Carbon Dioxide Extracted Ingredients for Fragrances

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In today's competitive world of fragrances, all creative perfumers are constantly seeking new, better ingredients or improvements in old ones.

Since the turn of the century, we have taken giant steps forward in the synthesis of aroma chemicals. Now, new low temperature technology is being used to improve the extraction of some old, well established, popular natural products, the essential oils. This new low temperature extraction technique employs carbon dioxide.

CO_2OL Extraction

The use of liquid carbon dioxide as a solvent in a selective extraction technique is not new; it has been known for decades. However, after several years of development, Pauls has reached the stage where we can confidently offer a commercial range of extracts to the creative formulators of the world. Cool extraction of essential oils utilises low temperature, between 0 and +10°C, and high pressure, between 8 and 80 atmospheres. This is a variable technique and the optimum conditions for each natural product are determined experimentally. (See Figure 1.)

At these low temperatures and high pressures carbon dioxide liquifies to become a non-polar selective solvent which is odourless, tasteless, colourless, easily removed and non-flammable: the ideal safe solvent.

The selectivity of carbon dioxide is demonstrated by the extraction of the essential oil plus the lighter fractions of the resin imparting the character of an absolute to the extract. It rejects protein, waxes, sugars, chlorophyl and pigments to yield an extract which more closely resembles the aroma of the botanical starting material than does that of the steam distilled equivalents.

The advantages of CO_2OL extracts compared to conventional oils prepared from the same batch of botanical starting material are:

- No solvent residues. Carbon dioxide is evaporated rapidly in the condenser-evaporator section of the extraction plant. Any traces which might remain are harmless, odourless and tasteless.

- No 'still notes.' Off-odours are sometimes found in freshly distilled essential oils. These 'still notes,' which are usually degradation products of the oil or botanical starting material, will usually evaporate or modify if the oil is allowed to mature. This can take varying lengths of time, which is inconvenient and incurs the cost of storage. CO_2OL extracts, because of their low temperature processing, do not form 'still notes' and do not need a maturation period.

- Lower monoterpene hydrocarbon levels. Extracts from the same starting material prepared using CO_2, compared to steam distilled oil, have much lower monoterpene hydrocarbon levels. These terpenes do not usually

contribute to the function of the oil in products which are water based. (For example, see Juniper berry oil. CO_2OL extracted chromatogram (fig. 2) and steam distilled chromatogram (fig. 3). A redrawn illustration of figures 2 and 3 plotting percentage component against retention index on a carbowax 20M stationary phase column is shown in figure 4.[2,3])

- More topnote. Low temperature extracts contain some components which are not present in steam distilled oils. This may be because they are soluble in the water phase, or just evaporate from the system during steam distillation. (For example, see hop oil CO_2OL extracted chromatogram (fig. 5) and steam distilled chromatogram (fig. 6). A redrawn illustration of figures 5 and 6 plotting percentage, component against retention index on a methyl silicone stationary phase column is shown in figure 7.[4])

- More backnote. The solvent character of carbon dioxide gives an extract consisting of essential oil and the top fraction of the resinoid. This imparts the character of the absolute to the extract but without the poorly soluble resins which impair its solubility. In the case of ginger roots, the steam distilled oil is colourless but the cool extract is a golden brown mobile oil. This is in contrast to the resinoid prepared with other nonselective solvents which is very dark brown and sometimes so viscous as to be solid. (See figure 8—ginger oil CO_2OL extracted and figure 9—ginger oil steam distilled. A redrawn illustration of figures 8 and 9 plotting percentage component against retention index on a methyl silicone stationary phase column is shown in figure 10.[4])

The carbon dioxide extracts are often more concentrated than steam distilled oils or extracts prepared with less selective solvents. They are also generally of finer odour and better fixed, hence longer lasting than steam distilled oils. Of course, conventional solvent extracts using smelly solvents like acetone, ethyl acetate or methanol are also longer lasting than steam distilled oils, but these solvent extracts are difficult to use in water-based products where their fat and wax contents cause them to precipitate. In soaps and detergents, conventional solvent extracts fulfil a fixing role very well if you use enough of them to compensate for their non-odourous content. However, in extrait perfumes

Figure 1.

