

Essential Oil of French Lavender— Its Composition and Its Adulteration

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The composition of oil of French lavender is extremely complex. Of the approximately 150 constituents presently identified, most are only present in trace quantities. However, they play a very important role in the overall fragrance of this oil. There are numerous other constituents still to be identified.

Among the numerous identified constituents are hydrocarbons, oxides, alcohols, esters, ketones, aldehydes, lactones and phenols.

Figure 1 is a chromatogram of a typical French lavender on which thirty-nine characterizing constituents are identified. The conditions under which the chromatographic analyses were made follow:

Apparatus: Perkin Elmer Sigma 3

Column: Fused silica, capillary; 50 meters long; 0.27 mm diameter

Stationary phase: OV 101

Detector: Flame ionization at 200 degrees C

Carrier gas: Helium; flow rate: 0.75 ml/min; head pressure: 22 psi (1.54 atmospheres)

Recorder: Intersmat ICR 1B

Temperature programs:

First: (for synthetic linalyl acetate ex beta-pinene) 65 degrees C to 180 degrees C at 1.5 degrees C/min; chartspeed: 8 mm/min

Second: (for synthetic linalool ex beta-pinene and synthetic linalyl acetate ex acetylene synthesis) 65 degrees C to 180 degrees C at 2.5 degrees C/min; chartspeed: 10 mm/min

Study of the composition of French lavender shows that the total amount of linalool and linalyl acetate often reaches 60% to 65% and in extreme cases 75% of the total oil. In numerous other essential oils, these percentages are similar and often exceeded. This is the case of lavandin, bergamot, petitgrain, neroli, shiu, and bois de rose.

In view of the importance of these two constituents, a number of chemists attempted to synthesize these chemicals in the early 1950s.

Two routes for these syntheses were quickly developed, the first which we will call acetylenic synthesis resulted in total synthesis from acetone and acetylene, and the second is a semi-synthesis starting with beta-pinene.

If the principle of total synthesis has changed little since, the semi-synthesis, on the other hand, has been subjected to numerous variations of which two can be pointed out. The first one uses myrcene obtained by pyrolyzation of beta-pinene, and the second one uses alpha-pinene directly. As a result, there is a surplus of beta-pinene on the international market place and, as a consequence, a lowering in price.

It is evident that these industrial syntheses do not produce a chemically pure linalool or linalyl acetate. These two products are contaminated with varying quantities and numbers of impurities. Among these impurities, some correspond to elements which are natural constituents of lavender and some are not found in pure lavender.

