became brown and possessed an unpleasant, amine odor after several days due to the polymerization or decomposition of unreacted trimethyl-5,6-dihydropyrazine. In the case of CuO addition (Figure 2), the formation of the pyrazine leveled off after 3.5 h of refluxing. Maximum yield peaked at 80% and trimethyl-5,6-dihydropyrazine disappeared completely. Also, the yield of pyrazine leveled off at 90% after 2 h and trimethyl-5,6-dihydropyrazine disappeared completely when MnO_2 was added (Figure 3). The formation of 2,3-dimethylpyrazine from 2,3-dimethyl-5,6-dihydropyrazine behaved in exactly the same manner as that of the formation of trimethylpyrazine in solutions containing no metal oxides, CuO, and MnO_2 (Figure 4, 5, and 6, respectively). It should also be pointed out that the rates of pyrazine formation in experiment no. 1, 5, 9, 21, 22, and 23 satisfy the equation of first-order reaction kinetics, which agrees with the results reported previously (Shibamoto, 1975).

CONCLUSION

The final reaction solution prepared by this method does not contain other pyrazines or dihydropyrazines. Therefore, pyrazines obtained from distillation of these solutions are over 99% pure and do not change their color or odor over long periods of storage. The best yield of a pyrazine was obtained from the oxidation of the corresponding dihydropyrazine in ethanol–KOH solution with a 3 molar ratio of CuO or MnO_2 to the dihydropyrazine. Pyrazines obtained by this method are useful as flavor ingredients because of their high purity and stability.

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Formation of Heterocyclic Compounds from the Reaction of Cysteamine and D-Glucose, Acetaldehyde, or Glyoxal

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The volatile compounds produced from the reaction of cysteamine and D-glucose, acetaldehyde, or glyoxal were extracted with methylene chloride using a liquid–liquid continuous extractor. Gas chromatographic and mass spectrometric methods were used to identify 24 compounds. The compounds identified were mainly heterocyclic compounds including pyrazines, thiazoles, thiazolines, and thiazolidines. *N*-Methylthiazolidine was identified by NMR spectra in addition to the GC–MS method. Most compounds identified in these model systems have previously been found in foods. Thiazolidines, which are reduced products of thiazoles and thiazolines, have not, however, been found in foods. The formation pathways of these heterocyclic compounds are also discussed.

Thiazole compounds are important flavor constituents in many foods, such as beef, beer, chocolate, coffee, and popcorn (Liebich et al., 1972; Buttery et al., 1967; Stoll et al., 1967; Walradt et al., 1970). A review of thiazoles in foods has been published (Maga, 1975). This review covers almost the entire range of roles of thiazoles in foods. The formation pathways of thiazoles are, however, not yet well understood. Several investigators have postulated reasonable formation pathways for thiazoles. For example, Mussinan et al. (1975) suggested that 2,4,5-trimethyl-3-thiazoline is formed from the reaction of diacetyl, hydrogen sulfide, and ammonia through the intermediate 2-keto-3-butanethiol. Assuming thiazoles form from thiazolines by dehydrogenation, the postulation of Mussinan et al. is quite a reasonable one. Shibamoto and Russell (1976) reported the formation of many thiazoles from the reaction of D-glucose, hydrogen sulfide, and ammonia. They proposed that D-glucose decomposes into various carbonyls, which subsequently react with hydrogen sulfide and ammonia to give thiazoles. The question remains, however: What are the sources of carbon, nitrogen, and sulfur atoms for this unique heterocyclic ring? It is obvious that the source of carbon atoms for thiazoles is D-glucose in the reaction of a glucose–hydrogen sulfide–ammonia model system. On the other hand, some researchers obtained thiazoles from the reaction of cysteine or cystine and ribose (Mulders, 1973; Fujimaki et al., 1969), and they have postulated that carbons 4 and 5 of the thiazole ring come from the amino acid and that carbon 2 comes from the sugar. For example, 2-acetyl-2-thiazoline, which has also been found in beef broth (Tonsbeek et al., 1971), would form from the reaction of cysteamine (decarboxylation product of cysteine) and pyruvaldehyde (product of sugar caramelization). In order to clarify the source of these atoms (C, N, S) of the five-membered heterocyclic ring in food systems, we investigated the reaction products of

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model systems consisting of cysteamine, which would come from the decarboxylation of cysteine, and D-glucose or aldehydes, which would come from the fragmentation of sugar. The formation pathways of the heterocyclic compounds obtained from this system were also studied.

