Recovery of Volatile Compounds from Butter Oil

D. A. FORSS and GWENDA L. HOLLOWAY,
Division of Dairy Research, C.S.I.R.O., Melbourne, Australia

Abstract

Three methods for the isolation of volatile compounds from oils and fats were compared using small concentrations (approximately 1 ppm) of added C_{3-12} *n*-alkan-2-ones and C_{2-10} *n*-alkan-1-ols in commercial butter oil. These were: high vacuum degassing, cold-finger molecular distillation and reduced pressure steam distillation. Several modifications were incorporated. The highest yields of all compounds were obtained by cold-finger molecular distillation but difficulties were encountered in subsequent analysis. It was more convenient to recover compounds boiling below 150C by either high vacuum degassing or reduced pressure steam distillation. The latter was more efficient for the higher boiling compounds. Extraction with organic solvents was not required in any of these techniques.

The combination of high vacuum degassing and cold-finger molecular distillation was found to be the best method of analyzing the complete range of model compounds.

Introduction

THE PURPOSE OF THIS STUDY was to develop efficient methods for the isolation of the aliphatic alcohols and carbonyl compounds from oxidized dairy products. This is an essential step if any quantitative assessment of their occurrence is to be made. Such information is necessary in establishing the role of these compounds in the many characteristic flavors encountered and in determining their mode of formation from unsaturated fatty esters.

de Bruyn and Schogt (2) reported that quantitative recovery by vacuum degassing from oils was limited to compounds boiling below 150C at atmospheric pressure. Hexan-2-one was the highest ketone that would distill completely; only 18% of undecan-2-one was recovered at 50C and pressures of 10^{-5} to 10^{-6} torr. In similar experiments Angelini et al. (1) obtained complete recovery of the C_{3-8} alkan-2-ones but only 12% of the C_{11} and 2% of the C_{12} alkan-2-ones from butter oil after 6 hours of continuous pumping.

de Bruyn and Schogt (2) obtained 100% yields of hexan-2-one and undecan-2-one on a cold finger filled with liquid nitrogen at 10^{-5} to 10^{-6} torr but the apparatus was limited to amounts of up to 200 g oil. Similarly, Lea and Swoboda (5) obtained complete recovery of the C_{3-12} *n*-alkanals from 10 g of fat at pressures down to 10^{-2} torr but had to introduce a number of steps such as freezing the oil and slow degassing through a capillary to obtain 100% recovery of the lower boiling aldehydes. Both the Dutch and English workers were able to complete their isolations in a relatively short time, 2–3 hr and 1 hr, respectively.

Chang (3) described a technique of countercurrent contact of soybean oil with steam in a 30 plate Oldershaw column (5 g steam through 150 g oil/hr at 80C and below 20 torr). Much of the reversion flavor was removed but the oil was not completely deodorized.

In an investigation of the aliphatic alcohols and aldehydes in oxidized dairy products, Stark and Forss (6) found that steam distillation of butter oil at 15 torr gave recoveries of 50–65% for the C_{1-6}; 40% for the C_7; 30% for the C_8 and less than 5% for the C_9 *n*-alkan-1-ols.

The levels of individual carbonyl compounds in oxidized dairy products are often below 1 ppm or 10 μmole/kg for a compound of mol wt 100. de Bruyn and Schogt (2) worked at levels of 40–400 ppm, Angelini et al. (1) at 10 ppm and Lea and Swoboda (5) at 100 μmole/kg, and in many cases they worked at elevated temperatures, e. g. 70C at which volatile compounds such as ketones may be generated from butter oil.

In the experiments reported here, studies were made of the relative recoveries of *n*-alkan-1-ols and *n*-alkan-2-ones by three methods: high vacuum degassing, cold-finger molecular distillation and reduced pressure steam distillation. Since in oxidized dairy products the alcohols and carbonyl compounds occur in low concentration (1 ppm), it was necessary to use relatively large amounts (900 g) of oil.