French Lavender

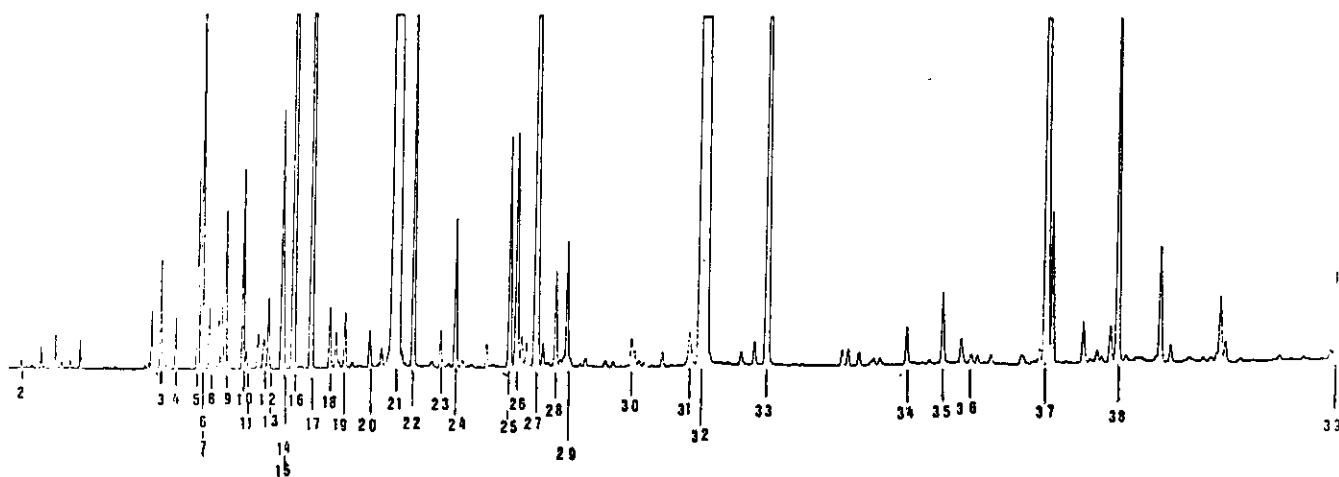


Figure 1. Typical French Lavender

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|--|---------------------------------|----------------------------|
| 1. Methyl Butenol Tertiaire | 14. Linonene | 27. Terpinene-1 Ol-4 |
| 2. Prenol | 15. Cineole-1, 8 | 28. α -Terpineol |
| 3. α -Pinene | 16. Cis β -Ocimene | 29. Butyrate d'Hexyle |
| 4. Camphene | 17. Trans β -Ocimene | 30. Nerol |
| 5. Octene-1 ol-3 | 18. γ -Terpinene | 31. Geraniol |
| 6. Octanone-3 | 19. ψ -Oxyde de Linalyle a | 32. Acetate de Linalyle |
| 7. Methyl Heptenone ? | 20. ψ -Oxyde de Linalyle b | 33. Acetate de Lavandulyle |
| 8. β -Pinene | 21. Linalol | 34. Acetate de Neryle |
| 9. Myrcene | 22. Acetate d'Octene-1 Yle-3 | 35. Acetate de Geranyle |
| 10. Acetate d'Hexyle | 23. Isobutyrate d/Hexyle | 36. Coumarine |
| 11. γ -Methyl γ -Vinyl Butyrolactone | 24. Camphre | 37. Caryophyllene |
| 12. α -Terpinene | 25. Borneol | 38. Humulene ? |
| 13. Paracymene | 26. Lavandulol | 39. Oxyde de Caryophyllene |

If a lavender oil is adulterated with a compound containing synthetic linalool and/or linalyl acetate, these abnormal impurities can be used as tracer elements. Using very definite and precise chromatographic conditions, these tracer elements will permit the detection of the fraud.

In the complete acetylenic synthesis of linalool, the key impurity is dehydrolinalool (1), partial and selective hydrogenation of which produces linalool (2). During hydrogenation, one observes the formation of a small quantity of a product of superhydrogenation, namely dihydrolinalool (3). A tracer element of nonhydrogenated dehydrolinalool also remains as well as some other minor impurities.

In figure 2, the upper portion shows a chromatogram of such a linalool and the lowest chromatogram represents that of a pure lavender. The two chromatograms in between represent oils of lavender with 1% and 5%, respectively, of linalool obtained by total synthesis.

In these chromatograms, the dehydrolinalool (1) was used as a tracer element. The dihydro-

linalool (3) shows up on the chromatogram together with a normal constituent of lavender and, therefore, under the conditions of this analysis, cannot be used as a tracer element.

The preparation of linalyl acetate by total synthesis also brings out dehydrolinalool. This linalyl acetate is directly acetylated by acetic anhydride in the presence of a mineral acid as catalyst. The acetate of dehydrolinalyl (4) is then hydrogenated to produce linalyl acetate (5) with small quantities of non-hydrogenated dehydrolinalyl acetate, acetate of dihydrolinalyl (6) and other minor components.

In this case, elements (4) and (6) can be used as tracer elements. In figure 3, the upper chromatogram represents that of a linalyl acetate obtained by acetylenic synthesis. The lowest chromatogram represents that of an oil of pure lavender, and the two intermediate chromatograms, those of oils of lavender to which have been added 1% and 5%, respectively, of linalyl acetate synthetic.

