</sup>; O---CH<sub>3</sub> at 1047 cm.<sup>-1</sup>) and several sesquiterpenes, the infrared spectra of which do not compare with any known compound.

Although care was taken to avoid isomerization on isolation, the trace amounts of the identified *cis*- and *trans*-alloocimene may be artifacts. The isomerization of ocimene to alloocimene on heating has been established (Wolinsky *et al.*, 1962; Hawkins and Hunt, 1951). The majority of the other identified components were detected on the chromatograms of the original oil.

A comparison was made of the several varieties of lavandin. Using an internal standard (carvone) with a

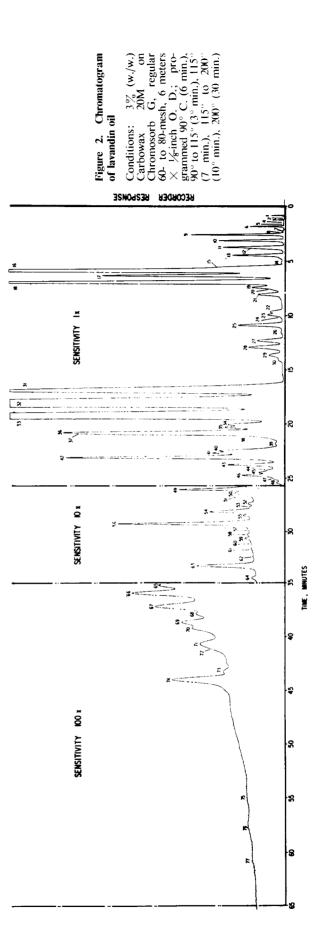


Table II. Compounds Isolated Irom Lavandin On									
Component	[α] <sub>D</sub>	Approx imate %	- Fraction Con- tained	GC Trapping Conditions <sup>a</sup>	Method of Identification	Source of Authentic Sample			
Terpenes									
Tricyclene		0.03	2A	1 (110°)	MS	Glidden			
$(+)$ - $\alpha$ -Pinene	+17	0.4	2A	1 (110°)	MS; IR	Turpentine; reported IR (Mitzner et al., 1965)			
(+)-Camphene	+67	0.3	2A	1 (110°)	MS; IR; 50° m.p.	Glidden; reported IR (Mitzner et al., 1965)			
$(+)$ - $\beta$ -Pinene	+3.4	0.3	2A	1 (75–90° at 2°/min.)	MS; 1R	Glidden; reported IR (Mitzner et al., 1965)			
β-Myrcene		0.3	2A	1 (110°)	MS; 1R	Glidden; reported IR (Mitzner et al., 1965)			
Sabinene		0.1	2A	1 (75°–90° at 2°/min.)	MS; 1R	Reported IR (Mitzner <i>et al</i> , 1965)			
3-Carene		0.02	2A	1 (75-90° at 2°/min.)	IR	Indian turpentine			
(+)-Limonene	+36	0.7	2A	1 (110°)	IR	Orange terpenes: reported IR (Mitzner et al., 1965)			
γ-Terpinene		TR.	2A	1 (165°)	MS; IR	Glidden; reported IR (Mitzner et al., 1965)			
cis-Ocimene		2.6	2A	1 (165°)	1 <b>R</b>	Reported IR (Mitzner <i>et al.</i> , 1965; Farnow and Porsch, 1961)			
trans-Ocimene		3.0	2A	1 (165°)	MS; IR	Opoponax reported IR (Mitzner et al., 1965; Farnow and Porsch, 1961)			
cis-Alloocimene		TR.	2A	1 (165°)	MS; IR	Reported 1R (Mitzner <i>et al.</i> , 1965)			
trans-Alloocimene		TR.	2A	1 (165°)	MS; IR	Reported IR (Mitzner <i>et al.</i> , 1965)			
Terpinolene		0.2	2A	1 (165°)	MS; IR	Hercules; reported IR (Mitzner et al., 1965)			
<i>p</i> -Cymene		0.04	2A	1 (110°)	1 <b>R</b>	Reported IR (Mitzner <i>et al.</i> , 1965)			
Sesquiterpenes $(-)$ - $\alpha$ -Santalene	- 19	0.2	6A-1A	1 (1 <b>5</b> 0°)	MS; IR; NMR <sup>b</sup>	Sandalwood; reported IR (Plivy et al., 1960)			
$(\pm)$ -Caryophyllene	0	0.7	6A-1B	1 (150195° at 2°/min.)	MS; IR; NMR	Clove; reported IR (Plivy <i>et al.</i> , 1960; Wenninger <i>et al.</i> , 1966)			
trans-β-Farnesene		0.3	6A-1D	1 (150–195° at 2°/min.)		Reported IR (Plivey <i>et al.</i> , 1960; Naves, 1966)			
γ-Cadinene Alcohols		TR.	6A	3 (165°)	MS; IR	Reported IR (Wenninger <i>et al.</i> , 1966; Sykora <i>et al.</i> , 1959; Buttery <i>et al.</i> , 1966)			
2-Methyl-3-buten-2-ol		<0.01	1	1 (75°)	MS	Aldrich			
3-Octanol		TR.	2D; 3D	$1(160^{\circ})$	MS	Spearmint			
1-Octen-3-ol			2D; 3D; 4D		MS; IR	Aldrich			
(–)-Linalool	-22	35	3C; 4D; 5B	3 (165°)	IR	Bois De Rose			
()·Lavandulol	-12	0.6	5C	1 (160°)	IR	Hoffmann-LaRoche; reported IR (Teisseire and Rinaldi, 1963)			
(+)-Borneol	+39	2.9	5C	1 (130–160° at 2°/min.)	IR	Orbis			
$\alpha$ -Terpineol		0.5	5C; 5D	1 (130–160 at 2°/min.)	IR	Reported IR (Mitzner and Lem- berg, 1966)			
trans-Linalool oxide		0.2	4D	1 (160°)	MS; IR	Hoffmann-La Roche; reported IR (Felix <i>et al.</i> , 1963)			
cis-Linalool oxide		0.1	4D	<b>1 (160°)</b>	MS; IR	Hoffman-La Roche, reported IR (Felix <i>et al.</i> , 1963)			
Ketones									
Acetone		0.01	1	1 (75°)	MS	Commercial			
3-Octanone		1.0	2C	3 (150°)	IR	Givaudan			
(+)-Camphor	+49.3 (C₂₄% C₂H₅OH)	8.9	3B; 4B	Recrystallized	Mixed m.p. 176°	Orbis			