Procedures and Results

Stock mixtures of approximately equimolar amounts of the C_{3-12} *n*-alkan-2-ones and the C_{2-10} *n*-alkan-1-ols were prepared. Ten microliters of the stock mixture was dissolved in 900 g (1000 ml) of commercial butter oil (water content less than 0.1%). The concentrates obtained by the various separation procedures were prepared as aqueous emulsions (10 ml) so that the complete range of compounds could be studied together, and analyzed by gas chromatography. Stainless steel columns (10 ft × 1/8 in. O.D.) packed with 2% Carbowax 20M on 100–120 mesh, acid-washed Chromosorb G were programmed from 60 to 160C at 6C/min using a hydrogen flame ionization detector. All joints were greased with Apiezon T to allow heating of the manifolds which increased recoveries slightly. With standard conditions of sampling the chromatographic analyses were reproducible.

High Vacuum Degassing and Cold-Finger Molecular Distillation

High vacuum degassing and cold-finger molecular distillation were carried out in the same apparatus (Fig. 1). The 10-liter flask (C) containing the butter oil was immersed in a water-bath at 50C and the contents stirred magnetically. The 2 traps (F and J) were cooled with liquid nitrogen and the apparatus was evacuated with a mechanical pump to a pressure of 10^{-1} torr (2 hr) through the capillary arm of the device (K) described by Lea and Swoboda (5) to minimize passage of volatile compounds through traps. The liquid nitrogen vessel was removed from trap F and evacuation continued with an oil diffusion pump to a pressure of 10^{-2} torr when the capillary arm was bypassed (½ hr). Pumping was continued for 3–5 hr at a pressure below 10^{-4} torr after which liquid nitrogen was added to the cold finger and pumping continued for 1 hr.

Three techniques were used to collect the compounds deposited on the cold finger. 1) Trap F was again cooled with liquid nitrogen and the liquid nitrogen in the cold finger (D) was allowed to evaporate.

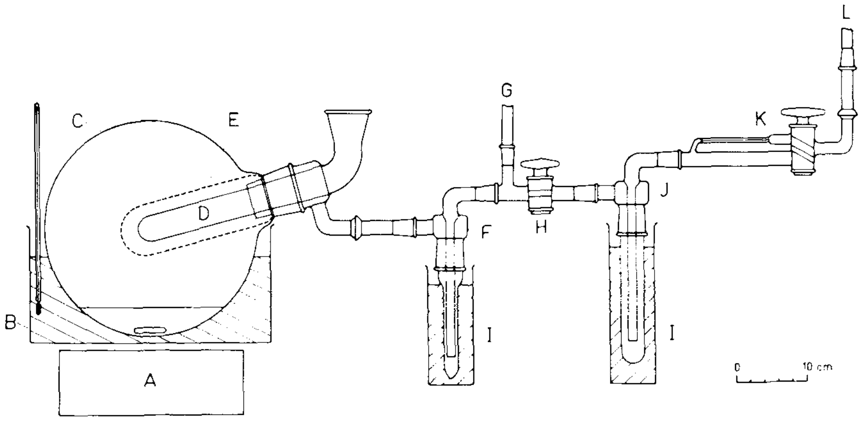

FIG. 1. Apparatus for high vacuum degassing and cold-finger molecular distillation of volatiles from butter oil. *A*, Magnetic stirrer and heater; *B*, water bath; *C*, 10 l flask with ₮55 neck; *D*, cold finger; *E*, test tube with ₮55 neck for distillation from cold finger; *F*, trap for collection of volatiles from cold finger; *G*, to Pirani gauge; *H*, stopcock, 9 mm bore; *I*, liquid nitrogen vessels; *J*, trap for volatiles from degassing; *K*, two-way stopcock with capillary; *L*, to mechanical and diffusion pumps.

