A Micromethod to Generate and Collect Odor Constituents from Heated Cooking Oils[1]

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ABSTRACT

A small stainless steel reactor about one-millionth the volume of a home kitchen, was built to generate odors from cooking oils heated to deep fat frying temperatures. This "microroom" was designed so that volatiles could be collected from 1-5 ml of heated oils (193 C) directly on a gas chromatographic column, cooled to -60 C and subsequently separated by temperature programing up to 250 C. Evaluations showed that heated oil odors from the microroom were similar to those room odors produced by heating to 193 C 300 ml of cooking oil in an open vessel; exposure to subambient conditions did not affect the separation efficiency of the gas chromatographic column. Provisions were made for three independent means of effluent monitoring: flame ionization detection, odor analyses and mass spectrometry.

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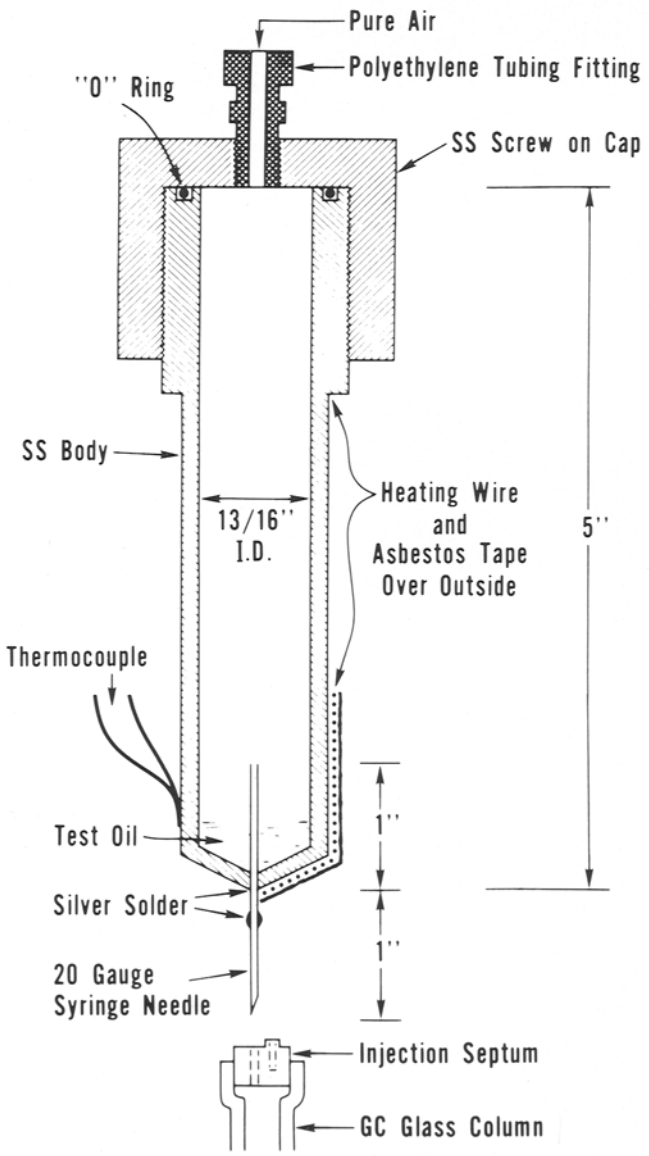

FIG. 1. Stainless steel reactor designed to simulate deep fat frying conditions and to collect directly on a gas chromatographic column odors from 1 to 5 ml of heated soybean oil for evaluation.

