The Composition of Volatile Oils Derived from Oleoresins[1]

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ABSTRACT

Essential oils and oleoresins derived from spices and herbs, by steam distillation in the former case or by solvent extraction in the latter case, are increasingly more important as flavoring constituents in heat-processed foods. Steam-distilled oils, when used for such purposes, tend to steam-distill during the heat processing due to moisture that is present. Oleoresins that contain the essential oil and natural fixatives tend to depress this volatilization and are preferred as flavoring materials in such cases. Subjective flavor panel evaluations are reported, showing the significance between oleoresins and essential oils as well as the corresponding spice or herb. Instrumental evaluation, primarily gas chromatography, will compare essential oils produced by direct steam distillation vs. those isolated form oleoresins. The difference in composition which can be related to the improved flavor effect from oleoresins is discussed.

INTRODUCTION

Growth of convenience foods during the past decade has resulted in greatly increased use of oleoresins for flavoring purposes in these products. Oleoresins are solvent-extracted materials from spices and herbs. The solvent is carefully removed by distillation under vacuum to conform to Federal Regulations on residual solvents (1). The spice or herb is prepared for extraction by grinding, which frees or ruptures the flavor cells to permit ready extraction. The solvent is circulated through the bed of spices or herbs and removes the flavor constituents (mainly as essential oil), resins, gums and other materials that are soluble in the solvent selected for the particular oleoresin to be produced. The solvent is then recovered, leaving behind a somewhat viscous material known as the oleoresin.

In the past, before oleoresin technology reached its modern stage, the only large volume spice or herb derivatives available to the food processor were the essential oils. In contrast to oleoresins, essential oils are produced by direct steam or water distillation from a spice or herb. The process makes use of the volatility of the essential oil constituents and their attendant insolubility in water. Distillation is carried on until the spice or herb is exhausted, that is, until no more essential oil can be detected in the distillate. After drying the essential oil and removing the water and in some cases rectifying the result, the essential oil was offered as a means of producing spice or herb flavors in food products and other applications. However, as noted above, essential oils by their very nature are volatile. The process used for isolation is steam distillation. Hence the food product incorporating them, especially when moisture was present and the food was heat-processed, often lost some of the flavoring components. Thus oleoresins have come to be preferred over essential oils for such food processing, since the extracted

