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Isolation, Identification, and Biogenesis of Bifunctional Compounds in Lavandin Oil

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Carbonyl compounds of lavandin were isolated by treating the oil with Girard T reagent in the presence of methanol and acidic ion exchange resin. The investigation of these materials resulted in the identification of 29 carbonyl compounds, of which 17 compounds are new in lavandin oil. They include ten aldehydes, four ketones, and three new bifunctional compounds. In another

experiment, less volatile lavandin residue, obtained by molecular distillation of the oil, was also analyzed by both column chromatography and glc methods. This resulted in the identification of two alcohols, three lactones, and three more bifunctional compounds. Biogenesis of bifunctional compounds has been discussed in the light of photooxidation of linalyl acetate.

Lavandin oil is produced commercially in southern France from a hybrid plant (*Lavandula hybrida* Reverchon). Due to its importance as a fragrance material, various investigators have studied this oil and identified many of its components (Steltenkamp and Casazza, 1967). The major components of this oil are linalool and linalyl acetate. In addition, there are small amounts of carbonyl compounds which have also been investigated by two workers in two different laboratories. Igolen (1955) studied this oil and identified six carbonyl compounds. In 1960 Stadler isolated the carbonyls of lavandin oil by Girard T reagent and identified 11 carbonyl compounds. The present paper reports the characterization of other carbonyl compounds of this oil, together with the constituents of less volatile residue.

EXPERIMENTAL PROCEDURE

Instrumental Methods. Glc analyses were performed on F&M 810 instrument using 10% Carbowax 20M and 10% SE-30 coated on Anakrom ABS (80-100 mesh) packed in a stainless steel column (8 ft \times 0.25 in. o.d.), unless specified. The following spectrometers were used: ir, Beckman IR-5A and IR-4; nmr, Varian 60 and HA 100 (CCl₄, TMS as internal standard); mass spectra, CEC Model 21-103 and AEI-MS9 for high-resolution spectra. Mass spectra major fragmentation peaks are recorded in decreasing order of intensity. Neutral alumina (Fisher Scientific, 80-200 mesh) was used for column chromatography.

Isolation of Monocarboxyls and Bifunctional Compounds from Lavandin Oil. A solution of lavandin oil (500 g) in methanol (5 l.) was treated with Girard T reagent (30 g) and acidic ion exchange resin (5 g) as described by Stanley *et al.* (1961), with regeneration of the carbonyls with purified formaldehyde (Hunter and Struck, 1962). The crude carbonyl compounds (4 g) thus isolated were first fractionated into 25 fractions (Figure 1) on a SE-30 column. Each fraction was collected from the end of the glc column in a Dry Ice-cooled glass tube and rechromatographed on a Carbowax 20M column. The pure compound thus isolated was analyzed by ir, nmr, and mass spectrometry.

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Isolation of Bifunction Compounds and Lactones from Lavandin Residue. Lavandin oil (5 kg) was distilled (25°, 0.1 mm) to separate the volatile material (4950 g) from a dark-colored gummy residue (50 g). This residue, which possessed strong lavandin odor, was chromatographed on neutral alumina (Activity I, 500 g). Benzene (2 l.) eluted 15 g of colored liquid possessing a strong odor. This liquid was again chromatographed on neutral alumina (Act. 1, 200 g) to obtain the fractions given in Table I. Fractions 1B, 1C, and 1D, which possessed lavandin odor, were further fractionated on a glc SE-30 column (0.25 in. \times 4 ft) and the major peaks of each fraction were collected and analyzed by ir, nmr, and mass spectrometry.

SYNTHESIS

Compound 1. Selenium dioxide oxidation of linalyl acetate **13** in ethyl alcohol (Sathe *et al.*, 1966) yielded **1**: ir (neat) 3.25, 3.38, 3.41, 3.5, 3.55, 3.7, 5.74 ($-\text{OCOCH}_3$), 5.9 ($\text{C}=\text{CCHO}$), 6.09, 6.9, 7.1, 7.3, 8.0, 8.52, 9.05, 9.25, 9.6, 9.7, 10.05, 10.65, 10.8, 12.2 μ ; nmr (CCl₄) δ 1.51 (s, 3 H, CH₃CO), 1.68 (s, 3 H, CH₃C=C), 1.93 (s, 3 H, OCOCH₃), 2.24 (m, 2 H, CH₂), 5.0-6.0 (m, 3 H, CH₂=CH), 6.28 (m, 1 H, $-\text{CH}=\text{C}=\text{O}$), 9.22 (s, 1 H, CHO); mass spectrum showed a peak at m/e 150 (M - 60) and major peaks at m/e 43, 41, 45, 93, 91, 79, 55, 67, 53.