Water at 95C was added to the cold finger and the most volatile compounds distilled into trap F. 2) Stopcock H was closed and the flask containing the butter oil was replaced by a closed tube (E) 3 cm greater in diameter than the cold finger. Trap F was cooled with liquid nitrogen and the apparatus evacuated to below 10^{-3} torr. Tube E was surrounded by water at 95C and the liquid nitrogen in the cold finger was replaced by water at 95C. The transfer of the ketones or alcohols into trap F was allowed to proceed for 1 hr. 3) The cold finger was removed from the flask, filled with water at 60C and the distillate was allowed to flow or was rinsed into a small flask with 1 ml quantities of acetone. Of the three techniques, the second was preferred as the lower boiling compounds were lost by evaporation in the third and the distillate tended to return to the butter oil in the first (Tables I and II).

de Bruyn and Schogt (2) used a test-tube similar to tube E with a capillary on the end for trapping the volatile compounds from their cold finger. This is the most efficient means of collecting a sample in a form suitable for gas chromatography. However, in our case, since the distillate was to be emulsified with 10 ml of water for analysis, it was more convenient to distill into trap F. Water was added to traps F and J to give final volumes of 10 ml and the emulsions were analyzed by gas chromatography.

Table I shows the percentage recoveries of ketones and Table II those of alcohols, first by vacuum degassing and then by vacuum distillation of the cold-finger molecular distillate in the absence of butter oil. The total recoveries of the ketones exceeded 75% in all cases and 90% with 5 of the ketones. Vacuum degassing alone gave recoveries of less than 50% of the C_{8-12} ketones. Table I also records the recoveries obtained by vacuum distillation of the cold-finger molecular distillate in the presence of butter oil; total recoveries were less than 65% for the C_{8-12} ketones.

TABLE I

Percentage Recoveries of *n*-Alkan-2-ones from Butter Oil by High Vacuum Degassing Followed by Distillation of the Cold-Finger Molecular Distillate in the Presence or the Absence of Butter Oil

Carbon no. of ketone	% Recoveries by high vacuum degassing	% Recoveries by cold-finger molecular distillation		Total % recoveries	
		a	b	a	b
3	95	....	....	95	95
4	82	....	....	82	82
5	90	3	3	93[c]	93[c]
6	69	14	14	83	83
7	55	36	44	91[c]	99[c]
8	22	35	56	57	78
9	12	52	75	64[c]	87[c]
10	7	18	83	25	90
11	5	8	92	13	97
12	6	8	82	14	88

[a] Distillation of cold-finger distillate in the presence of butter oil.
[b] Distillation of cold-finger distillate in the absence of butter oil.
[c] Inflated by ketones derived from butter oil.

The recoveries of alcohols are given in Table II. Total recoveries exceeded 50% in all cases but recoveries by vacuum degassing alone exceeded 50% with only the C_{2-5} alcohols.

Reduced Pressure Steam Distillation

n-Alkan-2-ones and *n*-alkan-1-ols were removed from butter oil (water bath at 50C) by steam distillation at 15 torr. The compounds in the distillate (500 ml) were concentrated by reflux through a vertical condenser at 0C and 0–20 torr into a trap cooled in liquid nitrogen (1–9 ml) as shown by Forss et al. (4). Recoveries were better than for high vacuum degassing but the isolation took 2 days. The efficiency of the second stage concentration of the steam distillate may be judged from Table III.

A combined apparatus (Fig. 2) was also used with continuous pumping through a capillary (E; 5 cm long × 0.5 mm bore; pressure at gauge (F) approximately 1 torr; the glass capillary regulates the rate of distillation and may be shortened to 2 cm to increase the rate.) The experiment could then be completed in one day with recoveries similar to those of the 2-stage distillation. The percentage recoveries of ketones from butter oil obtained with the combined apparatus are shown in Table IV.

As $C_{5,7,9,11}$ *n*-alkan-2-ones are formed in butter oil by heat in the presence of moisture, control experiments on the recoveries of ketones in the three methods

TABLE II

Percentage Recoveries of *n*-Alkan-1-ols from Butter Oil by High Vacuum Degassing Followed by Distillation of the Cold-Finger Molecular Distillate in the Absence of Butter Oil

Carbon no. of alcohol	% Recoveries by high vacuum degassing	% Recoveries by cold-finger molecular distillation	Total % recoveries
2	97	2	99
3	89	3	92
4	78	19	97
5	58	28	86
6	40	49	89
7	20	52	72
8	11	50	61
9	10	45	55
10	15	48	63