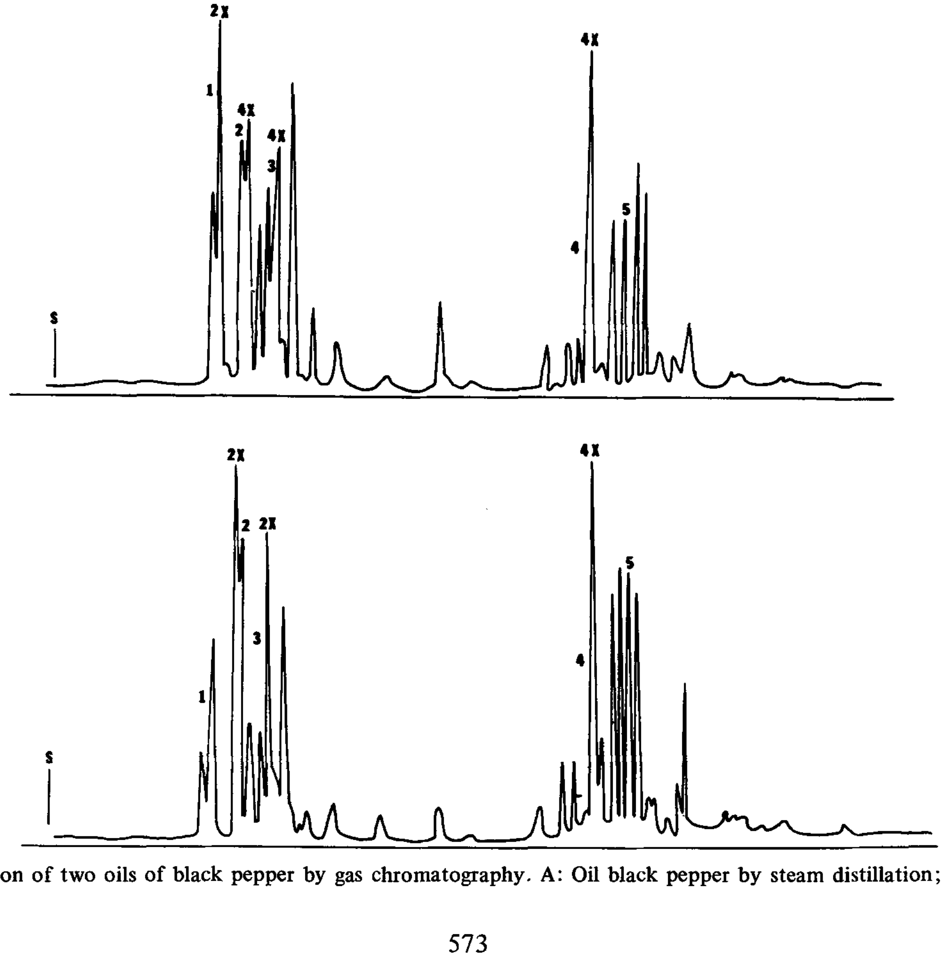

FIG. 1. Comparison of two oils of black pepper by gas chromatography. A: Oil black pepper by steam distillation; B: oil black pepper from oleoresin.

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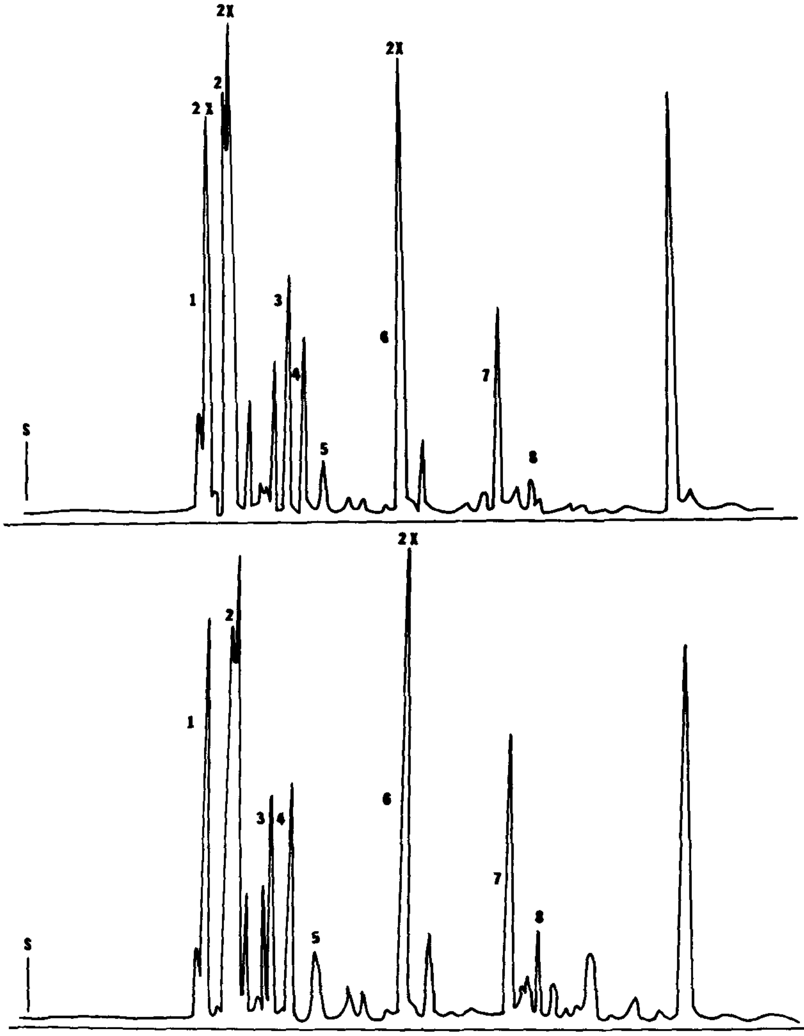