Compound 2. Selenium dioxide oxidation of lavandulyl acetate in the same way yielded **2**: ir (neat) 3.25, 3.4, 3.5, 3.7, 5.72 ($-\text{OCOCH}_3$), 5.9 ($\text{C}=\text{CCHO}$), 6.05, 6.9, 7.1, 7.25, 7.32, 8.1, 8.55, 9.6, 10.0, 10.3, 10.65, 11.15, 12.4 μ ; nmr (CCl₄) δ 1.7 (br s, 6 H, CH₃C=C), 1.99 (s, 3 H, $-\text{OCOCH}_3$), 2.5 (m, 3 H, CH₂C=C), 4.05 (br d, 2 H, CH₂OAC), 4.83 (br d, 2 H, C=CH₂), 6.3 (br, 1 H, CH=CCHO), 9.2 (s, 1 H, CHO); mass spectrum showed a peak at m/e 150 (M - 60) and major peaks at m/e 43, 44, 41, 93, 91, 55, 53, 107, 109.

Compound 3. Photooxidation of linalyl acetate **13**, as described below, yielded **3** as a minor component: ir (neat) 3.25, 3.36, 3.42, 5.75 ($-\text{OCOCH}_3$), 5.89, 5.96 ($\text{C}=\text{C}=\text{O}$), 6.08, 6.13, 6.98, 7.05, 7.3, 7.99, 8.05, 8.5, 9.05, 9.32, 9.55, 9.8, 10.18 (*trans*-CH=CH), 10.45, 10.75, 11.75, 12.6 μ ; nmr (CCl₄) δ 1.53 (s, 3 H, CH₃CO), 2.0 (s, 3 H, $-\text{OCOCH}_3$), 2.2 (s, 3 H, CH₃COC=C), 2.75 (d, 2 H, CH₂C=C), 5.0-6.5 (m, 5 H, CH=CHC=O and CH₂=CH); mass spectrum showed a peak at m/e 136 (M - 60) and major peaks at m/e 43, 91, 93, 119, 77, 121, 65.