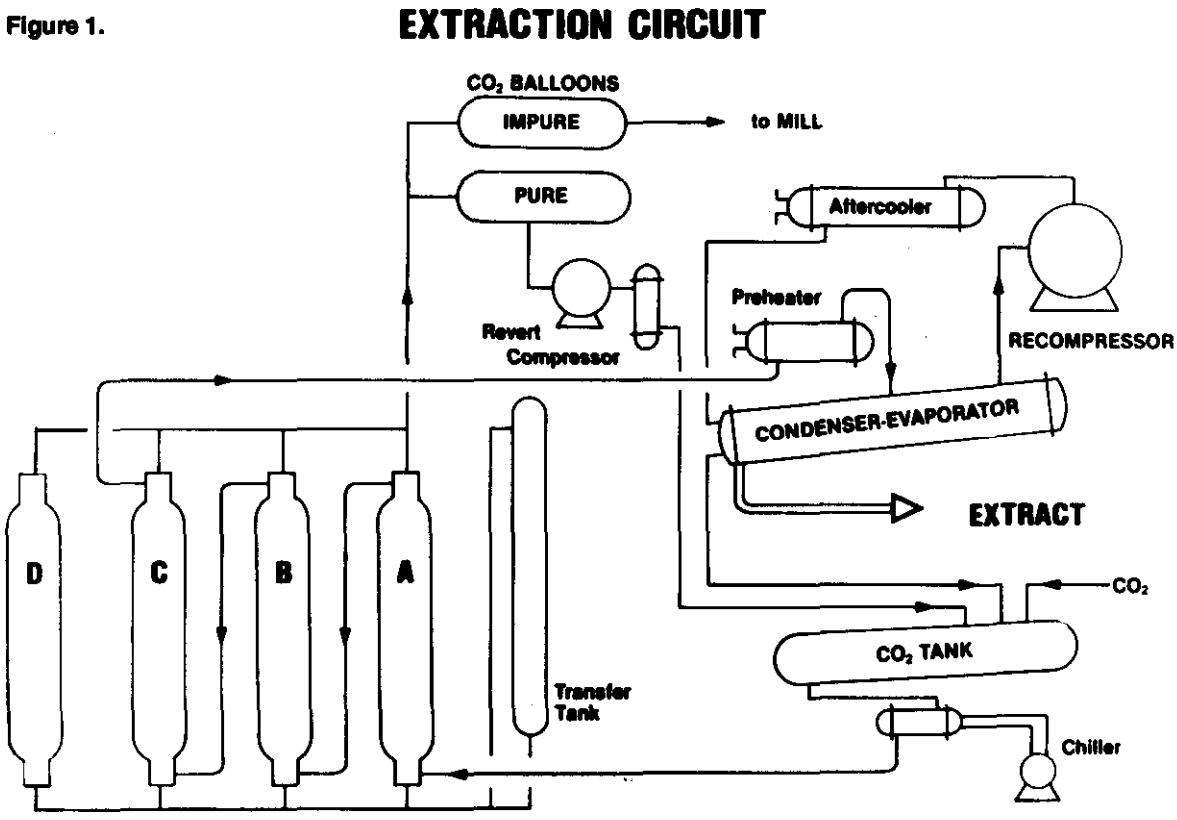


Figure 2. CO_2OL EXTRACTED JUNIPER BERRY OIL

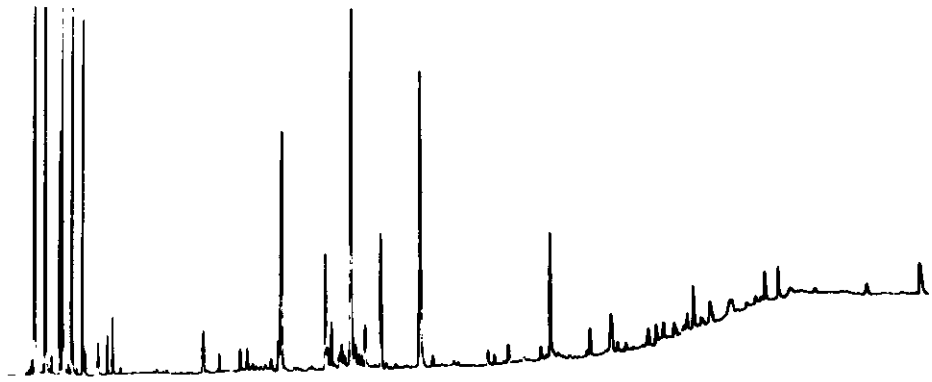


Figure 3. STEAM DISTILLED JUNIPER BERRY OIL

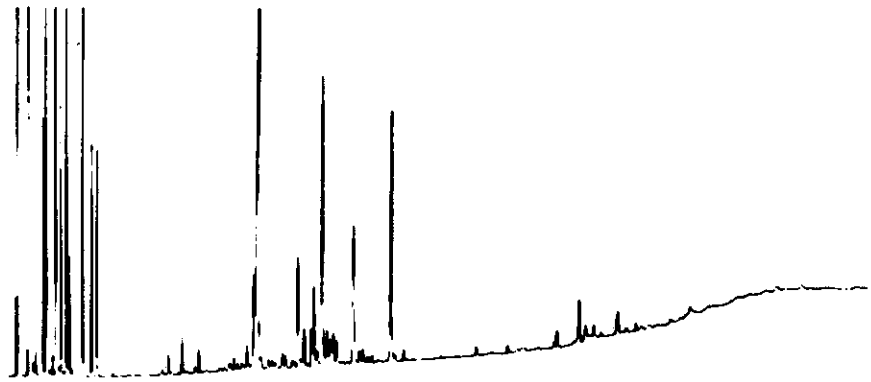


Figure 4.