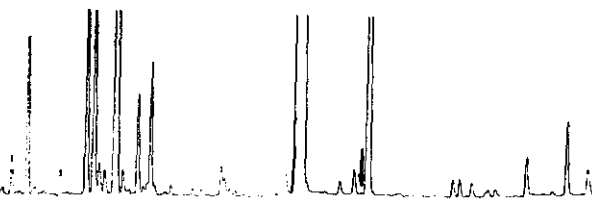
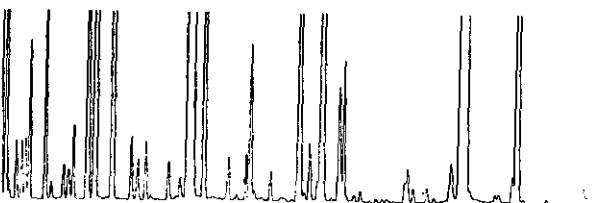
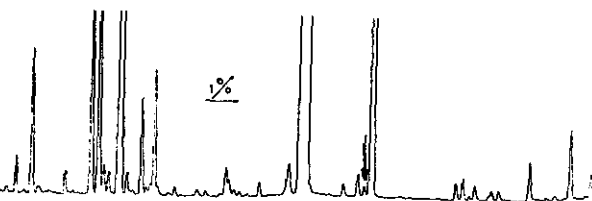
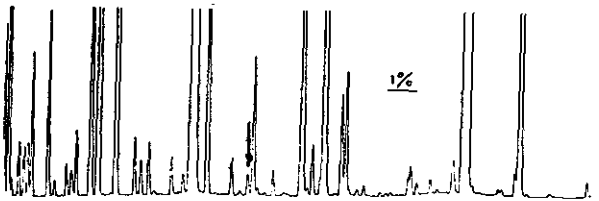
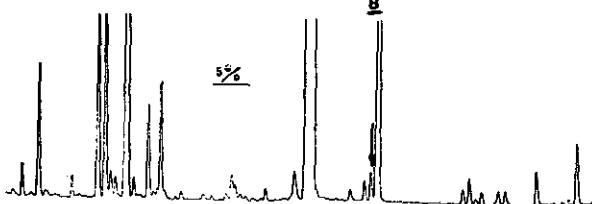
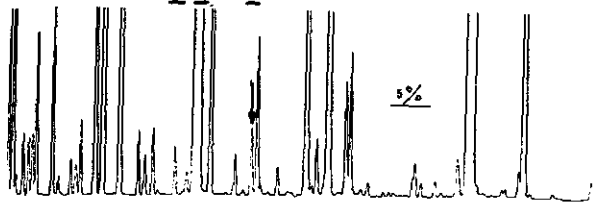
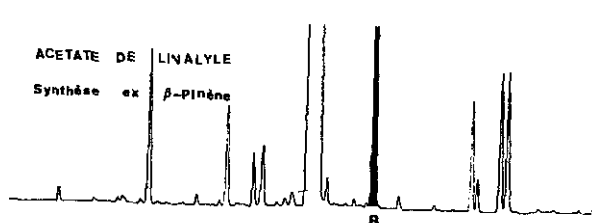
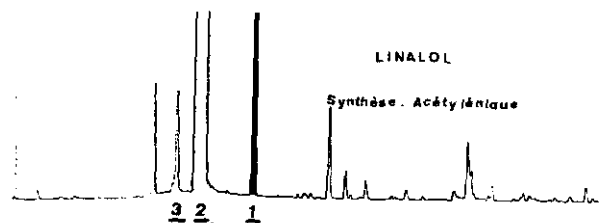