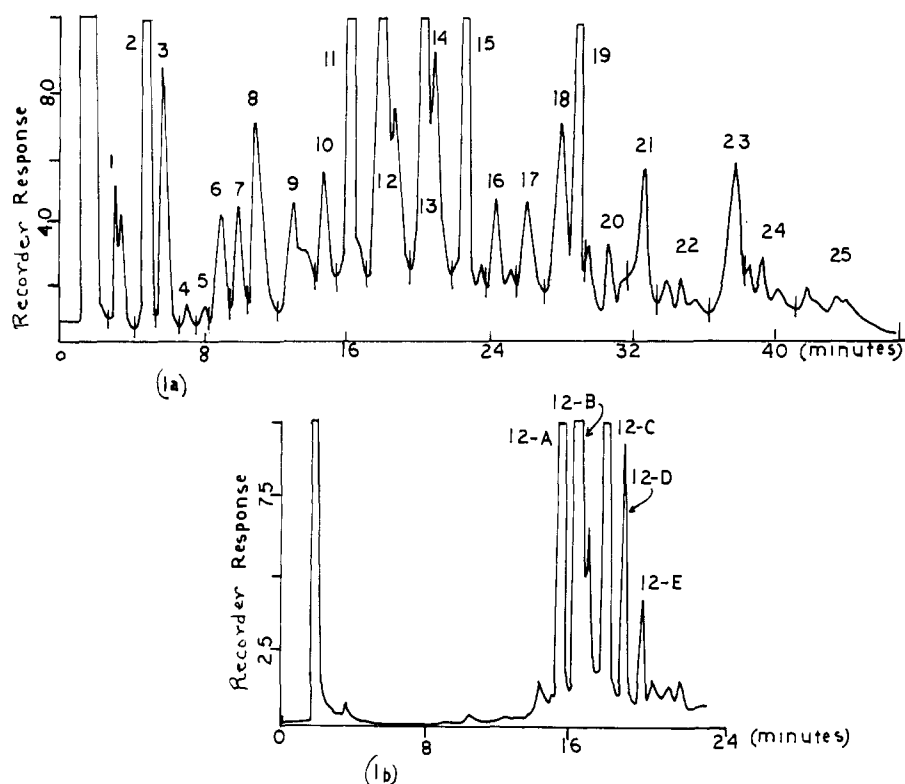


Figure 1 (a). Glc curve of the isolated carbonyl compounds of lavandin (10% silicone SE-30, 8 ft \times 0.25 in. o.d.) (b). Glc curve of the isolated peak 12 (10% Carbowax 20M, 8 ft \times 0.25 in. o.d.). For identity of peaks 12-B, 12-C, and 12-D see Table I.

Compound 4. Treatment of toluene with γ -valerolactone in the presence of aluminum trichloride, according to the procedure of Phillips (1955), yielded ketone 4 as a minor product: ir (neat) 3.32, 3.4, 3.49, 5.91 (α,β -unsaturated six-membered ring ketone), 6.2, 6.35, 6.65, 6.85, 7.09, 7.25, 7.38, 7.5, 7.65, 7.8, 7.99, 8.06, 8.18, 8.25, 8.35, 8.45, 8.6, 8.79, 9.05, 9.25, 9.55, 9.8, 10.0, 10.6, 11.05, 11.38, 12.0, 12.2 (st), 13.25, 13.7 μ ; (CDCl_3) δ 1.36 (d, 3 H, $\text{CH}_3\text{CC}=\text{C}$), 2.34 (s, 3 H, CH_3Ar), 2.5–3.1 (m, 3 H), 7.22 (m with an s at 7.22, 2 H, ArH), 7.8 (d, 1 H, HAr); mass spectrum showed the molecular ion peak at m/e 174 and major peaks at m/e 159, 118, 132, 27, 91.

Compound 7. Oxidation of linalyl acetate 13 with chromium trioxide in the presence of acetic acid (Buchi *et al.*, 1961) yielded lactone 7 (spectral data were superimposable with those published by Klein and Rojahn, 1967).

Compound 10. Treatment of linalyl acetate 13 with 1 mol of peracetic acid afforded 10: ir (neat) 3.25, 3.38, 3.42, 5.74, 6.09, 6.85, 7.05, 7.25, 7.29, 7.52, 8.0, 8.49, 8.9, 9.1, 9.6, 9.8, 10.05, 10.6, 10.8, 11.1, 11.39, 11.55, 12.5 μ ; mass spectrum showed a peak at m/e 152 ($M - 60$) and major peaks at m/e 41, 27, 43, 81, 39, 68, 67.

Compound 11. Photooxidation of linalyl acetate 13 afforded 11 as one of the major products: ir (neat) 2.93 (OH), 3.39, 3.41, 5.75 ($-\text{OCOCH}_3$), 6.09, 6.85, 6.95, 7.08, 7.3, 8.05, 8.65, 9.1, 9.7, 10.15, 10.25, 10.45, 10.85, 11.1, 11.8, 12.7, 13.0, 13.3 μ ; nmr (CCl_4) δ 1.25 [s, 6 H, (CH_3)₂CO], 1.49 (s, 3 H, CH_3COAC), 1.85 (s, 3 H, $-\text{OCOCH}_3$), 2.57 (b, 2 H, $\text{CH}_2\text{C}=\text{C}$), 5.0–6.0 (m, 5 H, $-\text{CH}=\text{CH}-$ and $\text{CH}_2=\text{CH}-$); mass spectrum showed a peak at m/e 150 ($M - 60$) and major peaks at m/e 91, 119, 43, 79, 41, 134, 77.