EXPERIMENTAL SECTION

Reaction of D-Glucose with Cysteamine. An aqueous solution (100 mL) containing 0.1 mol of D-glucose and 0.1 mol of cysteamine, which was previously converted from cysteamine hydrochloride by the addition of sodium hydroxide, was refluxed at 100 °C for 2 h. A dark-brown solution with a strong popcorn-like odor was obtained. This reaction mixture was extracted with 200 mL of methylene chloride in a liquid–liquid continuous extractor for 16 h, the extract dried for 12 h over anhydrous magnesium sulfate, and solvent was removed using a rotary flash evaporator. Approximately 0.2 g of brown oily material was obtained.

Reaction of Acetaldehyde and Glyoxal with Cysteamine. A Kjeldahl flask (100 mL) containing 0.3 mol of acetaldehyde or 0.3 mol of glyoxal and 0.1 mol of cysteamine (previously converted from cysteamine hydrochloride by the addition of sodium hydroxide) in 100 mL of deionized water was flame-sealed and the ampule was placed in an oven at 90 °C for 5 h. Prior to flame-sealing, each ampule was cooled in ice water and the contents were adjusted to pH 10 with 5 N NaOH solution. Following heat treatment, each reaction mixture was extracted for 24 h with 200 mL of methylene chloride using a liquid–liquid continuous extractor. The extracts were dried over anhydrous magnesium sulfate for 12 h, and solvent was removed using a rotary flash evaporator. Approximately 9.5 g of a pale-yellow, oily material (with an onion leek-like odor) and 2.5 of a dark-brown, oily material (with a popcorn-like odor) were obtained from the reaction of acetaldehyde–cysteamine and glyoxal–cysteamine, respectively.

Analysis of Volatiles. Identification of gas chromatographic peaks of reaction mixtures was made by comparison of their mass spectra and gas chromatographic retention indices to those of authentic compounds. A Hewlett-Packard Model 5710-A gas chromatograph equipped with a flame ionization detector, modified for capillary analyses, and a 100 m × 0.25 mm i.d. glass capillary column coated with Carbowax 20M was used. The column temperature was programmed from 70 to 170 °C at 1 °C/min. The nitrogen carrier gas flow was 0.6 mL/min. The gas chromatograph was fitted with an all-glass injector splitter of our own design to avoid any contact with metal surfaces and was operated with an injector split ratio of 100:1. The injector temperature was 250 °C and the detector temperature was 250 °C. Peak areas were integrated using a Hewlett-Packard Model 3385-A Automation System combined with the above gas chromatograph.

Some major peaks which could not be identified by the above method were trapped in semicapillary tubes cooled with dry ice using a Perkin-Elmer Model 900 gas chromatograph equipped with a thermal conductivity detector and a glass column (2 m × 4 mm i.d.) packed with 5% Carbowax 20M on Chromosorb W (60/80). The column temperature was programmed from 80 to 200 °C at 3 °C/min. The trapped materials were identified by comparison of their IR and NMR spectra, in addition to mass spectra and GC retention indices. The IR spectra were obtained with a Hitachi Model EPI-G3 grating infrared spectrophotometer. The NMR spectra were obtained with a Hitachi Model R-20A Magnetic Resonance Spectrometer (60 MHz) in deuteriochloroform with tetramethylsilane as an internal standard.

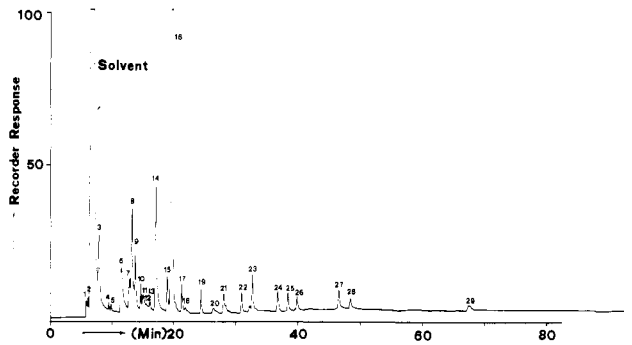

Figure 1. Gas chromatogram of volatiles formed by D-glucose–cysteamine model system. For chromatographic conditions see Experimental Section. For peak identification see Table I.