FIG. 2. Comparison of two oils of nutmeg by gas chromatography. A: Oil nutmeg by steam distillation; B: oil nutmeg from oleoresin.

material has been demonstrated repeatedly in actual use as more stable to heat processing than the essential oil. Furthermore solvent extraction removes from the spice or herb not only the essential oil which is primarily responsible for the flavor but also other constituents of a nonvolatile nature. These will be retained in the food product undergoing heat processing and at the same time tend to fix or stabilize the more volatile essential oil component. Fixation prevents evaporation or steam distillation of the volatile components during heat processing.

This phenomenon of stability of flavor produced by oleoresins has, up to now, been based primarily on empirical observation both in the laboratory and in commercial applications. Organoleptic comparison studies performed on foods have shown that an essential oil used for flavoring tends to be lost during heat processing, but where an oleoresin counterpart is used a more powerful flavor results, evidently more resistant to such losses under identical conditions.

In a paper presented by Downey and Eiserle (2), various oleoresins were compared to the corresponding spices and their essential oils in baked goods. Flavor panels were selected to evaluate the results, and in all cases the baked goods product flavored with the oleoresin was preferred for flavor over both the corresponding spice and essential oil. This illustrated that oleoresins were more stable in a food processed by baking, but no detailed explanation for the effect was presented at that time.

Widespread industrial use has also demonstrated the desirability of an oleoresin compared to an essential oil for flavoring heat-processed foods such as soups, sauces and meats. Basically this stability can be attributed to the fact that nonvolatile components are present in oleoresins but absent in essential oils. For some spices such as pepper, only the oleoresin is used since it contains the nonvolatile pungent principle, piperine, which gives the food this desirable flavoring characteristic of pepper spice. The corresponding essential oil of black pepper has a pleasant pepper-like aroma but none of the pungency. Other spices and herbs in which the nonvolatile components do not play as important a role for total flavor also exhibit greater stability. By analogy one can attribute this effect to the nonvolatile components, which in many cases are flavorless, but also tend to act as natural fixatives for the volatile oil constituent.

It occurred to us that, although this explanation is valid, it is not sufficient to explain the profound difference often noticed by flavor panels when essential oils were compared to oleoresins in heat-processed foods. For this reason we decided to compare the essential oil component as isolated from an oleoresin with an essential oil produced from the same spice by direct steam distillation. Classically oleoresins are analyzed for essential oil content by the Clevenger method of steam distillation. In this technique a weighed quantity of the oleoresin is mixed with water, and the mixture is stirred and heated allowing it to come to reflux, the essential oil being collected in a trap. The recovered essential oil, when examined for the usual physical and chemical properties, usually shows differences in these properties as compared to an essential oil produced by direct steam distillation. Therefore it was apparent that different concentrations of volatile components are present, even though the same raw material is used for the preparation of each product. Extraction techniques affect not only the composition of the product in regard to the nonvolatile components but also the concentration of the constituents of the volatile oil.

The Essential Oil Association (EOA) has prepared specifications for many essential oils produced directly by steam distillation and reports the specifications for such oils in their *Book of Specifications* (3). For example, Oil Black Pepper, EOA Specification No. 102, shows a refractive index at 20 C from 1.4795 to 1.4880, whereas EOA Specification No. 240 for Oleoresin Black Pepper shows a refractive index for the isolated oil derived by steam distillation which amounts to ca. 25 ml/100 oleoresin, as 1.4790 to 1.4890 at 20 C. It is noted that a slightly wider range is given with an increase on the higher side. Since terpenes have lower refractive indices than oxygenated components, the specification for the oil derived from the oleoresin seems to indicate that such oil may be lower in terpene content than one derived by direct steam distillation from the spice.