Compound 12. Treatment of 10 with aluminum isopropoxide according to the procedure of Eschinas (1968) yielded 12: ir (neat) 2.9 (OH), 3.27, 3.4, 3.43, 3.5, 5.78, 5.82 (double carbonyl absorptions, OCOCH_3), 6.05, 6.9, 7.1, 7.3, 8.1, 8.8 (br), 9.4, 9.6, 9.8, 10.05, 10.4, 10.55, 10.9, (br and st) μ ; nmr (CCl_4) δ 1.24 (s, 3 H, CH_3CO), 1.7 (s, 3 H, $\text{CH}_3\text{C}=\text{C}$), 1.98 (s, 3 H, CH_3COO), 4.8 (t, 1 H, CHO),

5.0–6.3 (m, 5 H, $\text{C}=\text{CH}_2$ and $\text{CH}_2=\text{CH}-$); mass spectrum showed a peak at m/e 152 ($M - 60$) and major peaks at m/e 43, 41, 67, 27, 39, 55, 71.

Compound 16. Photooxidation of linalyl acetate 13 yielded 16 as one of the minor products: ir (neat) 3.25, 3.38, 3.41, 3.55, 3.69, 5.74, ($-\text{OCOCH}_3$), 5.77 ($-\text{CHO}$), 6.05, 6.9, 7.05, 7.3, 8.0, 8.48, 8.65, 9.0, 9.8, 10.05, 10.55, 10.8, 12.0 μ ; mass spectrum showed the molecular ion peak at m/e 110 and major peaks at m/e 43, 27, 41, 29, 39, 41.

Photooxidation of Linalyl Acetate 13. Linalyl acetate (200 g) was photooxidized by bubbling oxygen at 50–60° for 106 hr under a low-pressure mercury lamp (made by Nester-Faust, Delaware, USA) to obtain 220 g of oxidized product. Glc analysis of this material showed the formation of several new peaks (Figure 5, microfilm edition) which were identified as: peak I (ocimene), peak II (limonene), peak III (*p*-cymene), peak IV (α ,4-dimethyl styrene), peak V (acetic acid), peak VI (linalyl acetate), peak VII (lactone 7), peak VIII (acetoxy aldehyde 16), peak IX (epoxide 10), peak X (acetoxy alcohol 11), peak XI (acetoxy ketone 3), and peak XII (acetoxy alcohol 12).

RESULTS AND DISCUSSIONS

Identification of Carbonyl Compounds in Lavandin Oil. Figure 1a represents the glc curve of the isolated carbonyl compounds from lavandin oil. The investigation of

Table I.

Fraction no.	Eluants, 500 ml/fraction	Wt of material, g
1A	Hexane	0.7
1B	Hexane	1.6
1C	5% ether-in-hexane	1.1
1D	25% ether-in-hexane	1.0
1E	Ether	2.1