Figure 2

Figure 3

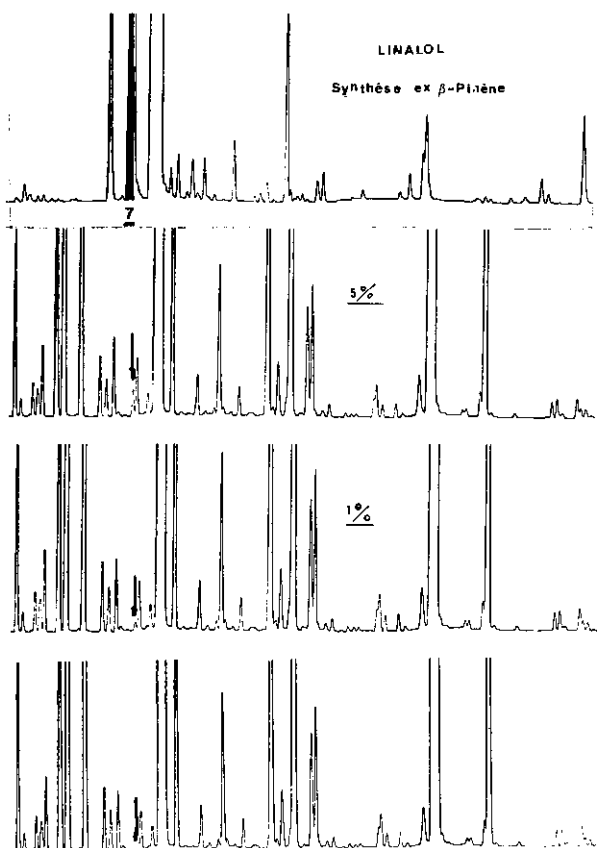


Figure 4

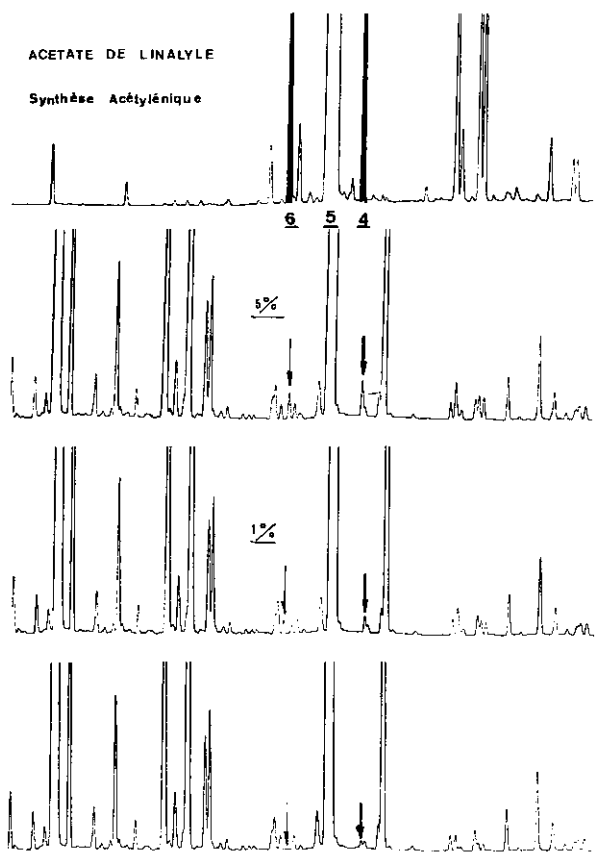
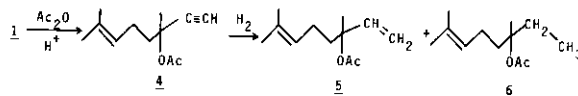
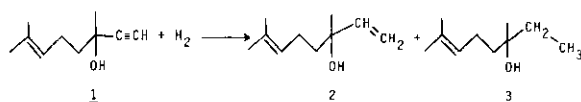


Figure 5



Impurities also show up during the manufacture of semi-synthetic linalool (peak 7 in figure 4) and linalyl acetate (peak 8 in figure 5) from myrcene.

As in the other examples, the upper chromatograms are of linalool (figure 4) and of synthetic linalyl acetate (figure 5) and the lowest chromatograms are of pure lavender. The chromatograms in between represent those of lavender oils to which have been added 1% and 5%, respectively, of linalool and linalyl acetate synthetic ex beta-pinene. (It is to be pointed out that of the chromatographic analysis conditions listed above, in the case of linalyl acetate ex beta-pinene the first temperature program is used, whereas in the other three cases it is the second temperature program that is used.)

We can conclude that, in using very well defined chromatographic analysis conditions, it is possible with a high degree of probability to detect the addition of even 1% of linalool and/or linalyl acetate synthetic in an oil of lavender and to detect with certainty the addition of a quantity of over 2% or 3%.

Finally, we must add that it is only recently that very pure synthetic linalool and linalyl acetate have been on the market. Furthermore, it should be obvious that the method we suggest would not be applicable to essential oils which would be adulterated by these new compounds.

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