# Table II. Compounds Isolated from Lavandin Oil

<sup>a</sup> Numbers refer to gas chromatographic columns given in Experimental. Column temperatures in centigrade are in parentheses. <sup>b</sup> Nuclear magnetic resonance, Varian A-60-A.

Component	[ <b>α</b> ]D	Approx imate %	Table II. - Fraction Con- tained	Continued GC Trapping Conditions <sup>a</sup>	Method of Identification	Source of Authentic Sample
Esters						
<i>n</i> -Butyl acetate		0.03	1	1 (75°)	MS	Verona
<i>n</i> -Hexyl butyrate		0.4	4A	3 (150°)	IR	К & К
<i>n</i> -Hexyl isobutyrate		0.09	4A	3 (150°)	IR	К & К
1-Octen-3-yl acetate		0.3	3A: 4A	1 (160°)	IR	Synthesized
(-)-Linalyl acetate	-11	27	5A	3 (165°)	IR	Hoffmann–La Roche
Lavandulyl acetate		1.0	6C	3 (185°)	IR	Hoffmann–La Roche
Lavandulyl butyrate		0.2	6B	3 (185°)	MS; IR	Synthesized
Lavandulyl-2-methyl		0.7	6B	3 (185°)	MS; IR	Synthesized
butvrate					.,	
Neryl acetate		0.7	6C	3 (185°)	IR	Givaudan; Glidden
Geranyl acetate		0.3	6C	3 (185°)	IR	Orbis
<i>n</i> -Hexyl tiglate		0.3	6C	3 (185°)	MS; IR	Fritzsche
MISCELLANEOUS				- ( )	,	
Dimethyl sulfide		< 0.01	1	1 (75°)	MS	Commercial
<i>n</i> -Butyl methyl ether		<0.01	1	1 (75°)	MS; IR	Synthesized
Cineole		7.6	2B; 3A	2 (110°)	IR	Eucalyptus
Caryophyllene oxide		0.3	6D	3 (185°)	MS; IR	Givaudan; reported IR (Plivy
				- ( )	,	<i>et al.</i> , 1960)
Coumarin		0.03	6E	Base extrac- tion of 6E	MS; IR	Universal Oil Products
Isocaryophyllene oxide		0.04	6D	3 (185°)	MS; IR	
Water		0.04	1	5 (105 )	1010, IIX	
., ator	Tent		signed True	e Volatile Comp	onents	
Acetal	dehvde	unitory As	signed fide	e volutile comp	3-Methylb	utanal
	uenyue				J-IVICIIIYIU	