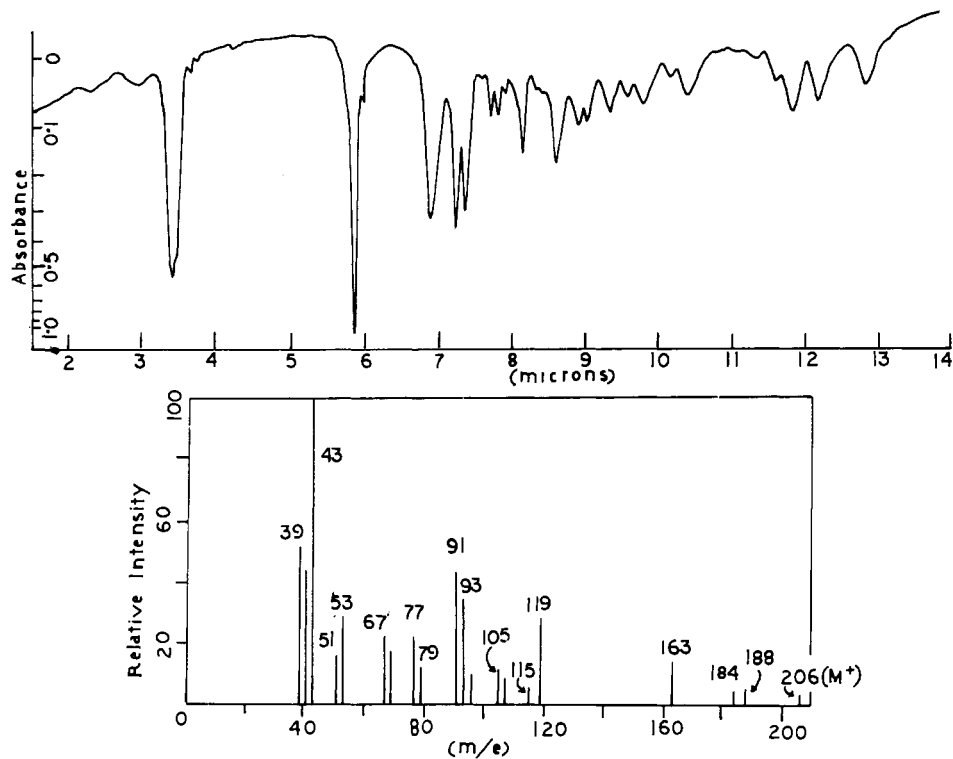


Figure 2. Ir and mass spectra of peak 21-A.

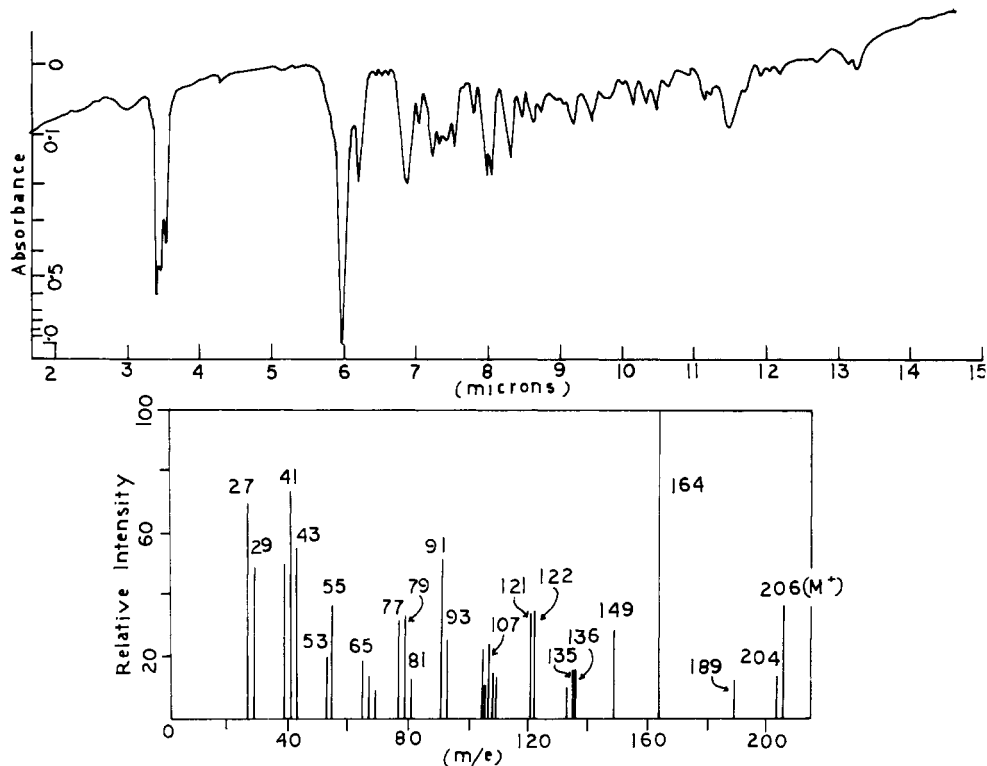
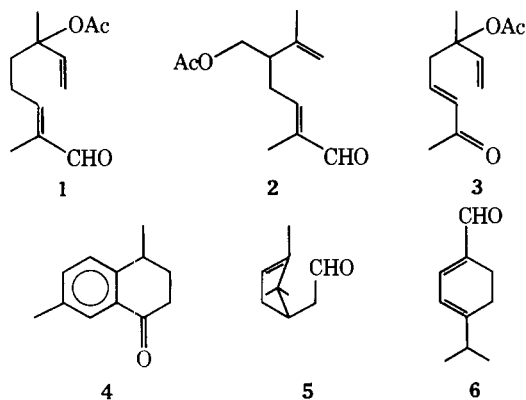