INTRODUCTION

Odor volatiles and the psychophysiological response to them frequently determine the acceptability of a food product. Introduction of a new or modified food item must also take into account cultural food patterns of the geographic area. For example in the Mediterranean region, attempts to substitute other edible oils for the familiar olive oil in deep fat frying raised strong objections. In 1968 under the sponsorship of the Soybean Council of America, samples of U.S.-made hydrogenated-winterized soybean salad oils were taken around the world. This soybean oil had retained the highest stability known after long term storage (1). Still when a manager of an Italian extraction plant, located near Rome, heated the American oil in a cast iron frying pan to 190 C, he characterized the odors that remained in an empty room after 1 min as unfamiliar and objectionable. This experience further showed the need for room odor tests in evaluating edible oils that would reflect the reactions of the potential user. The deficiency of the salad oil taken abroad in 1968 as a high temperature cooking oil was later confirmed in controlled odor panel evaluations (2) and could be corrected by the use of a copper hydrogenation catalyst (3). Identifying the characteristic fishy room odors that develop when unhardened soybean oil is heated motivated our investigation.

Prior investigations of room odors from heated cooking oil appear to be limited to those of Cowan et al. (3) and Evans et al. (2). In their studies, 20 experienced judges described odors generated in laboratory-size rooms on heating edible fats. In other investigations, separated constituents of heated oil odors have also been analyzed by collecting volatiles from 5 to 2500 ml of oil heated in the range of 155-210 C (4-11). Volatiles have been collected by passing an inert gas over or through the oil (6,7), by steam (10) and by vacuum (8) distillation. Although condensates can be separated by gas chromatography (GC), a transfer step is necessary from the collection apparatus to the GC column. One technique sweeps residual solvents and autoxidation products from a vegetable oil sample placed in a GC injection port liner directly onto a column (12). That technique was designed to analyze dissolved compounds in aging oil but not to collect and analyze room odor constituents arising from heated oils.

This paper describes a system for studying room odors that includes collection of heated oil volatiles, GC separation, sensory evaluation and mass spectrometric analysis of the separated compounds. The system employs an all stainless steel (SS) reactor which has roughly one-millionth the volume of a home kitchen and is referred to as a microroom. It was designed to achieve three objectives: (a) Only small quantities of oil (1-5 ml) are required; (b) room odors generated are comparable to those noted when larger volumes of oil are heated for cooking purposes; and (c) a transfer step is eliminated by trapping heated oil volatiles directly on a cold (-60 C) GC column.

EXPERIMENTAL PROCEDURES

The microroom designed for use in analysis of heated oil

odor was machined from a solid piece of SS (Fig. 1). A 2 in. piece of a 20-gauge SS syringe needle was inserted through a hole in the bottom of the container and silver-soldered into place. One inch of the needle protruded up into the microroom. This distance permitted taking odor samples from the vicinity of the oil surface but prevented hot oil from entering the GC system. The needle extending 1 in. below the microroom provided a means of injecting volatiles directly onto a cooled GC column. A bead of silver solder on the needle helped make a tight seal when the needle was inserted in the GC septum. The top of the microroom was sealed with an "O" ring and screw cap equipped with a 1/4 in. brass Poly-Flo polyethylene tube fitting (Imperial-Eastman). Insulated heating wire overwrapped with asbestos tape was wound around the microroom from the protruding needle up to the screw-on cap. A comparison of temperatures between the outside of the microroom (measured by a thermocouple soldered to it) and the oil contained in it showed only a 3 C difference at 193 C.

The commercial refined, bleached and deodorized soybean oil (SBO) used had a peroxide value of 0.0. When this oil was heated to 193 C in an open room, fishy and rancid odors were generated.

High purity dry air (The Mathison Co.) continually swept odors generated from oil heated in the microroom through the syringe needle onto a GC column held at -60 C. The sweeping air was measured with a flowmeter connected in series with the 1/4 in. polyethylene tubing leading from the compressed air tank to the fitting on the cap of the microroom.

An on-column injection GC (Packard 7400 series) was used to separate collected volatiles. Circuitry of the Model 873 deviation temperature controller unit was modified to allow the column oven to be cooled to -60 C and also to be temperature-programed from that level. To reach the -60 C temperature, dry ice was placed in a screen container located within the periphery of the 9 in. coiled glass column. Temperatures of the injection port and of the flame ionization detector (FID) oven were 180 and 250 C, respectively.