EXPERIMENTAL PROCEDURES

In order to substantiate whether the composition of essential oils produced by direct steam distillation differs from the essential oil isolated from an oleoresin, we decided to investigate the composition of such oils using gas chromatography. Significant differences were expected, particularly in the ratio of low boiling terpene constituents vs. high boiling components. On a commercial scale essential oils produced by steam distillation directly from the spice are normally distilled for ca. 30 hr to assure optimum yield and total recovery of the essential oil. During the time of distillation, the more volatile components are more readily isolated with the highest percentage of the oil being collected during the first several hours. In the remaining time only small percentages of oil are collected, but these are rich in high boiling constituents.

We examined essential oils and oleoresins from three different spices in this study: Tanzanian Clove, Malabar Black Pepper and East Indian Nutmeg. In the latter case, sound, whole nutmegs were used, since the usual commercial grade of East Indian Nutmegs used for the distillation of essential oil is commonly known as "wormy" nutmeg in which the nutmeg butter has been removed resulting in a somewhat porous matrix in which the essential oil cells are found. However by Federal Regulation Oleoresin Nutmeg cannot be produced from this quality of nutmegs, and hence the essential oil and the oleoresins were produced from sound East Indian Nutmeg commonly referred to as "grinders" in the trade.

I. Conditions for Gas Liquid Chromatographic
Analysis of Oil Black Pepper

A. 200 ft 0.03 in. ID OV-101 Capillary
B. 70 C to 110 C at 2 C/min
C. 110 C to 190 C at 4 C/min
D. 10 ml/min Helium
E. 12 psi Hydrogen, 50 psi air
F. Injection port: 280 C; detector: 260 C
G. Sample size: 0.04 μliters
H. Range: 100; attenuation: 8X
I. Chart speed: 20 ins/hr

Comparing the volatile oils from Malabar Black Pepper, we used a 200 ft capillary column in a Perkin-Elmer 900 Series gas chromatograph instrument using the conditions presented in Outline I. The resultant curves in Figure I show that the volatile oils are composed chiefly of two classes of compounds (the numbers in parentheses refer to Figure 1): the terpenes, including alpha pinene (1); beta pinene and sabinene (2); limonene (3); and the sesquiterpenes of which the main constituent is caryophyllene (4). Less than 5% of the oils are composed of oxygenated components. The differences between the two curves are seen to be quantitative rather than qualitative: the same constituents are present in each case except in different percentages. Oil Black Pepper distilled directly from the spice shows approximately twice the amount of low boiling terpene constituents and only two-thirds of the amount of the sesquiterpenes compared to the oil derived from the oleoresin. Hence the essential oil component of the oleroresin, which amounts to ca. 25% by weight, has a heavier character and is therefore of itself less volatile due to the diminished concentration of the low boiling terpene constituents. Likewise it should be less susceptible to oxidation, since terpenes are known to be more labile to oxidation and to polymerize more readily. Thus the oleoresin containing an essential oil of such a composition would be expected to be more stable and resistant to oxidation.