2-Methylpropanal 2-Methylbutanal

*n*-Heptane 2-Methylfuran Methyl propyl ketone

Table III. Relative Retention Times of Lavandin Components

Peak No. Figure 2)	Component	<b>1 (160)</b> <i>a</i>	<b>2 (80)</b> <sup>h</sup>	<b>2</b> (160) <sup>a</sup>	3 (165) <sup>a</sup>	4 (68) <sup>c</sup>	<b>4 (110)</b> <sup>d</sup>	4 (150)
-	Dimethyl sulfide	0.034	0.09	0.046	0.086	0.070	0.012	0.023
2 3 3 7 8	<i>n</i> -Butyl methyl ether	0.001	0.07	0.010	0.000	0.071	0.012	0.023
3	Acetone	0.045	0.15	0.062	0.087	0.107	0.017	0.034
7	2-Methyl-3-buten-2-ol	0.091	0.47			0.52	01011	0.089
8	Tricyclene	0.13	0.55	0.15	0.28	0.52	0.062	0.12
9	$\alpha$ -Pinene	0.14	0.59	0.15	0.28	0.58	0.068	0.12
10	<i>n</i> -Butyl acetate	0.14	0.73			0.72	01000	
10	Camphene	0.17	0.79	0.19	0.32	0.76	0.090	0.16
11	3-Pinene	0.21	1.00	0.23	0.38	1.00	0.108	0.19
12	Sabinene		••••			1.09	01100	0.19
13	3-Carene	0.23		0.24	0.41	1.31	0.13	0.23
13	β-Myrcene	0.22	1.33	0.22	0.36	1.46	0.13	0.20
15	Limonene	0.28	1.67	0.30	0.48	1.78	0.17	0.27
16	Cineole	0.31	1.86	0.36	0.50		0.19	0.29
17	cis-Ocimene	0.29		0.29	0.45		0.19	0.27
18	trans-Ocimene	0.32		0.33	0.49	2.59	0.21	0.30
18	γ-Terpinene				0.49		0.21	0.31
18	3-Octanone	0.33		0.40	0.42		0.22	0.31
20	<i>p</i> -Cymene	0.38		0.43	0.54		0.25	0.37
21	Terpinolene	0.41		0.41	0.62		0.26	0.38
23	<i>n</i> -Hexyl isobutyrate				0.77		0.36	0.44
25	1-Octen-3-yl acetate				0.71			0.50
25	3-Octanol	0.50		0.50	0.58		0.43	0.50
25	cis-Alloocimene	0.53						0.52
26	trans-Alloocimene	0.60						0.58
27	<i>n</i> -Hexyl butyrate				0.98		0.52	0.62
28	1-Octen-3-ol				0.59			0.64
29	trans-Linalool oxide	0.74		0.83	0.81		0.61	0.73
30	cis-Linalool oxide	0.82		0.94	0.88		0.70	0.82
31	Camphor	1.18		1.43	1.18		0.90	1.15

<sup>c</sup>  $\beta$ -Pinene = 1.00; point of injection = 0.00, <sup>d</sup> Linalool = 1.00; pentane = 0.00.