Hot oil volatiles were collected and separated on a 14 ft x 4 mm ID glass column packed with 10% OV-101 on 100/120 mesh Chromosorb WHP. Effluent from the column was split three ways: Approximately one-fourth went to the FID and three-fourths, to a 1/16-in. tubing (SS) held at 230 C equipped with a T connection that allowed a portion of the effluent to be drawn into a mass spectrometer for compound identification and into the atmosphere for "sniffing."

Since odor evaluation was an important phase of this study, special precautions were taken in heating and insulating the 1/16 in. SS tubing. The secondary coil of a transformer was connected directly to the ends of the electrically isolated 1/16 in. tubing that served as the resistive load or heating element. A thermocouple monitored the temperature. Glass wool and tape were used for insulation because when heated they contribute little or no interfering odors. A 250 ml beaker with a hole drilled in the bottom capped the end of the exit port, and just the tip of the tubing was exposed beyond the glass insulation. The beaker prevented hot oil odors from being absorbed and retained on the glass insulation, and also eliminated accidental burns while sniffing the GC effluent.

Adjacent to the GC exit port was an auxiliary chart recorder and a voltage dividing resistor taped with a 10 position switch which controlled the recorder's pen deflection. A man sitting at the GC exit port sniffing the effluent would turn the switch whenever an odor was detected in the GC effluent; how far he turned the switch depended upon the intensity of the odor detected. Also, a description of the odor was written on the auxiliary chart paper. Since both the GC and auxiliary recorders had identical chart speeds, odor descriptions could be easily assigned to particular GC peaks.

TABLE I

193 C Heated Soybean Oil (SBO) Room Odor Evaluations

Room[a] ft^3	SBO volume, ml	Air flow, cc/min	OIV[b] Fishy	OIV[b] Rancid
5820	300	—	1.9	0.93
1200	20	—	2.0	Yes
1200	13	—	2.0	Yes
1200	8	150	1.8	Yes
31	5	150	1.7	0.5

[a]The 5820 ft^3 room is a laboratory heated oil odor evaluation room, and procedures followed for room odor evaluation in it are described in Reference 2.

[b]Odor intensity value (OIV) = $\frac{\text{weighted summation of odor responses}}{\text{number of judges}}$. See Reference 2 for more detailed description of OIV. In the 1200 ft^3 room tests, judges were not asked to assign numerical ratings for intensities or rancid odor.

The following operating procedures are typical: Initially, the GC column oven was temperature-programed to 250 C to purge possible contaminants off the column with helium as the carrier gas. At the same time, the thoroughly cleaned microroom was charged with 1-5 ml oil, capped, connected to the pure air source and clamped into a standby position. After column purging was complete, the GC oven was cooled to -60 C with dry ice. Upon reaching the desired subambient temperature, the helium flow was stopped; the helium supply inlet probe was removed from the injection septum and replaced by the microroom's needle. The 1/16 in. hole that Packard column injection septums contain for the helium supply inlet probe also allows insertion of the 20 gauge needle and silver-solder bead without damaging a septum. Pure air was then passed through the microroom and GC column at 45 cc/min. At this time voltage was applied to the heating wires to raise the oil temperature from ambient to 193 C in 4 min and then readjusted to maintain that temperature. Volatiles from the hot oil were swept from the microroom onto the cold GC column for 10 min. After this collection period, the air was turned off, head pressure was allowed to bleed off and the microroom was removed. The helium supply probe was again inserted in the septum and the flow adjusted to 45 cc/min. Temperature-programing was then initiated from -60 to 250 C at 2 C/min. If odor descriptions of heated volatiles were desired, the judge would smell the GC effluent at the exit port and perform evaluations for intensity and quality of odor as described above.

