endogenous β-glucanase activity in barley and oats can greatly influence the solubility of β-glucans under certain extraction conditions.

It is notable that, for the potato and carrot, extraction following starch degradation at high temperature gave approximately 6-fold higher values than extraction with water at 38 °C. The exceptional susceptibility of the fibers in these two samples to solubilization at high temperature led to a significantly ($P < 0.001$) increased solubility of fiber in water at 38 °C following pretreatment by boiling in ethanol (Table II). With the exception of the potato and carrot samples, the values for soluble fiber extracted by the two methods designed to prevent endogenous enzyme activity, i.e. in acidic buffer or pretreatment with ethanol, were very similar. That extraction in acidic buffer gave numerically, and sometimes significantly, lower soluble fiber values than extraction in water at the same temperature for all samples could result from reduced solubility at lower pH or decreased endogenous enzyme activity (Åman and Graham, 1987).

The composition, as well as yield, of soluble fiber was also effected by extraction conditions. For example, the glucose to arabinose ratios in the soluble fiber in barley varied between 5.5 (method 4) and 11.3 (method 1), while the xylose to arabinose ratios remained around 1.4. Indeed the xylose to arabinose ratios in the soluble fiber were about 1.5 for all cereals, irrespective of extraction method.

The present study establishes that the determination of soluble dietary fiber is very dependent on the extraction method employed. It is also apparent that the relationship between different extraction methods depends on the sample under analysis. Which extraction method is most closely correlated to the physiological activity of soluble fiber is not known, although the solubility of nonstarch polysaccharides can increase greatly during passage through the small intestine (Graham et al., 1986). However, extraction by methods more relevant to physiological conditions may be more suitable than the high-temperature procedures most commonly employed.

Registry No. Klason lignin, 8068-04-0.

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Received for review November 10, 1986. Revised manuscript received August 10, 1987. Accepted December 14, 1987. This work was financially supported by the Swedish Council for Forestry and Agricultural Research.

Kinetic Study of Maillard Reactions in Milk Powder by Photoacoustic Spectroscopy

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Application of photoacoustic spectroscopy (PAS) to the analysis of milk or dairy products is reported. We have studied the kinetic aspects of the Maillard browning reactions in milk powder tablets. The reaction rate has been assessed by using the spectral ratio I_{335}/I_{280} (i.e., the PA intensity of the Maillard reaction products to that of proteins). The molar energy and enthalpy of activation were found to be 115 and 113 kJ mol^{-1} at 298 K, respectively. We discuss the relevance of the application of photoacoustic methodology in dairy research and the milk industry.

The nonenzymatic browning of Maillard reaction (Maillard, 1916) is very important in many respects such as food processing and storage, cataract formation, and diabetes. The primary reaction in Maillard browning is thermal condensation of an amino compound (i.e., protein amino acids, especially lysine) (Candiano et al., 1985) with the carbonyl group of a sugar in the open-chain form, probably to form a Schiff base, thereby reducing the amount of lysine available for nutrition. Loss of palatability often occurs. On the other hand, maple syrup owes its fine flavor and color to browning as the distinctive caramel and butterscotch flavors of dairy products derive from the browning of milk. This nonenzymatic browning of food products, which is different from caramelization, heat-induced browning of sugars in the absence of amino

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0021-8561/88/1436-0497$01.50/0

compounds, is the consequence of degradation of sugars and interactions of the degradation products. Some of the compounds formed by the Maillard reactions are reductones (Ledl and Fritsch, 1984) having an enediol conjugated with a carbonyl group, nitroso compounds (Roeper et al., 1984; Pool et al., 1984; Jadhav and Kulkarni, 1985), and pyrroles and derivatives (Hayase et al., 1985; Tressl et al., 1985a,b; Tressl and Gruenewald, 1986). Among the carbonyl compounds, some react with amines to form polymers called melanoidins, which are brown compounds of variable structure and solubility. They have unsaturated heterocyclic rings, which account for their absorption of UV light and for their fluorescence. Some of the products of the Maillard reactions, such as maltol, are somewhat volatile and contribute to the caramelized flavor in heated products. The intensity of browness is commonly assessed by measurements of reflectance of the products (Walstra and Jenness, 1984) or by absorbance of a tryptic digest (Utsunomiya et al., 1983; Walstra and Jenness, 1984). A great number of papers have been published on the biomedical (Perkins et al., 1982; Pinot, 1982; Lee et al., 1982, 1983; Jaegerstad et al., 1983, 1986; Pool et al., 1984; Anderson et al., 1984; Shibamoto, 1984; Shinohara, 1985; Otani et al., 1985), nutritional (Tanaka et al., 1977; Mori and Nakatsuji, 1977; Lee et al., 1977, 1982, 1983; Oeste and Sjoeding, 1984; Oeste et al., 1985, 1986; Plaskas et al., 1985), and toxicological (Lee et al., 1982; Lee and Chichester, 1983) aspects of Maillard reaction products, making it clearly obvious the importance of being able to measure routinely the Maillard browning in foods.