Figure 3. Ir and mass spectra of peak 23-A.

these materials resulted in the identification of 29 carbonyl compounds, of which 17 compounds are new in lavandin oil (Table II). They include 12 aldehydes and five ketones. Among them the bifunctional compounds 1, 2, and 3 and bicyclic ketone 4 are reported for the first time as constituents of a natural product. Acyclic aldehydes 5 (Lewis and Hedrick, 1965) and 6 (Kayahara *et al.*, 1968) are synthetically known materials and have only recently

been reported to occur in the oil from the fruit of *Juniperus communis* L. (Thomas, 1972) and cumin seed oil (Varo and Heinz, 1970), respectively. Bicyclic ketone 4 has been synthesized before (Phillips, 1955) but bifunctional compounds 1, 2, and 3 had neither been synthesized nor isolated previously. It should be noted that compounds 1 and 2 could exist in *cis-trans* forms, but no attempt was made to determine their stereochemistry.



During this carbonyl analysis, we also isolated two unknown norsesquiterpene ketones. These are peaks 21-A and 23-A of Figure 1a, whose ir and mass spectral fragmentation pattern are presented in Figures 2 and 3, respectively. Ir of peak 21-A showed absorption band at 5.84 μ due to $>C=O$ of a saturated ketone. The conspicuous feature of the ir spectrum was the strong doublet absorption of almost equal intensity at 7.25 and 7.39 μ . Since both *gem*-dimethyl and isopropyl groups show absorption bands at 7.22-7.39 μ (Bellamy, 1964), we could probably

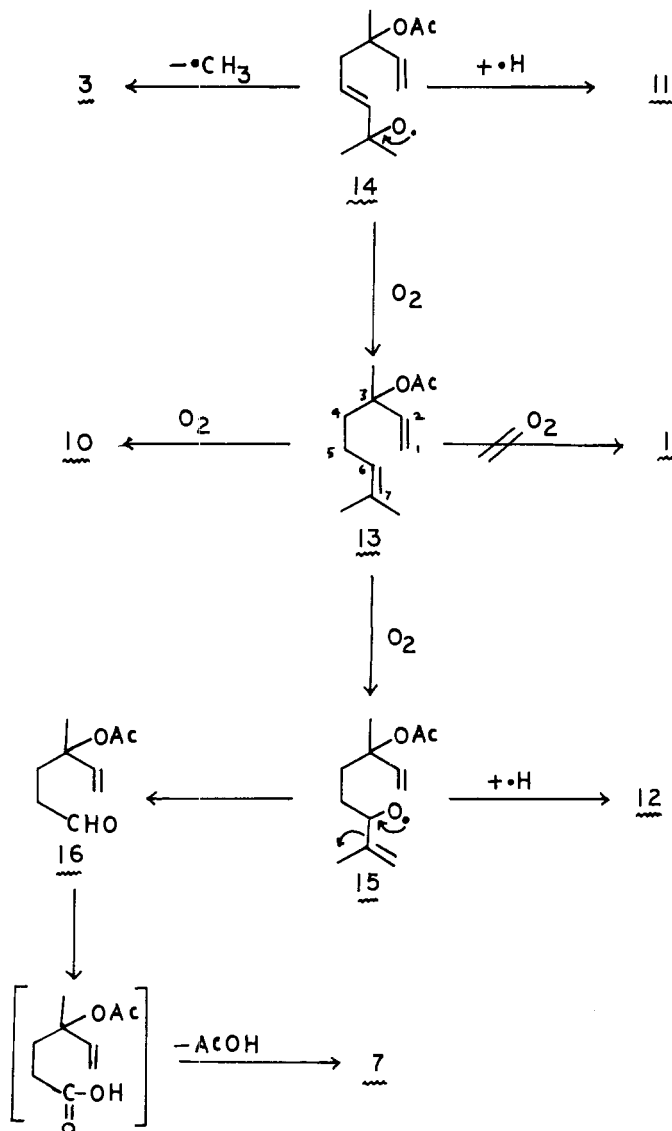


Figure 4. Biogenesis of bifunctional compounds.