Control runs were made following the procedure described except no oil was in the microroom, and the sensitivity of the FID electrometer was increased by a factor of 100. In those runs, no GC peaks were apparent nor were any odors noted in the effluent.

RESULTS AND DISCUSSION

Heated Oil Odors: Quantity and Room Volume Relationships

An objective for the design and use of the microroom was a search for the chemical identity of the fishy odor characteristic of heated SBO. While this odor can be produced quite readily from 300 ml SBO in an open room (2), it becomes elusive as the quantity of oil in the same room volume is decreased. A series of experiments was run to establish whether odors from 1 to 5 ml oil heated in the microroom were similar to those from 300 ml oil heated in

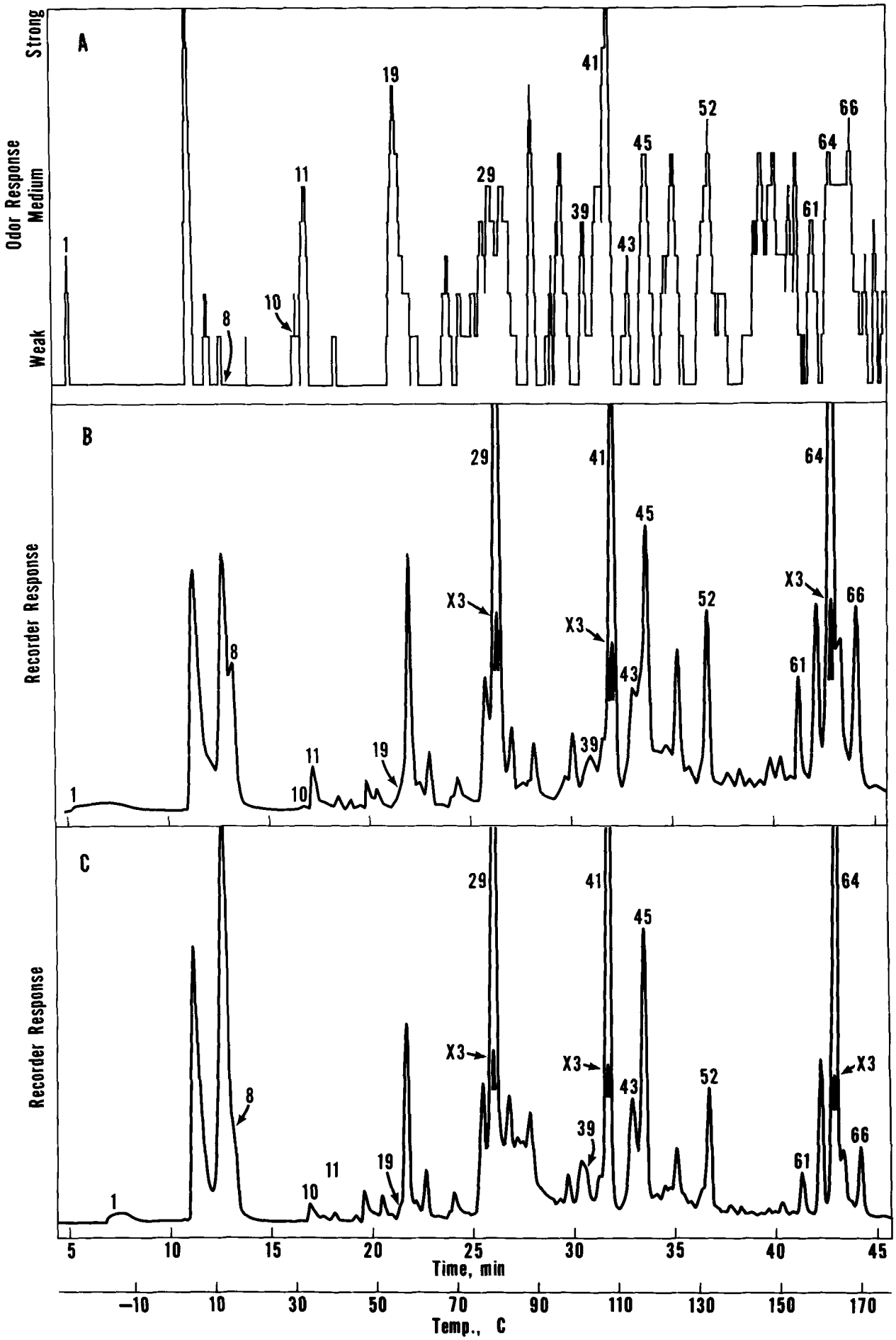

FIG. 2. A (Top):Odor intensigram or odor intensities of corresponding numbered peaks shown in B. B (Center): Chromatogram of volatiles from heated soybean oil collected for 10 min immediately after the oil reached 193 C. C (Bottom): Chromatogram of volatiles from heated soybean oil collected for 10 min after the oil had been continually heated for 2 hr, 30 min at 193 C.

TABLE II

Odor Descriptions of Separated Volatiles Collected from Heated Soybean Oil

Gas chromatographic peak[a]	Temperature eluted, C	Description[b]
1	-21	Sweet
4	+4	Lacrimal
10	33	Buttery
19	55	Grassy
29	82	Fruity
39	106	Sour
41	109	Peppermint-sweet
43	113	Metallic
45	118	Cinnamon
52	133	Caramel-dank
61	155	Moldy
64	163	Acrid-sour
66	169	Musty

[a]Gas chromatographic peak corresponds to numbered peaks in Figure 2.
[b]Best description of three-judge panel.

