Food Chemistry **12** (1983) 127–133

Interaction of Thiamine with Reducing Sugars

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(Received: 21 December, 1982)

ABSTRACT

The influence of reducing sugars (xylose, glucose and maltose) on the rate of thiamine destruction was studied at 95 °C in aqueous solutions buffered to pH 6·75. The rate of thiamine loss was found to be dependent on both the nature of the reducing sugar and on the concentration of the reducing sugar. Thiamine destruction rates, in the presence of a reducing sugar, decreased in the order: xylose > glucose > maltose. In addition, for the three reducing sugars studied, thiamine loss was enhanced as reducing sugar concentration increased. It was found that, when a reducing sugar was present, the rate of thiamine loss increased by as much as 37%.

INTRODUCTION

Since thiamine is the most sensitive of the B vitamins, detailed information concerning the degradation of this vitamin is required to ensure that adequate levels remain in the processed or formulated food products. Farrer (1955) has extensively reviewed the literature concerning thiamine stability in foods for all work up to that time. More recently, Dwivedi & Arnold (1973) outlined the possible mechanisms leading to

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Food Chemistry 0308-8146/83/$03·00

thiamine degradation and, in most cases, it has been found that thiamine destruction in both model and real food systems can be described by first order kinetics.

Thiamine loss in model and real food systems is dependent on many factors. Feliciotti & Esselen (1957) and Maga & Sizer (1978) have shown that increasing the severity of a heat treatment accelerates thiamine destruction. Mulley *et al.* (1975) and Morfee & Liska (1971) studied thiamine retention as a function of pH and found that, as pH increased, thiamine stability decreased. Other factors which have been implicated in thiamine destruction in foods include: sulfite treatment (Leichter & Joslyn, 1969), polyphenol oxidases (Chan & Hilker, 1974) and water activity (Dennison *et al.*, 1977).

One aspect of thiamine chemistry which has received very little attention, however, is the interaction of thiamine with a reducing sugar in a Maillard-type of browning reaction. By virtue of the amino group on the pyrimidine ring of the thiamine molecule, reducing sugars are susceptible to nucleophilic attack by the thiamine molecule. De Lange & Mijll Dekker (1954) were the first to observe that the darkening of a dry thiamine–glucose mixture at 85 °C was paralleled by a decrease of the thiamine content in the mixture. Van der Pole (1956) found that aqueous solutions containing thiamine and glucose darkened at 75 °C. More definite proof that thiamine was, in fact, capable of condensing with a reducing sugar came from the work of Lhoest (1958) who, using paper chromatographic techniques, identified glucothiamine as a condensation product of glucose and thiamine.

An inspection of the scientific literature from 1958 to the present time reveals that further investigations, relating to thiamine loss through reaction with a reducing sugar, have not been carried out even though indirect evidence does show that this type of reaction is indeed plausible. For example, Wai *et al.* (1962) noted that thiamine activity in vitamin preparations containing dextrose decreased by 90 % during 30 days of storage at 45 °C, whereas losses of thiamine with substances such as sucrose and mannitol (both non-reducing) were negligible during the same storage period. Dennison *et al.* (1977) postulated that the brown colour formation and loss of thiamine in dry or aqueous products might be due to the involvement of thiamine in a Maillard-type of browning reaction; however, these investigators did not pursue the aspect further.

This study was undertaken to ascertain the extent to which the rate of thiamine destruction was influenced by the presence of the reducing sugars, xylose, glucose and maltose.

MATERIALS AND METHODS

Materials

Thiamine hydrochloride xylose, glucose and maltose were reagent grade and were used as received. Thiamine hydrochloride was dried over phosphorus pentoxide in a desiccator for 24 h prior to use. All solutions were prepared immediately before use. Glass distilled water was used for the preparation of all solutions.

Methods

All kinetic studies were conducted at $95 \pm 0{\cdot}1$ °C (Haake, FK-2). Ten-millilitre aliquots of solution containing thiamine hydrochloride and reducing sugar were pipetted into a 1000-ml round bottom flask containing approximately 700 ml of phosphate buffer of pH 6·75. This flask and its contents were immersed in the water bath for sufficient time to allow the buffer solution to reach the desired temperature (95 °C), at which point the thiamine or reducing sugar containing solutions were added. After the solutions were added, the flask was shaken to ensure thorough mixing. This procedure ensured that, at the time of mixing of thiamine and reducing sugar, the temperature of the reaction mixture reached 95 °C almost instantaneously. The flask was equipped with a water cooled condenser to prevent loss of water by evaporation during the course of the experiment.

Immediately after the addition and mixing of the thiamine and sugar containing solutions to the flask, 10·0-ml aliquots were withdrawn for thiamine analysis. Ten-millilitre aliquots were also removed at 45-min intervals for a 3-h period. At each particular time interval three aliquots were removed, one aliquot to serve as a blank and the other two samples for thiamine determination. The thiamine content was determined by the thiochrome method (AOAC, 1975). A Coleman model 12-C fluorometer was used to measure fluorescent intensities. All kinetic runs were performed at least in duplicate.