Photoacoustic spectroscopy (PAS) is a technique for the study of the energy emitted as heat following the absorption of modulated light by a sample. In contrast with absorption spectroscopy where the signal measured is determined by the sample's optical constant, the thermal properties of the sample usually play the central role in the photoacoustic signal (Parker, 1973; Rosencwaig, 1975). The intensity of the photoacoustic signal is proportional to three parameters: i.e., the radiant power absorbed, radiationless conversion efficiency, and thermal-transfer efficiency. The sample contained in a sealed cell is illuminated through a transparent window by a chopped monochromatic beam. Oscillatory heating at the chopper frequency due to the absorption of the modulated light by the sample is communicated to the surrounding gas where pressure oscillations are generated and sensed by a microphone.

Photoacoustic spectroscopy has long been utilized to study the absorption of light by gases, but since recently has its use been extended to liquids and solids. Since its first application by Rosencwaig (1973) and other researchers (Harshbarger and Robin, 1973; Kaya et al., 1975) a number of papers covering the theoretical (Rosencwaig and Gersho, 1976; Afromowitz et al., 1977; McDonald and Wetsel, 1978; Wrobel and Vala, 1978) and experimental (Dewey, 1974; King and Kirkbright, 1976; Munroe and Reichard, 1977; Adams et al., 1977; Aamodt et al., 1977; Bard, 1978; Somoano, 1978; Blank and Wakefield, 1979) aspects of PAS have been published. To our knowledge, PAS has never been applied elsewhere to dairy products, a field where there is a real need for analytical instruments other than absorption ones, for direct, rapid, and precise measurements of opaque and light-scattering samples. In the present paper we report kinetic and thermodynamic data of the Maillard reactions in milk powder by use of PAS.

MATERIALS AND METHODS

Photoacoustic (PA) measurements were performed on a homemade PA spectrometer (Ducharme et al., 1979; Boucher and Leblanc, 1985; Boucher et al., 1986) consisting of a 1000-W xenon lamp (Schoeffel Instrument Corp., Westwood, NJ) and a monochromator driven by a variable-speed motor. The monochromatic beam was modulated by a mechanical chopper at a frequency that could be varied from 20 to 1000 Hz, and it was focussed and reflected into the PA cell.

The kinetic study of the Maillard reactions was carried out on tablets made out of lyophilized raw milk containing about 3% water (w/w); the tablets were 1.25 cm in diameter and 0.03 cm in thickness. Two series of measurements were done, one on tablets heated in a controlled-temperature oven (Fisher Scientific Co., Montréal) at 383.5 and 391.5 K for different periods of time, and other series of tablets heated 5 min at 378.5, 388.5, and 393.5 K. The PA spectra were run from 250 to 600 nm at a modulation frequency of 40 Hz. The scan speed was 50 nm min^{-1}, and the time constant of the lock-in amplifier was set at 1.25 s. The bandwidth of the light beam was 10 nm. All of the PA measurements were performed at room temperature, i.e., 298 ± 1 K.

RESULTS

Milk, as well as most dairy products, presents a PA spectrum in the UV. An example giving PA spectra of tablets of milk powder (Figure 1A, curve 1) displays one peak at 280 nm corresponding to the absorption of proteins and a smaller band in the visible (400–500 nm) that might be assigned to milk carotenoids. When heated, the tablets gradually turn brown with a concomitant change in the PA spectra (Figure 1A, curves 2–6). As evidenced in this figure, a new PA band appears around 335 nm as a consequence of the Maillard reactions. At the very beginning of the reaction, a decrease of the protein band as a consequence of protein denaturation is observed (Figure 1B, curve 1 vs curve 2) followed by an increase of the protein band (Figure 1B, curve 4 vs curve 3), due to the contribution of the reaction products. In Figure 1C are examples of the differences of spectra of milk tablets after and before heating. The difference spectra for different temperatures and duration peak at 335 nm. It can also be noticed that as the heating time is prolonged, the difference spectra become broader and broader at the red side of the spectrum. This could be the sign of many other reactions occurring in the sample, considering the complexity of the composition of raw milk.