an all-aluminum frypan (Sunbeam Model No. RS-3, 10 cm deep) in an open room. Empty offices (1200 ft^3) and an aluminum foil enclosure (31 ft^3) were used to study oil quantity-odor concentration relationships. In the office rooms from 8 to 20 ml SBO in petri dishes was heated on a hot plate. As shown in Table I, a fishy room odor was noted when 13 to 20 ml oil was heated and evaluated in the 1200 ft^3 room. The odor intensity value (OIV, see equation in Table I, footnote b) was comparable to that realized from 300 ml oil heated in a deep fat fryer and evaluated in a 5820 ft^3 room. For quantities of SBO less than 13 ml, it was necessary to blow air (compressed, high purity) at 150 cc/min into petri dishes to develop the fishy odor. For some tests when helium was substituted for air, only hay-like odors were noted.

Attempts to use the empty office rooms to evaluate odors from 1 to 5 ml SBO heated in the microroom produced only slight deiscernible odors. Apparently the amounts of odoriferous materials from the 1 to 5 ml oil were just at detectable levels, and therefore a smaller room volume was required. An aluminum foil enclosure (31 ft^3) was then constructed, and just the needle of the microroom was inserted through the foil. Under the restricted volume conditions and in five replicate trials, experienced judges smelled the fishy odor. In each trial, fishy OIV ranged from 1.0 to 2.0.

For a sensation to be considered significant, at least 50% of the judges had to concur that a particular odor was present. Though a limited number of judges were asked to make evaluations, data in Table I, which shows the results of one test, do indicate both 1 to 5 ml and 300 ml quantities of heated SBO produce similar room odors. Interestingly, while the tests were being conducted different room odors were noted as the oil progressed to 193 C, i.e., buttery, grassy-beany then acrid, and the fishy odor was not apparent until the oil temperature was held at 193 C for 30 min. This preliminary study of odor-generating conditions assured us that the volatiles produced from vegetable oils on a microscale mirrored practical conditions.