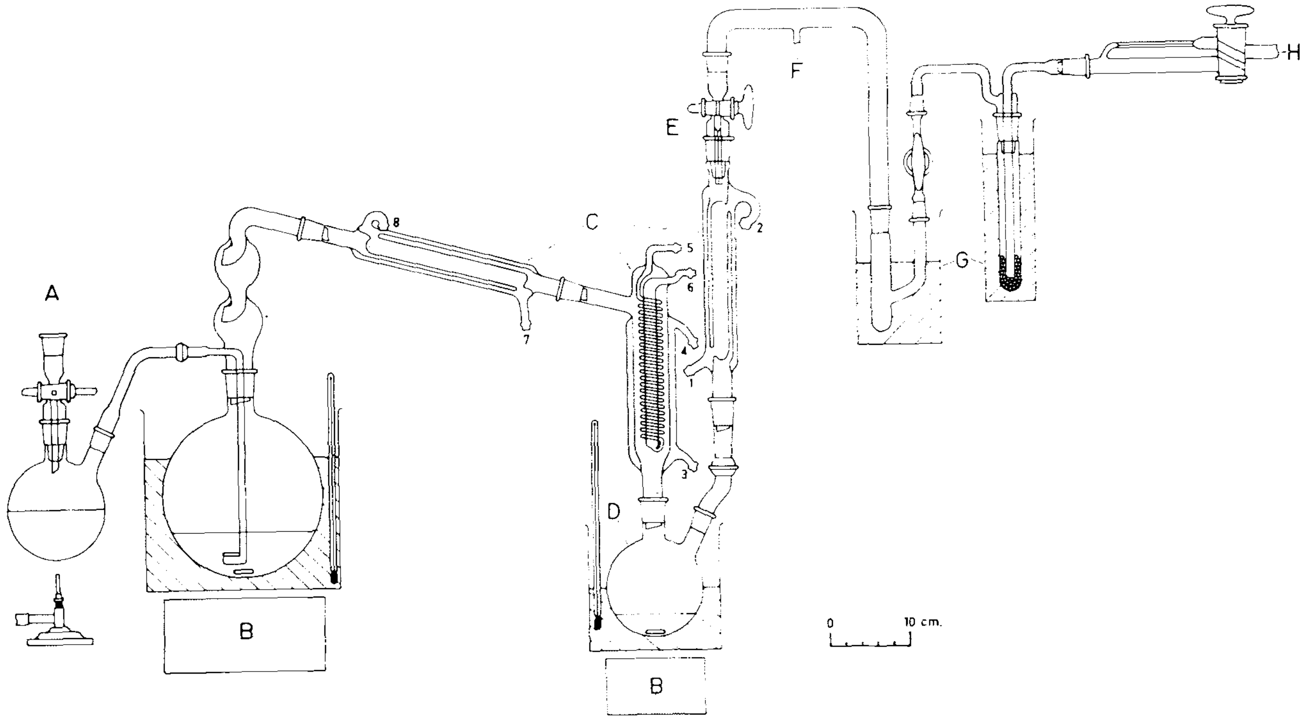

FIG. 2. Apparatus for reduced pressure, steam distillation of volatiles from butter oil, and concentration of distillate. *A*, Steam generator, 1-liter flask; *B*, magnetic stirrer and heater; *C*, condensers, numbers indicate flow of coolant (0C); *D*, flask, 1 liter; *E*, stopcock with capillary (5 cm long × 0.5 mm bore); *F*, to vacuum gauge (0–20 torr); *G*, liquid nitrogen containers; *H*, to mechanical pump.

of isolating volatile compounds were run. The amounts of $C_{5,7,9}$ ketones obtained seldom exceeded 10% of the amounts of synthetic compounds later added.

The recoveries of $C_{2\text{-}10}$ *n*-alkan-1-ols by reduced pressure steam distillation (Table V) were of the same order as those of the ketones.