The chemical kinetics of the Maillard browning can be followed in two ways. One is by plotting the spectral ratio I_{335}/I_{280} (ratio of PA intensity at 335 nm to that of 280 nm) versus time (t). The second is to draw the PA intensity difference between the spectra of the heated and the nonheated tablets. For the latter method to be valid, all tablets should have exactly the same PA signal before heating (initial signal). In the present study, an attempt to obtain reproducibility of the initial signal was unsuccessful due to the difficulty in reproducing the exact conditions in the preparation of the tablets. The spectral ratio method has therefore been adopted. The kinetic curves obtained by using this method are shown in Figure 2, curves 1 and 2, at 383.5 and 391.5 K, respectively. A straight line is obtained at the beginning, which starts to curve from about 10 min in both cases and saturates at about 20 min. The slope of the straight region yields the initial rate, v_i, of the reaction. The kinetic curve being linear through 10 min, it is not necessary to measure the PA signal through a longer interval of time to determine the initial rate. The initial rate at the three other temperatures (i.e., 378.5, 388.5, and 393.5 K) has therefore been

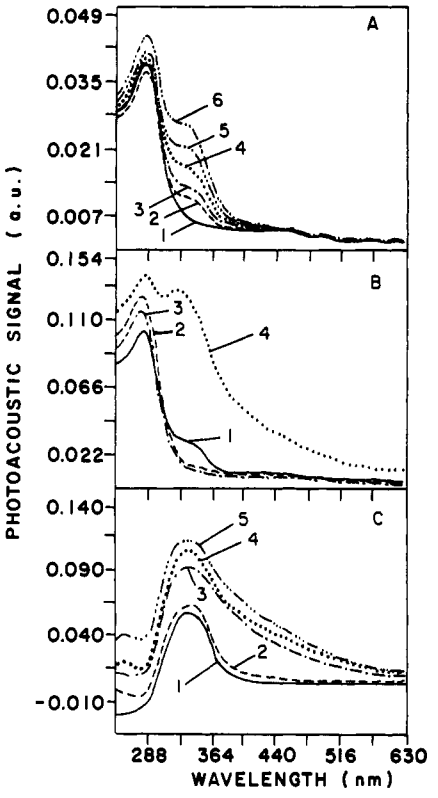

Figure 1. (A) Spectral evolution of Maillard reactions in a milk tablet with time at 393.5 K obtained by photoacoustic spectroscopy: 0 min (curve 1), 5 min (curve 2), 10 min (curve 3), 20 min (curve 4), 35 min (curve 5), 45 min (curve 6). (B) PA spectra obtained during Maillard reactions in milk tablets showing the decrease of the protein band at 280 nm in the heated tablet (curve 1) compared with the nonheated tablet (curve 2) followed by an increase of the 280-nm band for a tablet heated for a longer period of time (curve 4) compared with the nonheated tablet (curve 3). The measurements were conducted at 383.5 K. (C) PA difference spectra obtained for five milk tablets heated 10 min at 383.5 K (curve 1), 10 min at 391.5 K (curve 2), 60 min at 383.5 K (curve 3), 60 min at 391.5 K (curve 4), and 90 min at 391.5 K (curve 5), showing a maximum at 335 nm and a broadening of the difference spectra as the tablets are heated for longer periods of time and at higher temperatures.

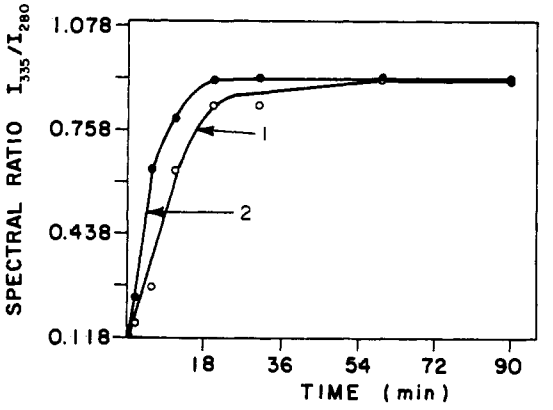

Figure 2. Kinetic curves of the Maillard reactions in milk tablets heated at 383.5 K (curve 1) and 391.5 K (curve 2).

calculated by using the spectral ratio for 5-min heating.