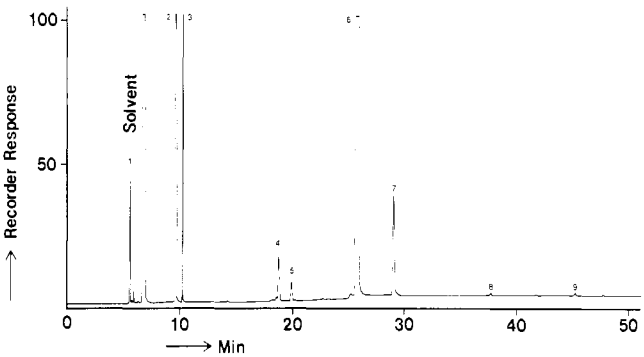

Figure 2. Gas chromatogram of volatiles formed by acetaldehyde–cysteamine model system. For chromatographic conditions see Experimental Section. For peak identification see Table I.

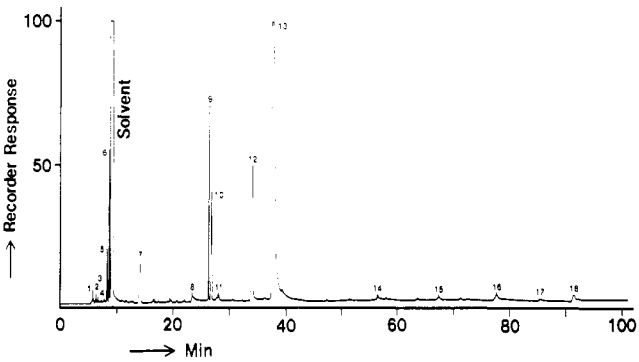

Figure 3. Gas chromatogram of volatiles formed by glyoxal–cysteamine model system. For chromatographic conditions see Experimental Section. For peak identification see Table I.

RESULTS AND DISCUSSION

The formation of sulfur- and nitrogen-containing heterocyclic compounds has been studied by many investigators (Boelens et al., 1974; Mussinan and Katz, 1973; Buttery et al., 1973; Pittet and Hruza, 1974). Boelens et al. (1974) reported the formation of nine heterocyclic compounds from the reaction of fatty aldehyde, hydrogen sulfide, thiols, and ammonia. They suggested that the acetaldehyde, hydrogen sulfide, and ammonia, which were derived from cysteine, could be the precursors of these heterocyclic compounds. Mulders (1973) identified eight thiazoles from his cysteine/cystine–ribose system. Our model system, which consisted of cysteamine and D-glucose, acetaldehyde, or glyoxal, produced 14 sulfur- and

Table I. Compounds Identified from D-Glucose, Acetaldehyde, or Glyoxal and Cysteamine Model Systems

compound	D-glucose (Figure 1) peak area, %	no.[l]	acetaldehyde (Figure 2) peak area, %	no.	glyoxal (Figure 3) peak area, %	no.	occurrence in food	MS references
acetaldehyde	1	0.89	1	3.40			popcorn,[a] cocoa[b]	Stenhagen et al. (1974a)
ethylene oxide					5	0.49		Stenhagen et al. (1974b)
ethylene sulfide	2	1.09			6	1.81		Porter and Bladas (1971a)
isobutyl alcohol	3	3.38					peanuts[c]	Stenhagen et al. (1974c)
acetoin	6	3.29					coffee,[d] pork liver,[e] beef[f]	Ferrietti and Flanagan (1971)
cis,cis-2,4,6-trimethyl-*s*-trioxane			2	27.76				Pouchert (1970a)
cis,trans-2,4,6-trimethyl-*s*-trioxane			3	5.05				Pouchert (1970a)
pyridine	4	0.45					popcorn,[a] peanuts[c]	Porter and Baldas (1971b)
N-methylaziridine	10	1.07						Porter and Baldas (1971c)
azetidine	12	0.11						Porter and Baldas (1971d)
pyrazine			7	0.46			popcorn,[a] peanuts[c]	Bondarovich et al. (1967)
2-methylpyrazine	5	0.45					popcorn,[a] peanuts[c]	Bondarovich et al. (1967)
furfural	13	0.45					popcorn,[a] peanuts[c]	Stoll et al. (1967)
2-acetylfuran	15	2.65					coffee,[g] beef[h]	Stoll et al. (1967)
furfuryl alcohol	20	0.40					popcorn,[a] coffee[g]	Mussinan and Walradt (1974)
2-acetylthiazole	21	1.45					beef,[j] potato[j]	Pittet and Hruza (1974)
2-thiazoline	9	3.50			10	2.29		Ledl (1976)
2-methyl-2-thiazoline	7	2.34						Kato et al. (1973)
2-methyl-3-thiazoline (tentative)	8	7.59						
2-ethyl-2-thiazoline	11	0.67						Kato et al. (1973)
2-formyl-2-thiazoline (tentative)	23	2.56			15	0.08		
2-acetyl-2-thiazoline	22	1.18			14	0.08		Tonsbeek et al. (1971)
thiazolidine	16	46.17	7	1.03	13	86.04		Pouchert (1970b)
2-methylthiazolidine	14	9.23	6	61.21	12	2.80		Fujimaki et al. (1969)
2-ethylthiazolidine	17	2.00						
2-*n*-propylthiazoline	18	0.27						Ledl and Severin (1973)
2-acetylthiazolidine (tentative)	24	1.38						
2,3-dihydro-6*H*-1,4-thiazine (tentative)					9	3.96		
N-methylthiazolidine					11	0.22		