Discussion

As preliminary experiments had shown that *n*-alkanals, *n*-alk-2-enals, *n*-alka-2,4-dienals and *n*-alkan-2-ones of similar chain lengths distilled in approximately equal amounts, the ketones were chosen for their greater stability. Stark and Forss (6) had demonstrated the presence of the $C_{1\text{-}8}$ *n*-alkan-1-ols in oxidized butter and had reported that reduced pressure steam distillation was unsuitable for the isolation of the higher homologues. However, our success in recovering the C_9 and $_{10}$ *n*-alkan-1-ols in moderate yield may be due to the use of double the amount of steam and distilling four times longer.

Reduced pressure steam distillation has become less frequently used for the isolation of food flavors because of the difficulty of recovering the organic compounds from a large volume of distillate. Redistillation (4) through a vertical condenser at 0C largely overcomes this problem and moreover affords a fairly quantitative picture of the lower boiling compounds which can be lost when organic solvents are used to extract the steam distillate.

Reduced pressure steam distillation is generally more suitable for samples which contain more than 1% water, e.g. butter. The water phase (e.g. butter serum) may be distilled separately and the distillate combined with that from the fat phase. If necessary the residual fat may be subjected to cold-finger molecular distillation for the isolation of the highest boiling flavor compounds. If it can be proved that the compounds of interest are concentrated in the fat phase, the aqueous phase may be discarded. In this case it may be advisable to degas to 10^{-2} torr and to commence the cold-finger molecular distillation at a relatively high pressure. The volatiles in the aqueous fraction may be concentrated either by distillation through a vertical microcondenser at 0C or preferably by vacuum sublimation through a trap at −55C into a liquid nitrogen trap (4).

From the results of this experiment and from ex-

TABLE III

Percentage Recoveries of *n*-Alkan-2-ones (10 µl) from Water (500 ml) by Distillation through a Vertical Condenser at 0C at 1 torr

Carbon no. of ketone	% Recoveries in first trap	% Recoveries in second trap	Total % recoveries
3	78	2	80
4	88	4	92
5	88	5	93
6	75	3	78
7	81	6	87
8	74	8	82
9	67	12	79
10	58	12	70
11	49	9	58
12	36	8	44
Volume of Distillate	4.2 ml	4.7 ml	8.9 ml

TABLE IV

Percentage Recoveries of *n*-Alkan-2-ones from Butter Oil by Reduced Pressure Steam Distillation and Simultaneous Concentration of the Distillate

Carbon no. of ketone	% Recoveries in concentrated steam distillate (9 ml)
3	82
4	77
5	81[a]
6	76
7	91[a]
8	75
9	79[a]
10	48
11	25
12	12

[a] Inflated by ketones derived from butter oil.

TABLE V

Percentage Recoveries of *n*-Alkan-1-ols from Butter Oil by Reduced Pressure Steam Distillation and Concentration of Distillate

Carbon no. of alcohol	% Recoveries in concentrated steam distillate (3 ml)
2	74
3	71
4	79
5	96
6	100
7	93
8	76
9	50
10	30

perience in this laboratory, failure to obtain 100% yields of the lower boiling alcohols and ketones from butter oil is mainly due to incomplete trapping. With small samples, freezing of the oil, evacuating the system and carrying out the initial degassing in a closed system (e.g. Lea and Swoboda (Ref. 5) facilitate quantitative collection of lower boiling compounds. However, with samples of 900 g of oil, freezing in liquid nitrogen is cumbersome. As a means of minimizing losses of the lower boiling compounds cooling of the cold finger with liquid nitrogen during the degassing and allowing it to warm up when the pressure is below 10^{-1} torr is better than cooling the trap (*F*; Fig. 1) nearest to the flask.

The results of this investigation indicate that the combination of high vacuum degassing and cold-finger molecular distillation is the best method of analyzing the complete range of model compounds. Cold-finger distillation alone is inadequate because even with a water content in the oil as low as 0.1% there is a great tendency for the deposit to fall off or be blown off the cold finger. Redistillation of the cold-finger molecular distillate avoids the collection of high boiling compounds such as fatty acids and lactones which are of little importance in studies on oxidized flavor in butter oil.

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