In order to derive thermodynamic parameters of the Maillard reactions, we have used the Arrhenius law (eq 1), where k is the rate constant, A the preexponential factor, E^* the energy of activation, R the ideal gas constant, and T the absolute temperature (K).

$$k = A \exp(-E^*/RT) \quad (1)$$

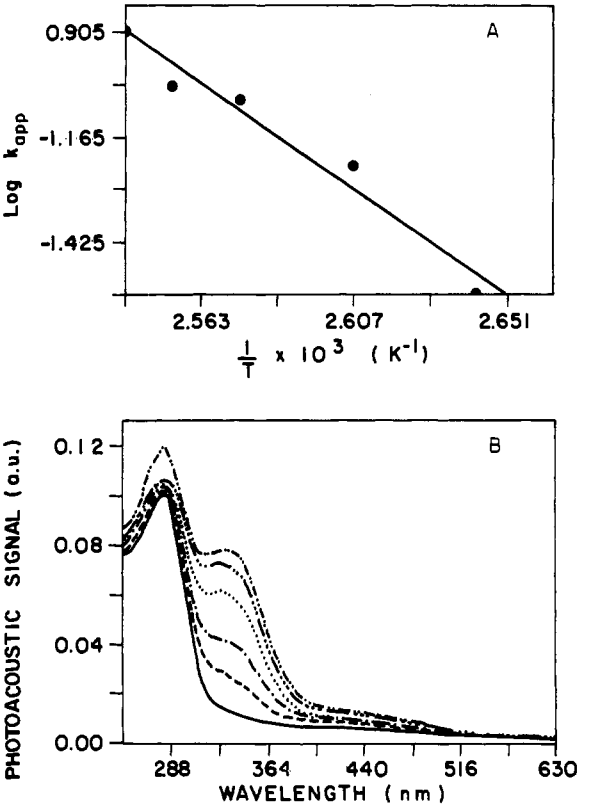

Figure 3. log k_{app} vs $1/T$ plot for the Maillard reactions in milk tablets (A) with the corresponding PA spectra (B).

Rearranging the terms, we obtain eq 2. Hence, plotting log k vs $1/T$ gives a straight line, the slope of which corresponds to $E^*/2.303R$, thereby giving the energy of activation, E^*. In these experiments, the rate constant, k,

$$\log k = \log A - E^*/2.303RT \quad (2)$$

is not easy to determine. But, since k is proportional to the initial rate, i.e., the slope of the curve I_{335}/T_{280} vs t, the latter reactional parameter, which we name apparent rate constant, k_{app}, can be conveniently used in the log k vs $1/T$ plot. The results obtained therein are shown in Figure 3A. As indicated, a straight line is obtained with a correlation coefficient higher than 0.98 (the corresponding PA spectra are given in Figure 3B). The data shown in Figure 3A allow us to find the molar activation energy, E^*, to be 115 kJ mol^{-1} ± 11% at the 95% confidence level. The molar enthalpy of activation (H^*), which can be obtained from eq 3, is found to be 113 kJ mol^{-1} at 298.5 K. The temperature dependence of a reaction could

$$H^* = E^* + RT \quad (3)$$

also be expressed as Q_{10}, which represents the factor by which the rate of a reaction is increased when the temperature is raised by 10 °C (Walstra and Jenness, 1984) (eq 4). According to our measurements, Q_{10} is equal to 2.7 at 373.5 K.

$$Q_{10} \simeq 1.03 \exp(10\Delta H^*/RT^2) \quad (4)$$

As for the Z value (Walstra and Jenness, 1984), defined as the temperature rise (K) needed to increase the rate of a reaction by a factor of 10 (eq 5), we obtained 23.6 K at 373.5 K.

$$Z = 10/\log Q_{10} \simeq 2.303RT^2/H^* \quad (5)$$

DISCUSSION

The rates at which the several manifestations of Maillard reactions occur in milk as well as in dairy products highly depend on pH, temperature, time, and water activity (a_w).