Heated Oil Volatiles: Collection, Separation and Odor Descriptions

Efficient GC separation requires injection of a sample as a narrow plug onto the GC column. Theoretical predictions are that a compound on a column 30 C below its elution temperature does not move appreciably. Since a 10 min interval was used to collect the heated volatiles directly on the -60 C column, it was suspected that separation efficiency might be affected. To test the effect of the 10 min collection time, two 0.5 μl samples of an equal volume mixture of saturated C_5-C_{15} hydrocarbons were injected onto the -60 C GC column 15 min apart. The column oven was then temperature-programed under identical conditions used to separate collected volatiles from heated SBO. At 12 C a broad pentane peak was discernible as a major peak and shoulder. At 39 C a single hexane peak was recorded, which showed only slight tailing. The remainder C_7-C_{15} hydrocarbon peaks showed no indication of the double injection. It then can be assumed that the 10 min volatile collection period should have a negligible effect on the column separation efficiency for compounds eluting at a temperature higher than pentane.

Further evaluation of the microroom included the actual on-column collection of SBO volatiles with their subsequent separation and detection. An odor "intensigram" (a chart recording of odor intensities of separated heated oil volatiles as judged by a monitor sniffing at the GC exit port) and GC of volatiles from 1 ml heated SBO are shown in Figure 2A and B, respectively. These curves, simultaneously recorded by the procedure described above, show the correspondingly numbered odor intensity and GC peaks. Chromatogram B is one out of 10 reproducible GC patterns obtained of collected volatiles from 1 to 5 ml oil and reflects the number of compounds involved in heated oil odors. Comparison of the intensigram and chromatogram of Figure 2A and B shows that olfactometric and FID responses differ for the same compounds; therefore odor significance of eluted material cannot be directly correlated to GC peak heights. For example, while the large GC peak no. 8 was being recorded (Fig. 2B), no odor was noted by the judge monitoring the effluent at the GC exit port (Fig. 2A). The reverse situation is evident in Figure 2A and B for peak no. 11 where the nose shows greater sensitivity than the FID. Similar observations were noted by Gaudagni et al. (13) when correlating sensory and GC measurements of separated apple essence.

Effluent odor descriptions listed in Table II correspond to numbered peaks in Figure 2. This partial list represents descriptions given by a three-judge panel. Each judge was asked to note odors in the GC effluent in the manner described above during two complete GC separations of collected SBO volatiles. Some peaks were always given the same odor description by each judge; e.g., GC peak 10 was always associated with a buttery odor; other peaks stimulated a pleasant and sweet response, like GC peak 41; and still others were given such divergent descriptions that a general odor category assignment was impossible. Such a situation invariably occurred with unfamiliar odors.

Some of the odor descriptions listed in Table II were not anticipated from separated heated SBO volatiles. However it is not uncommon to find odors of separated volatiles not related to starting substances. Buttery et al. (14) and Flath

et al. (15) reported similar experiences in sensory evaluation of separated volatiles from bell peppers and delicious apple essence. Only a few separated volatiles had characteristic aromas resembling their original materials. Parallel to their reports, only odors associated with GC peaks, 10, 19, 29, 39, 43, 64 and 66 can be related to unfractionated room odors of heated SBO.

The chromatogram in Figure 2C is also of SBO volatiles collected for 10 min on a -60 C GC column after the oil had been continually heated in the reactor at 193 C for 2 hr, 30 min. Similarities between the curves in Figure 2B and C are quite apparent and disclose that the composition of the volatiles does not change appreciably with continual heating once the oil reaches 193 C. This similarity was corroborated by room odor evaluations made according to the procedures described by Evans et al. (2). Comparative room odor tests were run on 300 ml samples of oil for each room. One sample was heated for 20 min and the other for 2 hr, 30 min before odor panel evaluations. Results from the test showed similar odor scores for each room (4.5 vs. 5.0) and that the same prominent odors were present in both test rooms, i.e., fishy, rancid, acrid, burnt and hot oil; and except for the acrid odor, their intensities were in approximately the same relative proportions. Apparently once an oil reaches 193 C the exact time volatile collection begins is not critical in obtaining representative samples.

Identification of volatiles collected from SBO via gas chromatography and mass spectrometry and the instrumentation and methodology will be the subject of another paper.

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