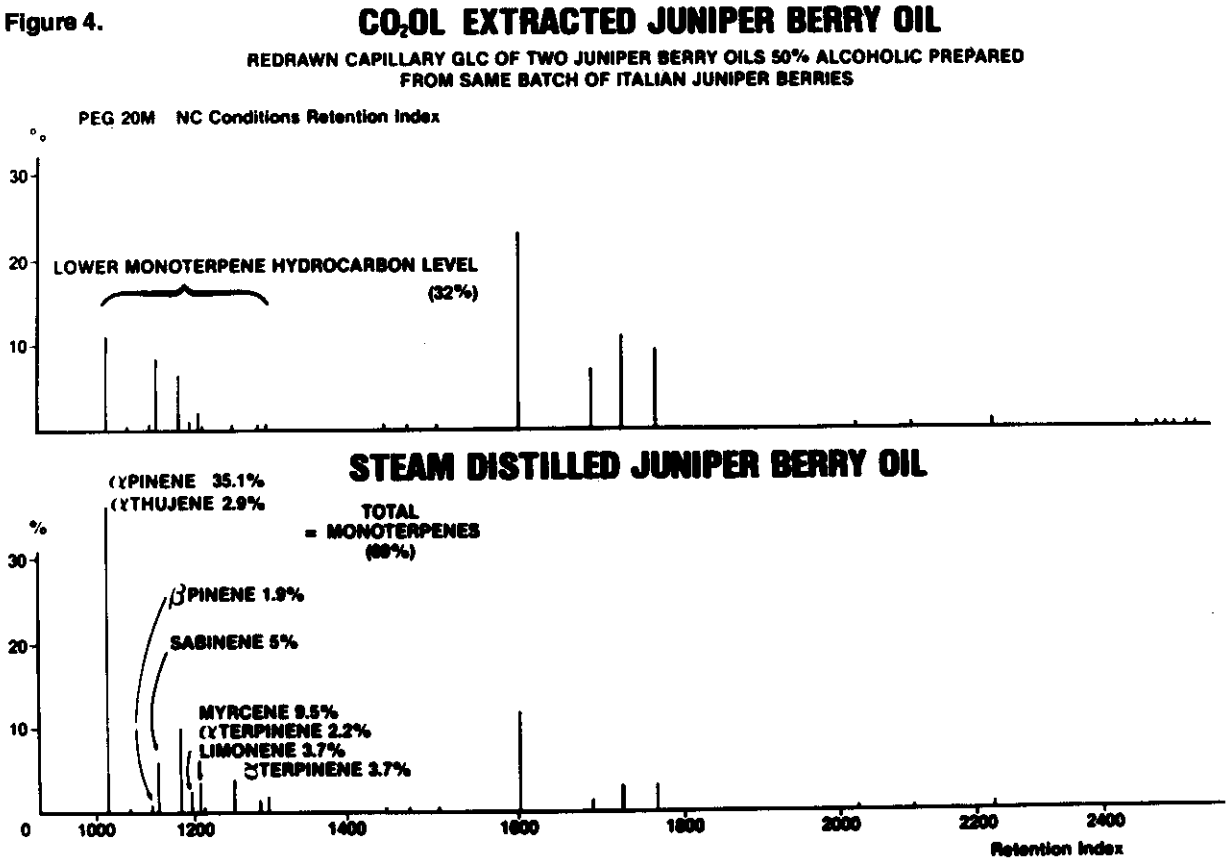


Figure 5. CO_2OL EXTRACTED HOP OIL

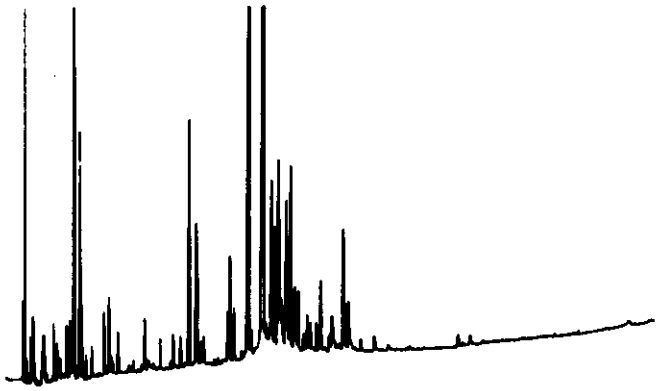
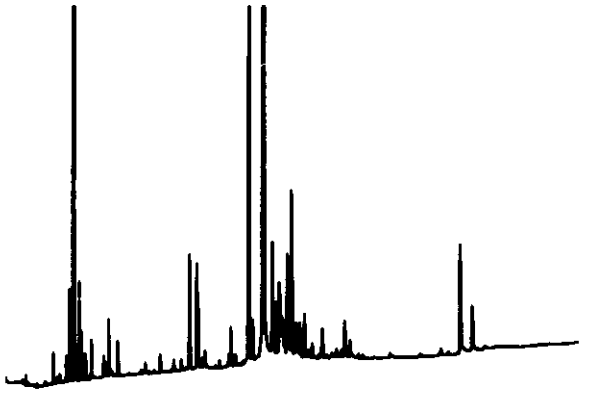


Figure 6. STEAM DISTILLED HOP OIL



or colognes, a selective extract is a cleaner, altogether more elegant ingredient. Where many creations contain a preponderance of aroma chemicals, the benefit of using new natural products to give soul to a fragrance skeleton is readily appreciated.

Uses

Truly terpeneless essential oils can be prepared from CO_2OL extracts by using the additional technique of extremely high vacuum molecular distillation with the minimum of heat. This process removes the 'absolute character' of the carbon dioxide extract to give an ingredient which is terpeneless. A terpeneless extract in which the terpenes were never generated is completely different from conventional terpeneless oils in which the oil is steam distilled from the botanical with heat, and then heated again to fractionate off the terpenes. The cool method is so much more refined and gives an ingredient of superior odour and solubility in which the terpenes were never formed. (For example, ginger oil terpeneless CO_2OL extracted chromatogram (fig. 11) and conventional chromatogram (fig. 12). A redrawn illustration of figures 11 and 12 plotting percentage component against retention index on a methyl silicone sta-

Figure 7.