Table III. Continued									
Peak No. (Figure 2)	Component	<b>1 (160)</b> <sup>a</sup>	<b>2</b> (80) <sup>b</sup>	<b>2</b> (160) <sup>a</sup>	<b>3 (165)</b> <sup>a</sup>	<b>4</b> (68) <sup>c</sup>	<b>4 (110)</b> <sup>d</sup>	<b>4 (150)</b> <sup>d</sup>	
32	Linalool	1.00		1.00	1.00		1.00	1.00	
33	Linalyl acetate	1.16			1.47		1.08	1.13	
34	$\alpha$ -Santalene			1.32	2.65			1.34	
35	Lavandulyl acetate				1.73			1.38	
36	Caryophyllene	1.65		1.65	2.88		1.34	1.58	
38	<i>n</i> -Hexyl tiglate				2.11			1.52	
40	Lavandulol			1.60	1.60		2.00	1.84	
41	trans-β-Farnesene							1.80	
42	Borneol	2.15		2.06	1.89		2.16	2.11	
42	$\alpha$ -Terpineol	2.05		2.09	1.83		2.03	2.14	
43	Neryl acetate				2.71			2.30	
45	Geranyl acetate	2.67		2.42	3.04			2.62	
45	Lavandulyl butyrate				3.66			2.53	
46	Lavandulyl-2-methyl butyrate				4.32			2.71	
51	$\gamma$ -Cadinene							4.04	
54	Isocaryophyllene oxide								
56	Caryophyllene oxide							6.70	
74	Coumarin							-	

Table IV. Analytical Data on Lavandula Oils

		14010	and and	, tical Data	on Davanut			
	No. of Samples	$\alpha$ -Pinene	Camphene	Linalool	Camphor	Linaly1 Acetate	Optical Rotation	Refractive Index, 20° C.
Lavandin								
Abrialis	10	0.20-0.60 0.43	0.20-0.40	24.3-38.6 33.1	8.9-10.0 9.4	25.6-35.4 29.4	-2.36 to $-4.52-3.78$	1.4615–1.4641 1.4625
Super	5	0.10-0.25 0.15	0.10-2.20 0.13	27.7–36.2 31.7	4.8-5.6 5.0	43.5-49.6 46.0	-7.30 to $-8.14-7.68$	1.4570-1.4578 1.4573
Standard	3	0.40-0.50 0.43	0.40	37.2–45.4 43.0	9.3–9.8 9.5	17.0–25.3 21.4	-4.50 to $-4.81-4.67$	1.4634–1.4639 1.4637
Maime Epis Tete	1	0.3	0.3	52.4	7.6	23.7	- 7.66	1.4624
Commercial lavandin Abrialis	200	0.20-1.10	0.15-0.88	26.7-43.4	5.6-10.6	20.5-35.5	-2.23 to -5.12	1.4599-1.4640
(over 5-yr.period)		0.57	0.42	33.9	8.7	27.3	-3.77	1,4622
Lavender	9	TR	TR	24.0-37.0 32.1	TR-0.5 0.2	33.9-55.2 46.1	-7.63 to $-10.21-8.64$	1.4567–1.4630 1.4606

Ucon 550-Tween 20 substrate (column 3) at  $165^{\circ}$  C., the three major components, linalool, camphor, and linalyl acetate, were cleanly resolved and were determined quantitatively. The smaller components,  $\alpha$ -pinene and camphene also were determined. The differences between several varieties of lavandin are shown in Table IV. This procedure has been used for the routine quality control of lavandin and the results based on acceptable commercial samples received over the past 5 years are summarized. The results of several French lavender samples are included for comparison with the lavandin. The major difference in lavender compared with lavandin appears to be the absence or presence of only trace amounts of cineole and camphor.

Besides these quantitative differences in the major components of the lavandin varieties listed, sizable differences in ratios of *cis*- and *trans*-ocimene, cineole, and 3-octanone also occur even within the same variety. The lavandin Maime variety showed 4.5% *cis*-ocimene with only a trace of *trans*-ocimene, while several abrialis varieties and a super

1068 J. AGR. FOOD CHEM.

variety showed nearly equal ratios of the two ocimene isomers. The data are not sufficiently complete to categorize these differences according to variety but do indicate that wide differences occur with authentic samples of these oils. These differences are apparently due to changes in variety along with agricultural conditions. The sesquiterpenes from several varieties which were easily recovered by elution with pentane (cut 6A) were also examined. The amount of sesquiterpenes isolated averages 2.5% of the total oil. Caryophyllene was the major sesquiterpene in the oils analyzed except for a 1965 Lavandin abrialis, where  $\alpha$ -santalene was predominant. The sesquiterpene,  $\gamma$ -cadinene, was not observed in many of the oils.