Table II. Carbonyl Compounds Identified in Lavandin Oil

Peak no.	Name of the compounds	Reference
Aldehydes		
1-B	Hexanal	Igolen (1955)
2-B	<i>trans</i> -2-Hexenal	
3-B	Heptenal	
8-A	Octanal	Igolen (1955)
8-B	<i>trans</i> -2, <i>trans</i> -4-Heptadienal	
11-B	Nonanal	
12-B	α -Campholenal	
13-A	Decanal	
13-B	Myrtenal	
14-E	Cuminaldehyde	Igolen (1955); Stadtler (1960)
15-C	Phellandral	Stadtler (1960)
15-D-1	Perillaldehyde	
15-D-2	1,4- <i>p</i> -Menthadien-7-al (compound 6)	
16-A	<i>trans</i> -2, <i>trans</i> -4-Decadienal	
Ketones		
4-5-B	6-Methyl-3-heptanone	
7-B	3-Octanone	Igolen (1955); Stadtler (1960)
10-A	6-Methyl-5-hepten-2-one	Stadtler (1960)
11-G	6-Methyl-3,5-heptadien-2-one	Stadtler (1960)
12-B	Camphor	Igolen (1955); Stadtler (1960)
12-C	Nopinone	Stadtler (1960)
12-D	Sabinaketone	Stadtler (1960)
13-C	Cryptone	Stadtler (1960)
13-E	<i>p</i> -Methyl-acetophenone	
14-D	Carvone	Stadtler (1960)
17-E	<i>p</i> -Isopropyl-acetophenone	
21-C	1-(2 <i>H</i>)-Naphthalenone-3,4- dihydro-4,7-dimethyl (compound 4)	
21-A	C ₁₄ -Unknown-saturated ketone	
23-A	C ₁₄ -Unknown- α,β -unsaturated ketone	
Bifunctional compounds		
17-F	3,7-Octadien-2-one-6-hydroxy- 6-methyl acetate (compound 3)	
20-B	2,7-Octadienal-6-hydroxy-2,6- dimethyl acetate (compound 1)	
20-C	2-Heptenal-7-hydroxy-5-isoprenyl- 2-methyl acetate (compound 2)	

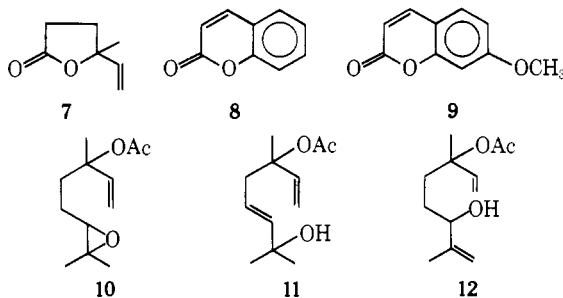
Table III. Compounds Identified in Lavandin Residue

		Reference
Alcohols		
Lavandulol		Naves (1945)
<i>p</i> -Cymene-8-ol		
Lactones		
γ -Methyl- γ -vinylbutyrolactone (compound 7)		Klein and Rojahn (1967)
Coumarin (compound 8)		Igolen (1955)
7-Methoxycoumarin (compound 9)		
Bifunctional compounds		
1-Octene-3-ol-6,7-epoxy-3,7-dimethyl acetate (compound 10)		
3-7-Octadiene-2,6-diol-2,6-dimethyl- 6-acetate (compound 11)		
1,7-Octadiene-3,6-diol-2,6-dimethyl- 6-acetate (compound 12)		

assign the absorption at 7.39μ in conjunction with the carbonyl band at 5.84μ to a methyl ketone group ($\text{CH}_3\text{C}=\text{O}$; Silverstein and Bassler, 1964). Another interesting feature of ir spectrum was the absence of absorption band at $6.97\text{--}7.12 \mu$, which suggested that the molecule did not contain an α -methylene group (CH_2CO ; Silverstein and Bassler, 1964). The weak absorptions at 3.3 , 6.98 , and 12.1μ could be due to the presence of a tri-substituted double bond ($\text{RC}=\text{CHR}$). The mass spectrum showed the molecular ion peak at m/e 206 ($\text{C}_{14}\text{H}_{22}\text{O}$) and major peaks at m/e 43, 39, 41, 91, 93, and 119 (Figure 2).