[a] Walradt et al. (1970). [b] vanPraag et al. (1968). [c] Walradt et al. (1971). [d] Stoffelsma et al. (1968). [e] Mussinan and Walradt (1974). [f] Liebich et al. (1972). [g] Stoll et al. (1967). [h] Persson and vonSydow (1973). [i] Wilson et al. (1973). [j] Buttery and Ling (1974). [k] Tonsbeek et al. (1971). [l] The peak numbers on Figures 1-3 which do not appear in Table I are unknowns.

nitrogen-containing compounds. These compounds are listed in Table I and their gas chromatograms are shown in Figures 1–3. We obtained thiazolidines in large amounts (total area: 57% from cysteamin-D-glucose; 62% from cysteamine–acetaldehyde; 88% from cysteamine–glyoxal).

Bonner and zu Reckendorf (1961) obtained 2-[D-glucopentahydroxypentyl-(1)]thiazolidine from the reaction of D-glucose and cysteamine in methanol. Some thiazolidines, with a sugar moiety attached to their 2 carbon, have been obtained from the reaction of cysteine and sugars by many researchers (Schubert, 1939; Weitzel et al., 1959). These experiments were conducted at room temperature, which might not promote sugar fragmentation either before or after formation of thiazolidines containing a sugar moiety. Consequently, they did not isolate any thiazolidines lacking a sugar moiety. Some thiazolidines lacking sugar moieties were isolated and confirmed, however, in our heated model system. Fujimaki et al. (1969) reported that pyrolysis of cysteine produced 2-methylthiazolidine and they postulated that this compound was produced from the reaction of cysteine or cysteamine, which had formed from cysteine following decarboxylation, and acetaldehyde. Our results indicate that their speculation may be correct. If we replace acetaldehyde with formaldehyde or pyruvaldehyde, then unsubstituted thiazolidine or 2-acetylthiazolidine, respectively, would be formed. We found both compounds in our reaction mixture, and unsubstituted thiazolidine from the reaction of D-glucose or glyoxal and cysteamine was a major component (area: 46 and 86%, respectively), but was a minor component from the reaction of acetaldehyde–cysteamine (area: 1.0%).

It is well known that the fragmentation of sugars produces a large number of carbonyl compounds including formaldehyde, acetaldehyde, glyoxal, and pyruvaldehyde (Hodge, 1967). Tonsbeek et al. (1971) isolated 2-acetyl-2-thiazoline from beef broth. 2-Acetylthiazole was also found in ground beef and pork liver (Wilson et al., 1973; Mussinan and Walradt, 1974). These two acetyl derivatives are dehydrogenation products of 2-acetylthiazolidine. We found both 2-acetyl-2-thiazoline and 2-acetylthiazole in our glucose–cysteamine reaction mixture and 2-acetyl-2-thiazoline was also found in our glucose–glyoxal reaction mixture.