Fluorescent intensities obtained at each time interval were plotted according to the equation:

$$\ln \frac{(I)}{(I_0)} = -kt$$

where I is the fluorescent intensity at time t(min) and I_0 is the measured fluorescent intensity at time $t = 0$. The first order rate constants for thiamine destruction, k (min^{-1}) were obtained from a linear regression of the resulting plot. Within the range of thiamine concentrations employed in this study, fluorescent intensities were shown to be directly proportional to the thiamine concentration.

RESULTS AND DISCUSSION

Figure 1 illustrates the experimentally obtained thiamine destruction curves in the presence of xylose. As illustrated, the kinetic runs are quite reproducible. The high correlation coefficients (r) obtained in these and other experiments indicate that the destruction of thiamine follows first order kinetics. Previous studies have demonstrated that the loss of amine in the Maillard reaction follows first order kinetics, at least during the initial stages of the reaction. Warmbier *et al.* (1976) studied the loss of

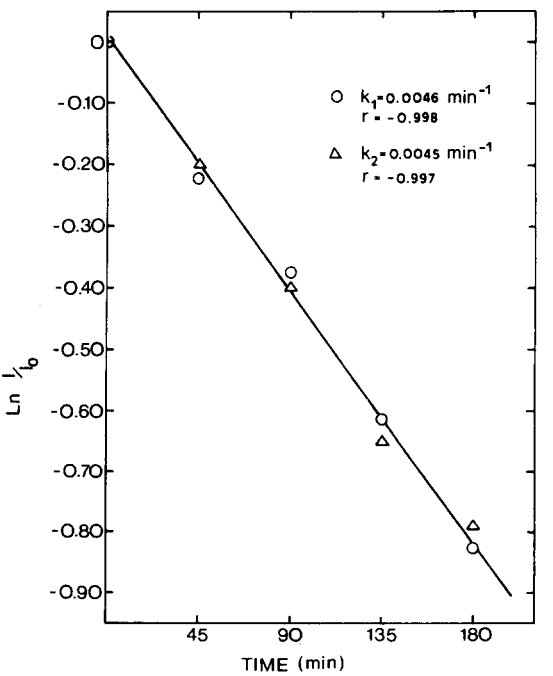

Fig. 1. Rate of thiamine destruction in the presence of xylose at 95 °C at pH 6·75, ○ and △ representing duplicate kinetic experiments.

TABLE 1
Reaction Rate Constants (min^{-1}) for Thiamine Destruction as a Function of Reducing Sugar Type and Concentration

Reducing sugar	*Reducing sugar concentration (μg/ml)*		
	0	*6*	*8*
Xylose	0·003 5	0·004 6	0·004 8
Glucose	—	0·003 8	0·004 3
Maltose	—	0·003 4	0·004 2

available lysine in an IMF system containing casein, glucose and glycerol and found that the initial loss rate of available lysine (and glucose) followed first order kinetics. Wolf *et al.* (1977) concluded that, in a model system composed of soybean protein and glucose, the reaction resulting in the initial rapid phase of available lysine loss occurred by first order kinetics. In the present study, it should be remembered that not only does thiamine degrade through interaction with reducing sugars, as do other amine compounds, but it is also destroyed by heat. Thus, the assumption that thiamine loss follows first order kinetics may be considered a simplification to what is otherwise a very complex situation.

The results presented in Table 1 show that the rate of thiamine loss is enhanced when reducing sugars are present in solution. Moreover, it is apparent that the rate of thiamine loss is dependent not only on the concentration of reducing sugar but depends on the type of reducing sugar as well. Table 1 shows that the rate of thiamine loss increases as the concentration of the reducing sugar increases for the reducing species used in this study. At a concentration of 8 μg/ml, xylose is seen to enhance the rate of thiamine destruction by almost 40 %.

In addition, Table 1 shows that the rate of thiamine destruction is a function of the type of reducing sugar present in solution. More specifically, the rate of thiamine loss is seen to increase in the order maltose (reducing disaccharide) < glucose (hexose) < xylose (pentose). It is well known that the nature of the reducing sugar plays a major rôle in determining the activity of a sugar in a non-enzymatic browning reaction. The rate of condensation of an amino compound with a reducing sugar is dependent on the rate at which the cyclic sugar structure opens to form the acyclic reducible form. As outlined by de Man (1976), the fact that pentoses are more reactive than hexoses which, in turn, are more reactive

than reducing disaccharides, is attributable to the amount of open chain structure which follows the order: pentose > hexose > reducing disaccharide. Katchalsky & Sharon (1953) have reported that the rate of lysine interaction with a variety of aldoses followed a similar order: arabinose > xylose > galactose > lactose > glucose > maltose. Thus, the rates of thiamine loss are consistent with results to be expected on either the bases of equilibrium sugar tautomeric distribution or conformational instability.

In view of current trends to replace sucrose with other sweetening agents, e.g. fructose, we feel that this aspect of thiamine chemistry warrants further study.

CONCLUSION

Studies were conducted to evaluate the influence of reducing sugars on the loss of thiamine in aqueous solution. It was found that the rate of thiamine loss increased when reducing sugars were present. The rate of thiamine loss was influenced by type and concentration of reducing sugar.

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