The ir spectrum of peak 23-A showed absorptions at 5.95 and 6.19μ , due to the presence of an α,β -unsaturated ketone group. The absorption at 7.02μ was due to the presence of an α -methylene group ($\text{CH}_2\text{C}=\text{O}$). The mass spectrum showed the molecular ion peak at m/e 206 ($\text{C}_{14}\text{H}_{22}\text{O}$). The base peak at m/e 164 ($M - 42$) suggested that the molecule contains a partial cyclohexenone structure containing $\text{C}=\text{CCOCH}_2$ group (Budzikiewicz *et al.*, 1967). The major peaks were at m/e 41, 27, 43, 91, and 39 (Figure 3). Due to the lack of material, nmr analyses of both these peaks could not be performed and therefore a structural assignment was not possible.

Identification of the Noncarbonyl Constituents of Less Volatile Lavandin Residue. Analyses of the different column chromatographic fractions of lavandin residue resulted in the identification of lavandulol (Naves, 1945), 8-cymenol, butyrolactone 7 (Klein and Rojahn, 1967), coumarin 8 (Igolen, 1955), 7-methoxycoumarin (9), and bifunctional compounds 10, 11, and 12 (Table III). 7-Methoxycoumarin 9 has been found in lavender oil before (Brown, 1962) but not in lavandin. Among bifunctional compounds, compound 10 is synthetically known, but 11 and 12 have neither been isolated from any natural product nor synthesized before. Ir, nmr, and mass spectra of compounds 1, 2, 3, and 11 (Figures 6-9) were deposited in the microfilm edition.

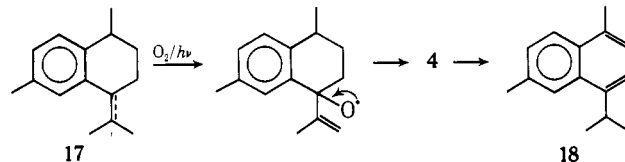


Biogenesis of Bifunctional Compounds (Figure 4). Most of the bifunctional compounds, including lactone 7, thus identified in lavandin oil could arise from further transformation of linalyl acetate 13, which is one of the main components of this oil. According to either autoxidation (Farmer, 1946; Khan, 1954a,b) or photooxidation (Schenck, 1957) theory, oxygen could directly attack the tri-substituted (C_6 and C_7) double bond of linalyl acetate 13 to form the epoxide 10. At the same time, oxygen could attack the carbon-7 to generate the free radical 14, which could not only abstract a proton to form hydroxyacetate 11, but also could undergo disproportionation to give acetoxy ketone 3. Similarly, the attack of oxygen at carbon-6 would give rise to another free radical 15, which could generate both hydroxy acetate 12 and acetoxy aldehyde 16. On further oxidation, compound 16 could generate an intermediate acid which could undergo cyclization to produce the lactone 7 (Figure 4).

Photooxidation of linalyl acetate 13 yielded all the compounds discussed above. It should be noted that acetoxy aldehyde 1 was not found among the photooxidative decomposition products of linalyl acetate. This suggests that acetoxy aldehydes 1 and 2 are produced enzymatically

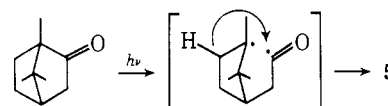
from linalyl acetate and lavandulyl acetate, respectively. Whether or not the other bifunctional compounds are enzymatically or artificially produced is an open question.

Origin of Bicyclic Ketone 4 and α -Campholenal 5. Ketone 4 has not been previously isolated from any natural product, but it is synthetically known. Its structural similarity with known sesquiterpenes (*viz.* calamenene) led us to believe that 4 is probably also a photooxidative degradation product of dehydrocalamenene-type material 17.



Interestingly, it should be mentioned that Johnson and Jones (1947) made 4 and converted it to another sesquiterpene cadalene 18.

Similarly, α -campholenal 5 is probably the photolysis product of camphor (Takeshita and Fukazawa, 1968), which is one of the major carbonyl compounds of lavandin oil.



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