Neither thiazolidine nor its analogues have been found in foods, although alkylthiazolidines have been used as flavor ingredients to create meat-like flavor when mixed with pyrazines and cyclohexenones (Firmenich, 1974, 1975). Our proposed reaction mechanisms for the formation of heterocyclic compounds obtained from D-glucose, acetaldehyde, or glyoxal and cysteamine are summarized

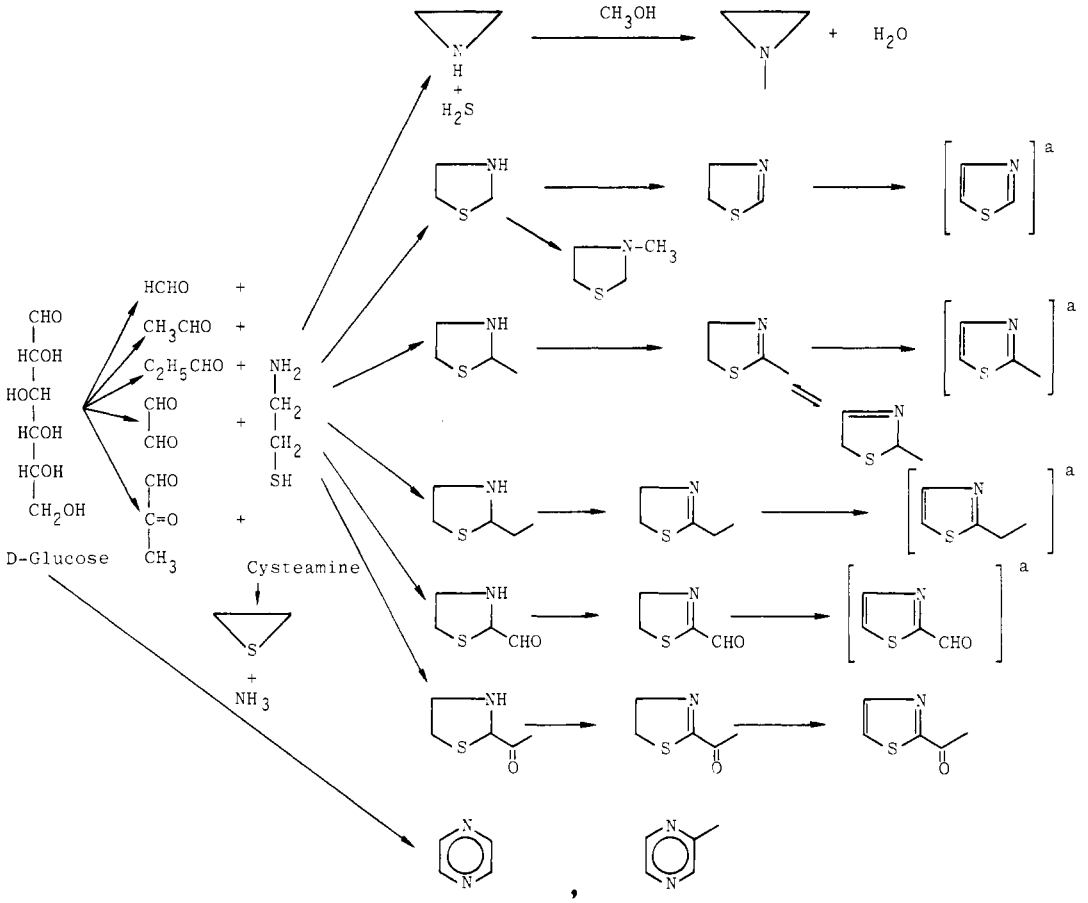

Figure 4. Proposed formation pathways of heterocyclic compounds obtained from cysteamine and D-glucose, acetaldehyde, or glyoxal model systems. (a) Have not been found in these model systems.

in Figure 4. We did not obtain any 4- or 5-substituted thiazolidines. We conclude, therefore, that the 4 and 5 carbon atoms in the thiazolidine ring come from cysteamine and that the 2 carbon atom comes from glucose. We also found numerous other heterocyclic compounds including ethylene sulfide, *N*-methylaziridine, azetidine, 2,3-dihydro-6*H*-1,4-thiazine (tentative), in addition to several thiazolidines, thiazolines, and thiazoles.

N-Methylthiazolidine (peak no. 11, Figure 3) was identified from its NMR spectrum in addition to its mass spectrum and gas chromatographic retention index. The reaction of cysteamine and formaldehyde produced this compound as the main product. Approximately 1 mg of this compound was isolated from the above reaction mixture using the preparative gas chromatograph for NMR analysis. The NMR and mass spectral data for *N*-methylthiazolidine are as follows: NMR (in $CDCl_3$ with respect to tetramethylsilane) 2.30 ppm (singlet, 3 H, *N*-methyl), 2.95 ppm (multiplet, 4 H, C-4 and C-5 methylene), 4.05 ppm (singlet, 2 H, C-2 methylene); mass spectrum (*m/e*, followed by intensities in parentheses) M^+ = 103 (100), 102 (22), 70 (3), 61 (2.5), 60 (8), 57 (67.5), 44 (16.5), 43 (9.2), 42 (30.0).