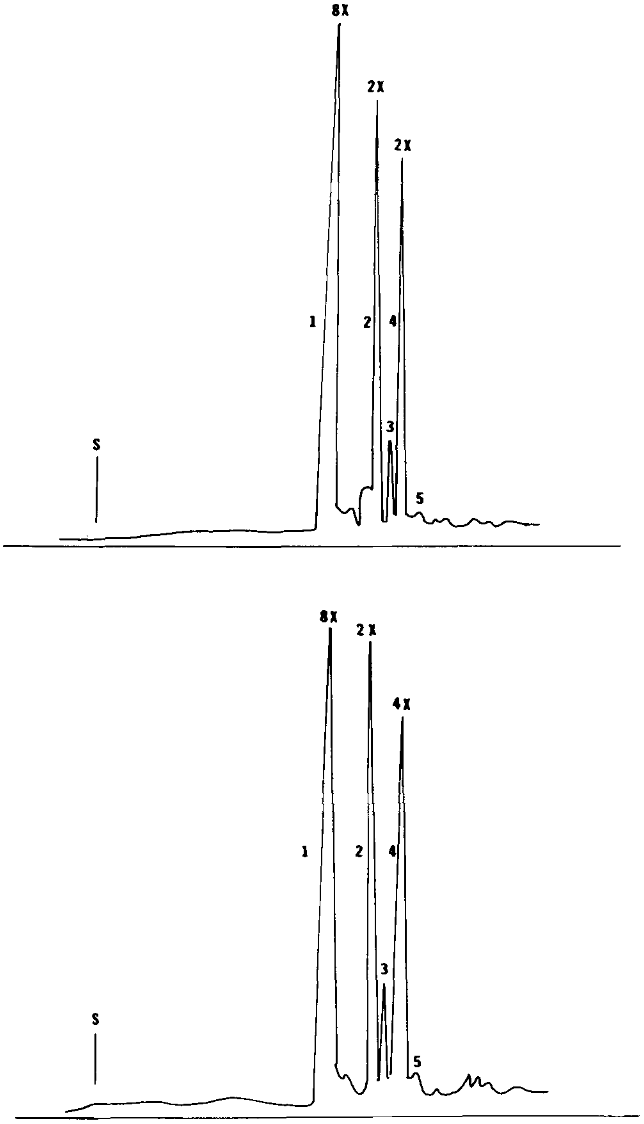

FIG. 3. Comparison of two clove oils by gas chromatography. A: Oil clove by steam distillation; B: oil clove from oleoresin.

An explanation for this difference in composition can be traced to the method of isolation. You will recall that we stated the steam distillation process takes ca. 30 hr, the first third of which isolates the more volatile components with the remaining operation isolating more high boiling constituents. In the oleoresin all materials are extracted simultaneously and have relatively the same solubility in the solvent used for extraction. Thus the sesquiterpenes ought to be present in an oleoresin at a higher concentration. During steam distillation the sesquiterpenes would distill very slowly toward the end of the process, and more could probably be collected if the time were extended to greater than 30 hr. Commercially, however, this would be uneconomical and impractical.

II. Conditions for Gas Liquid Chromatographic Analysis of Oil Nutmeg

A. 200 ft 0.03 in. ID OV-101 Capillary
B. 70 C to 90 C at 2 C/min
C. 90 C to 190 C at 4 C/min
D. 10 ml/min Helium
E. 12 psi Hydrogen; 50 psi air
F. Injection port: 280 C; detector: 260 C
G. Sample size: 0.04 μliters
H. Range: 100; attenuation: 8X
I. Chart speed: 20 ins/hr

The East Indian Nutmeg Oils were examined on the same 200 ft capillary column and instrument as were the Black Pepper Oils described above, but using the conditions as described in Outline II. We note more profound differences in composition in Figure 2. Nutmeg oil consists chiefly of terpenes, but the oxygenated components characterize the flavor of the oil more specifically than in the case of Oil Black Pepper. When the oil is distilled directly from the spice, more of the low boiling terpene components were present than in the oil isolated from the oleoresin (the numbers in parentheses refers to Figure 2): alpha pinene (1), beta pinene and sabinene (2) are present in greater concentration in the essential oil as compared to the oleoresin. However those terpenes which are less volatile, mainly limonene (3), gamma terpinene (4) and terpinolene (5), are found at approximately the same concentration in both oils. Surprisingly the major alcoholic constituent, terpinen-4-ol (6), which has an intermediate vapor pressure, is present in both oils in approximately the same concentration. The other oxygenated components such as eugenol (8) and other phenolic ether derivatives (7) are at a much higher concentration in the oleoresin, as compared to the essential oil produced by direct steam distillation. Since phenolic constituents are known to exhibit antioxidant effects, this may account for the comparative stability of the oleoresin compared to the essential oil. Higher concentrations of such components in the oleoresin would tend to stabilize the terpene constituents to a greater degree, particularly since their concentration is relatively lower. Furthermore these phenolic derivatives are less volatile and have a characteristic nutmeg odor and flavor, and their higher concentration would tend to make the oleoresin truer to the flavor of the natural spice than the essential oil, in which terpenes predominate and the phenolic derivatives are at a lower concentration. In addition the oleoresin contains appreciable concentrations of nonvolatile myristic acid esters, possibly trimyristin, which act as a sort of carrier for the essential oil component. Of itself, it has little nutmeg flavor, but is a solvent for the oil and tends to act as a fixative.