The rates of these reactions increase with increasing concentrations of milk solids, reach a maximum at a water activity of about 0.61 (i.e., 10% water), and then decline (Walstra and Jenness, 1984). Besides, Maillard reactions increase exponentially with pH increase (Patton, 1952) and reach a maximum at around pH 10 (Ashoor and Zent, 1984). The influence of pH is particularly important during the course of Maillard reactions in another respect. Indeed, because of the production of acid compounds during the Maillard reactions, they are self-inhibiting to some extent. Consequently, it clearly appears important to keep all other factors constant when the effect of any one of them is studied.

That the PA determination of Maillard reaction rate is adequate and reliable is strongly stressed by the excellent agreement of our results with data available in the literature. For instance, the values of energy of activation published for the Maillard reactions range from 65 to 180 kJ mol^{-1} (Herrmann and Nour, 1977; Stamp and Labuza, 1983; Walstra and Jenness, 1984), depending on the reaction system involved, compared with our value, i.e., 115 kJ mol^{-1}. Besides, the published values (Stamp and Labuza, 1983; Walstra and Jenness, 1984) for Q_{10} at 373.5 K are between 1.9 and 5.0, against 2.7 for this study. The agreement of our results with published data indicates that the use of the spectral ratio I_{335}/I_{280} for the apparent rate constant in this study is quite appropriate and accurate. It is noteworthy that the PA band that we recorded for the Maillard browning products (i.e., 335 nm) is in agreement with the absorption band (i.e., 330 nm) obtained in solution for a mixture of glucose and poly-L-lysine when heated at 374.5–443.5 K for Maillard browning (Hansen and Millington, 1979), which clearly shows that Maillard reactions have been measured.

Despite the accordance of these results with those published elsewhere, one should be aware that chemical changes in milk often involve many separate reactions, e.g. protein denaturation, fouling (formation of skin on the surface of liquid milk), mutarotation of lactose, conformation change of protein, crystallization of fat, association or dissociation of casein, browning, dephosphorylation of caseinate, heat coagulation of milk, enzyme inactivation, and killing of vegetative bacteria and spores etc., each with its own E^* and H^*. All these reactions may depend in different ways on environmental conditions; a particular reaction may therefore depend on conditions of the reaction that is rate determining. Consequently, an activation energy obtained from the temperature dependence of a reaction rate should be considered as an apparent, average one (Walstra and Jenness, 1984). However, as common practice, temperature-dependent reaction rate is used to determine the energy of activation (Walstra and Jenness, 1984). For the particular case of Maillard reactions, as far as we know, they do not seem to be rate-limited by another reaction occurring in milk. Therefore, these thermodynamic parameters could be considered as true values. So, photoacoustic analysis of milk and dairy products appears to be very promising in that it is precise, rapid, and direct: there is no need for special preparation of the sample (milk, cheese, butter, yogurt, milk powder, etc.) such as extraction, solubilization, and so on (Martel et al., 1987). PAS can be applied to transparent as well as to opaque or light-scattering materials. Besides, the photoacoustic spectroscopy allows depth profiling of the sample by changing the modulation frequency. By this way, useful information can be obtained on the structure, the composition, and the optical and thermal properties of the sample from different depths of the sample, representing a real advantage over other existing spectroscopic methods used in dairy research.

CONCLUSION

We have demonstrated how easily photoacoustic spectroscopy can be applied to dairy products, especially for the study of the kinetic aspects of Maillard reactions, using the spectral ratio methodology. From a qualitative point of view, this method will also be very useful to measure the extent of heat damage to nutritional capacity of dairy products, particularly those designed for babies, in the different processes of sterilization and industrial preparations as far as the Maillard browning reactions are concerned. Being a direct, rapid, and above all a nondestructive spectroscopic method, PAS is welcome in dairy research and the milk industry as it is now in many other fields.

ABBREVIATIONS AND SYMBOLS

A, preexponential factor in Arrhenius law; a_w, water activity; E^*, energy of activation; H^*, enthalpy of activation; I_{λ_i}, photoacoustic intensity at a given wavelength, λ_i; k, rate constant; PA, photoacoustic; PAS, photoacoustic spectroscopy; Q_{10}, factor of increase of a reaction rate when the temperature is raised by 10 °C; R, ideal gas constant; T, temperature (K); Z, temperature rise (K) to increase the rate of a reaction by a factor of 10.

ACKNOWLEDGMENT

This work was supported by the Natural Sciences and Engineering Research Council of Canada and Agrinove, Coopérative agro-alimentaire.

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Received for review February 4, 1987. Accepted November 3, 1987.