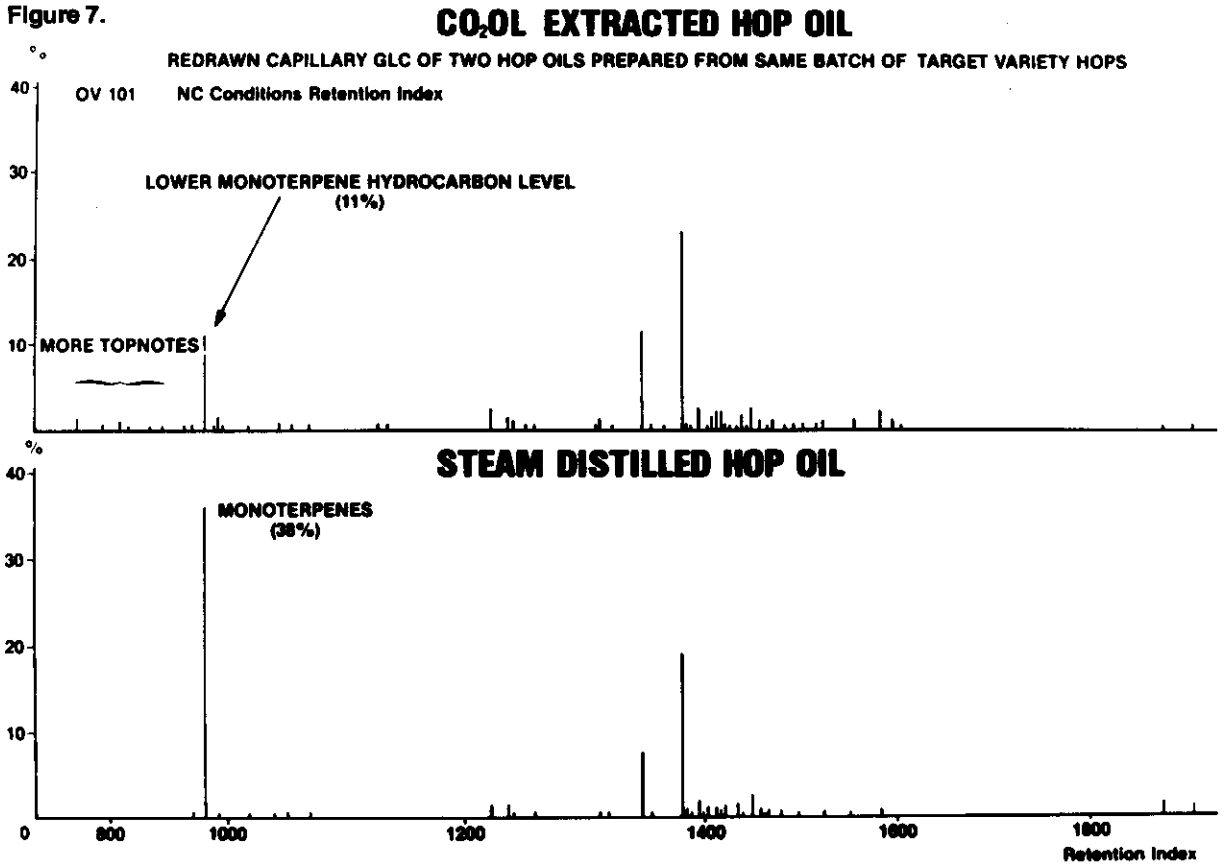


Figure 8. CO_2OL EXTRACTED GINGER OIL

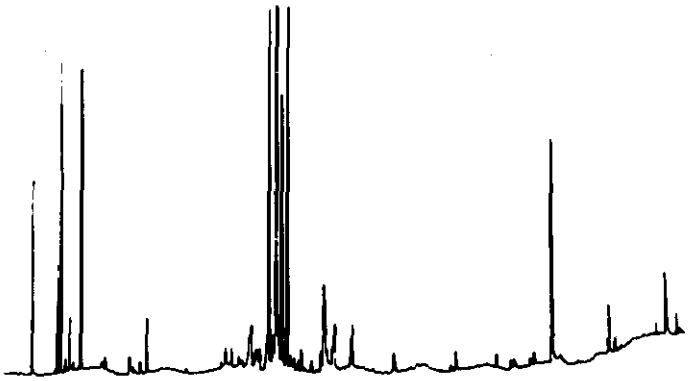


Figure 9. STEAM DISTILLED GINGER OIL

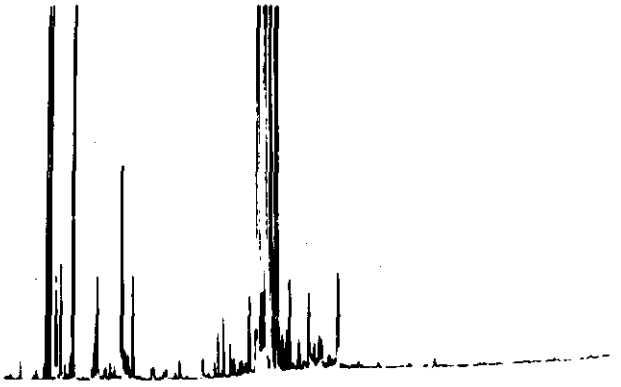


Figure 10.