The presence of pyrazine and 2-methylpyrazine indicates the production of ammonia in these model systems (Shibamoto and Bernhard, 1976). The amount of ammonia produced in these systems should be very small because we obtained only a small amount of pyrazine and 2-methylpyrazine (peak area: 0.46 and 0.45 in Figures 2 and 1, respectively). 2-Methylpyrazine is the main constituent of the volatiles obtained from the D-glucose–ammonia model system (over 85% of total products; Shibamoto and Bernhard, 1976). Since thiazolines and thiazoles have been found in foods, thiazolidines should form in foods also. The heat treatment may, however, convert most of the thiazolidines into thiazolines or thiazoles. It is necessary to further investigate this dehydrogenation process from thiazolidine to thiazoline and thiazole in order to clarify the formation pathways of thiazole compounds in foods.

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Production of Volatile Flavor Compounds in Ultrahigh-Temperature Processed Milk during Aseptic Storage

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Volatile flavor compounds in ultrahigh-temperature (UHT) processed milk were investigated to determine their role in off-flavor development during aseptic storage. The milk samples were processed at 145 °C for 3 s with and without added ascorbic acid and stored at 3, 22, and 35 °C for 5 months. Flavor isolates were prepared through steam vacuum distillation and subsequent extraction of the distillate with dichloromethane. The isolates were analyzed using gas chromatography and mass spectrometry. The milk was regularly analyzed by various chemical methods and evaluated by a taste panel during storage. Twenty-six compounds were identified, seven of which were not previously reported in UHT milk. Gas chromatographic profiles indicated that 2-pentanone, 2-heptanone, 2-nonanone, and *n*-hexanal increased most in concentration during storage. The rate of increase in odd carbon-numbered methyl ketones (C_{3-13}) was dependent upon storage temperature, whereas the rate of increase in aldehydes was dependent upon both oxygen content and temperature of storage. Although methyl ketones were the most abundant class of compounds, aldehydes appeared to be most important in contributing to the off-flavor of stored UHT milk.

Development of stale and/or oxidized flavors during storage is a primary deterrent for acceptability of ultrahigh-temperature (UHT) processed milk. The flavor often appears within a month at room temperature and increases gradually as a function of time. Ashton (1965) reported that, at higher temperatures of storage (21–38 °C), the UHT milk packed aseptically in waxed paper–polyethylene laminates showed signs of developing an incipient oxidative rancidity or cardboardy flavor at about 19 days. Kirk et al. (1968) observed that in UHT milks the rate of staling was a function of storage temperature and paralleling the development of staleness were increases in carbonyl compounds as well as the disappearance of many unidentified components. Ashton et al. (1969) reported that the course of off-flavor development was not only associated with storage temperature but affected by light and oxygen as well. Zadow and Birtwistle (1973) reported that the major factors influencing flavor changes during storage of UHT milk were the level of dissolved oxygen present in the product after processing and the storage temperature. The influence of initial oxygen content on the flavor of samples stored at 2 °C was comparatively minor, most samples being considered "very good" independent of their oxygen content. For samples stored at 20 °C an initially low oxygen content resulted in a poor flavor performance during the first few weeks of storage while an initially high oxygen content resulted in the development of oxidized or rancid flavors at the early stages of storage. Samples with an intermedate initial oxygen content (P_{O_2} 60–100 mmHg) were preferred to achieve a balance between these extremes. Storage at 38 °C resulted in marked visual browning of samples and a rapid decrease in acceptability of flavor independent of oxygen concentration. Thomas et al. (1975) investigated the effect of dissolved oxygen content on flavor and chemical changes during storage of indirectly heated UHT milk. Flavor acceptability increased to a maximum after a few days of storage and then declined with storage. The increase was associated with less off-flavor described as cabbagy and the decrease with more "stale" off-flavor descriptions. Milks with higher initial oxygen contents were preferred up to 8–13 days, but thereafter acceptability was independent of initial oxygen content.

Several workers have studied the volatile compounds present in stored dairy products (Arnold and Lindsay, 1968; Arnold et al., 1966; Bassette, 1958; Bingam, 1964;

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