III. Conditions for Gas Liquid Chromatographic Analysis of Oil Clove

A. 1/8 in. OD x 0.10 in. ID Stainless steel
B. 18 ft 5% OV-101 Chromosorb W HP 80/100 mesh
C. 120 C to 230 C at 4 C/min
D. 30 ml/min Helium
E. Injection port: 270 C
F. Detector: 280 C
G. Sample size: 0.5 μliters
H. Chart speed: 15 ins/hr

When Clove Oils were examined by gas chromatography, an 18 ft 1/8 in. packed column was used employing the conditions given in Outline III. Clove spice itself contains insignificant trace amounts of terpenes, and hence the essential oils produced either directly by steam distillation or from the oleoresin show practically no monoterpenes present. Yet there are significant differences of a quantitative nature found mainly in the concentration of eugenyl acetate. When Clove Buds are steam distilled to isolate the essential oil, this phenol ester is usually present in the range of 5 to 12%. In the oil from the oleoresin, the concentration is greater than 18% (the numbers in parenthesis refers to Figure III): all other components, mainly free eugenol (1), beta caryophyllene (2) and beta humulene (5) (the sesquiterpene components) are approximately equivalent in concentration in both types of oils. There is a minor amount of isocaryophyllene (3) in the oil derived by direct steam distillation, whereas the oil isolated from the oleoresin exhibits only a trace of this component. Other minor quantitative differences due to uncharacterized components are seen, but the major difference is found in the eugenyl acetate (4) concentration. This can be explained readily by reviewing the method of preparation. We believe that high concentrations of eugenyl acetate must naturally be present in the spice. However steam distillation, especially the use of high pressure steam distillation, would tend to hydrolyze the eugenyl acetate, and the resultant oil would show lower concentrations of this ester, the free eugenyl increasing proportionately. Likewise some of the naturally occurring caryophyllene could isomerize under these slightly acidic conditions and show up as isocaryophyllene. Thus the extracted product is not subject to hydrolysis, and the processing for oleoresin would remove from the spice that which is actually present without alteration. Since eugenyl acetate is often used for its fixative properties both in flavors and perfumery, the fact that it is present at ca. 50% higher concentration in the oil isolated from the oleoresin would account for the unusual stability and truer flavor character of the oleoresin as compared to the steam distilled essential oil.

DISCUSSION

In reviewing our results we have shown that differences both in concentration and constituents are found in oils derived from an oleoresin as compared to the corresponding steam-distilled oils. A single explanation cannot be given for the empirically demonstrated greater stability of oleoresins compared to essential oils. However a common thread does run throughout all these observations: namely, that higher boiling constituents, be they sesquiterpenes, oxygenated derivatives or esters having higher boiling points, are present in greater concentration in the essential oil portion of oleoresins. Conversely, essential oils produced by direct steam distillation seem to have higher concentrations of low boiling constituents, and these essential oils would be expected to be more volatile than the corresponding essential oil obtained from an oleoresin. We believe that this exercise, using the gas chromatograph to identify components of essential oils prepared directly by steam distillation compared to those present in oleoresins, lends a more scientific, rational basis to what has been observed empirically for many years. Oleoresins are truer to the spice or herb in flavor character and tend to withstand high temperature processing to a greater extent than comparable essential oils. This phenomenon can now also be attributed to the composition of the essential oil present in an oleoresin, in addition to the influence of the nonvolatile constituents.

REFERENCES

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