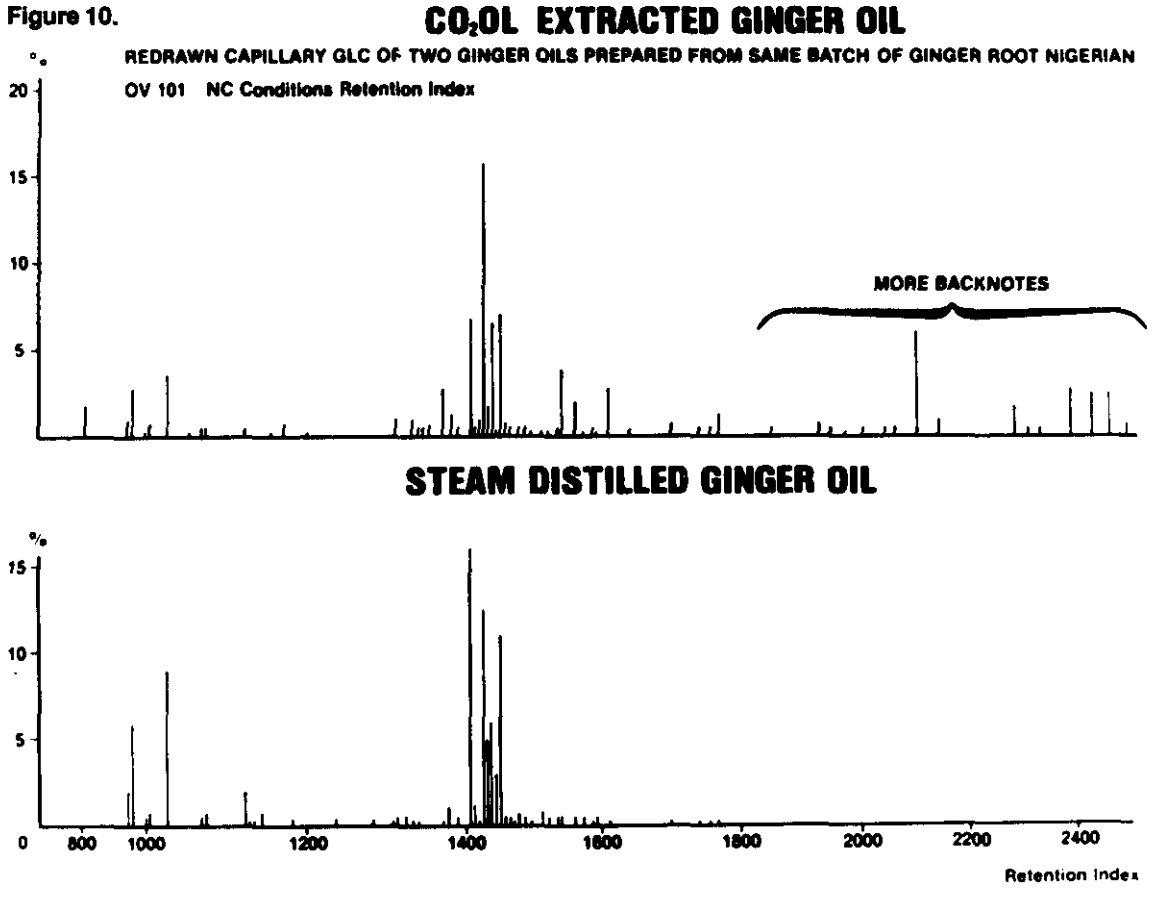


Figure 11. CO_2OL TERPENELESS GINGER OIL

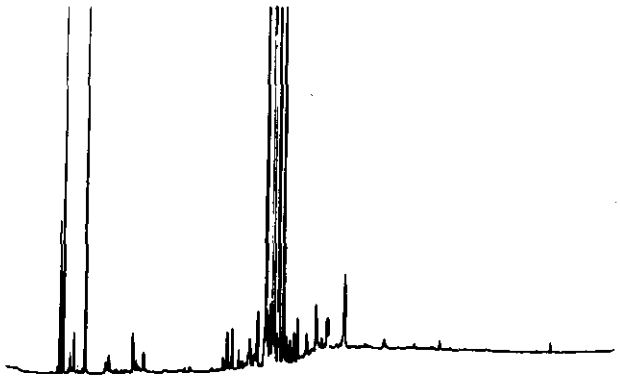
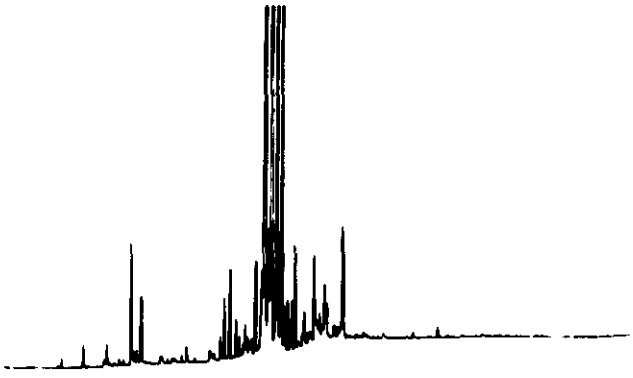


Figure 12. STEAM DISTILLED + FRACTIONALLY DISTILLED TERPENELESS GINGER OIL



tionary phase column is shown in figure 13.[4] Note here the similarity in profile, but the extra top notes in the 'cool terpeneless' oil.)

Summary

CO_2OL extraction is the use of low temperature and high pressure liquid carbon dioxide to prepare fine quality essential oils without using heat. These extracts have clear advantages which when built into new creations could help create new winning fragrances.

References

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3. Fingerprinting of essential oils Carbowax 20M stationary phase, Analytical Methods Committee of The Chemical Society, Essential Oil Subcommittee, The Analyst (London), 205, 262-273, 1980
4. Fingerprinting of essential oils Methyl silicone stationary phase, Analytical Methods Committee of The Chemical Society, Essential Oil Subcommittee, The Analyst (London), 106, 448-455, 1981

Figure 13. CO_2OL TERPENELESS GINGER OIL

REDRAWN CAPILLARY GLC OF TWO TERPENELESS GINGER OILS PREPARED FROM SAME BATCH OF GINGER ROOT NIGERIAN