The analytical data from several hundred commercial samples which were acceptable on odor and analysis are summarized in Table IV. Many of the commercial samples received, however, were unacceptable because of appreciable adulteration. 3,5,5-Trimethylhexanol and the corresponding acetate have been isolated and identified in numerous commercial samples offered in the United

States and other countries. These samples also have been found to contain an abnormally high terpene content ( $\alpha$ -pinene up to 5%). Adulteration seems obvious, since the samples obtained in southern France from various varieties and locations were never found to contain any trace of this alcohol or acetate or to contain over 1.2% $\alpha$ -pinene. To our knowledge, neither this alcohol nor the acetate has ever been reported as a natural constituent of any essential oil. The authors hope this report will establish standards for lavandin oil.

#### ACKNOWLEDGMENT

The authors are indebted to E. M. Emery and K. Kellenbach for assistance with the mass and infrared spectral interpretations. They acknowledge the technical assistance of S. P. DeGulis and the cooperation at the management level of G. H. Fuller and S. J. Shymon.

#### LITERATURE CITED

- Benezet, L., Igolen, G., Parfumerie 1, 208 (1943).
- Buttery, R. G., Lundin, R. E., Ling, L., Chem. Ind. (London) 18, 1225 (1966).
- Calvarano, I., Essenze Deriv. Agrumari 34, 169 (1964). Farnow, H., Porsch. F., Dragoco Rept. 8, 183 (1961).

- Felix, D., Melera, A., Seibl, J., Kovats, E. sz., Helv. Chim. Acta
- Henry, D., Melera, A., Seloi, J., Kovats, E. S., Herr. Chim. Acta
  46, 1513 (1963).
  Guenther, E., "The Essential Oils," Vol. III, pp. 492–504, Van Nostrand, New York, 1949.
  Hawkins, J. E., Hunt, H. G., J. Am. Chem. Soc. 73, 5379 (1951).
  Igolen, G., Soap, Perfumery & Cosmetics 28, 525 (1955).
  Mitzner, B. M., Lemberg, S., Am. Perfumer Cosmetics 81, 25 (1965).

- (1966). Mitzner, B. M., Theimer, E. T., Freeman, S. K., Appl. Spectroscopy 19, 169 (1965).

- copy 19, 169 (1965).
  Naves, Y. R., Helt. Chim. Acta 28, 1220 (1945a).
  Naves, Y. R., Helt. Chim. Acta 28, 1231 (1945b).
  Naves, Y. R., Helt. Chim. Acta 42, 2744 (1959).
  Naves, Y. R., Helt. Chim. Acta 49, 1029 (1966).
  Naves, Y. R., Angla, B., Ann. Chim. Anal. 23, 203 (1941).
  Peyron, L., Benezet, L., Compt. Rend. 262, 1105 (1966).
  Plivy, J., Horak, M., Herout, V., Sorm, F., "Die Terpene I Sesquiterpene," Akademie Verlag, Berlin, 1960.
  Ripert, J., Ann. Fals. Fraudes 342, 284 (1937).
  Sfras, I. Vanderstreek L. Parfumerie 1 (9) 235 (1943)

- Staller, P. A., Helv. Chim. Acta **43**, 1601 (1967). Staller, P. A., Helv. Chim. Acta **43**, 1601 (1960). Sykora, V., Herout, V., Collection Czech. Chem. Commun. **24**, 1732 (1959).
- Teisseire, P., Recherches (Paris) 4, 51 (1954). Teisseire, P., Rinaldi, M., Recherches (Paris) 13, 4 (1963).

- WINDER, F., KITARUI, M., Recherches (Paris) 13, 4 (1963).
  Vinot, M., Bouscary, A., Recherches (Paris) 14, 57 (1964).
  Wenninger, J. A., Yates, R. L., Dolinsky, M., Proc. Sci. Sect. Toilet Goods Assoc. 46, 44 (1966).
  Wolinsky, J., Chollar, B., Baird, M. D., J. Am. Chem. Soc. 84, 2775 (1962).
- Received for review April 26, 1967. Accepted June 23, 1967.