Dietary fibers have water solubility-associated, different physiological effects (1): most water-soluble dietary fibers (SDF) markedly decrease serum cholesterol level, whereas most water-insoluble dietary fibers (IDF) don’t have such effect (2). In spite of the importance of interaction between dietary fiber and water, the interaction has not been satisfactorily considered in detail. Therefore, a rapid hydration measurement based on proton spin-spin relaxation behavior has recently been utilized for a basic investigation of the above interaction at the molecular level and as an immediate means for hydration change. This method was applied to an analysis of commercial dietary fibers in water, resulting in three patterns for the relaxation curve (3). The three patterns were characterized by “sodium alginate type,” “polydextrose type,” and “cellulose type,” which corresponded well to high molecular weight SDF (H-SDF), low molecular weight SDF (L-SDF), and IDF, respectively. This classification may reflect differences in the mechanism of dietary fibers on serum cholesterol level; for example, the cholesterol-lowering action of H-SDF arise mainly from their direct effects on the viscosity of the solution (1, 4), whereas the effects of L-SDF are mostly based on the fermentability by bacteria and not the direct viscosity effect, and there are no such actions for most IDF. Although the different proton behaviors in water were measured by \(^1\)H-NMR at 30°C (3), those after heat treatment remained uncertain. Information about the effect of heat treatment on interaction between dietary fiber and water is important because many foodstuffs containing dietary fibers are consumed after heat treatment. These facts were revealed by examination of the heat effect on interaction between dietary fiber and water using the \(^1\)H-NMR technique. Dietary fibers commercially available as food additives were adopted for the rapid measurement of \(^1\)H-NMR relaxation (3). When necessary, they were named with different numbers if they had the same ingredients but different physicochemical properties such as viscosity and dispersibility as described in literature (3). Twenty micrograms of dietary fiber powder was added to 300 μL of distilled water. The mixture was allowed to stand at 30°C for one day and then heated at 85°C for 30 min, followed by the measurement of spin-spin relaxation behavior observed in conformity with the Carr-Purcell-Meiboom-Gill’s pulse sequence (5) using a Bruker PC120 pulsed NMR-spectrometer (20 MHz) at 30°C. This heating condition (85°C, 30 min) was adopted to compare the relaxation behaviors in the water of dietary fiber in spite of virtual differences of cooking temperature and time for each foodstuff. Analytical items were the relaxation curve, relaxation time, and proton population. The proton relaxation time was estimated from the slope of linear regression for natural logarithms of signal amplitudes in NMR against delay times (6, 7). The proton populations consisted of the fast and slow components with 0-100 and 250-430 ms delay times, respectively. The population for the fast component was not discussed because of a simple calculation required from the value of the slow component. The average of duplicate measurements was obtained for each sample because the proton relaxation behavior could be assumed to be invariable as a result of repeated measurements in the previous experiment (3).

Relaxation curves for polydextrose and cellulose-1 in water before and after heat treatment are shown in Fig. 1 as typical examples of L-SDF and IDF, respectively. Polydextrose gave the same mono-phase relaxation curve before and after heat treatment at 85°C for 30 min. On the other hand, cellulose-1 gave a relaxation pattern different from L-SDF, i.e., a multi-expo-
Fig. 1. Typical relaxation curves of dietary fibers in water. The curves are for samples after incubation at 30°C for 1 d (○) and its subsequent heat treatment at 85°C for 30 min (●). L-SDF, low molecular weight water-soluble dietary fiber; IDF, water-insoluble dietary fiber.

Fig. 2. Proton populations for the slow relaxation component in various dietary fibers. Commercially available dietary fibers were adopted without further purification as samples for rapid hydration measurement by 1H-NMR relaxation (3). The properties of these dietary fibers such as their suppliers, sources, viscosity in water and so on were the same as shown in the literature (3). Open and closed bars indicate samples after incubation at 30°C for 1 d and its subsequent heat treatment at 85°C for 30 min, respectively. The average of duplicate measurements was shown for each sample because the proton relaxation behavior could be assumed to be invariable as a result of repeated measurements in the previous experiment (3). Abbreviations were the same as in Fig. 1.
treatment. Thus, 70–80% of protons varied from the slow component to the fast one after heating at 85°C. Such a considerable change in the proton population held only for agar probably through proton exchange between the fast and slow components. To address such a possibility, the relaxation times for their components were further investigated as below.

As shown in Fig. 3, all of the relaxation times for H-SDF in water were much less than those for L-SDF or IDF, although being almost constant before and after heat treatment. The slow relaxation time of agar in water after heat treatment at 85°C for 30 min could not be ascertained because its value, calculated from the slope of the linear regression line (Fig. 1), was beyond that of distilled water (2,300–2,500 ms). The slow relaxation times of other fibers could be reasonably calculated as shown in Fig. 3.

The fast relaxation times could be obtained from the decay curves for proton relaxations in either all IDF or a few H-SDF such as sodium alginate-1, pectin-1, and pectin-2 (Fig. 4). Most of them were somewhat similar to one another before and after heat treatment. However, the fast relaxation times in agar were obtained as 68 and 22 ms before and after heat treatment, respectively. Such a large difference in this respect was specific to agar.

Thus, the parameters for the proton relaxation behavior of dietary fibers except agar were almost constant before and after heat treatment. Agar lost the slow relaxation component after heat treatment, while its relaxation time became even faster. Such changes in proton relaxation caused by heat treatment are explained to reflect the chain flexibility of agarose and its related polysaccharides (8, 9). Lee et al. used non-linear transverse magnetization decay to indicate the presence of several pore sizes in the system (7). It is therefore reasonable to consider that there are different pore-size distributions in agar before and after heat treatment. Although the $T_2$ relaxation time is influenced by proton exchange processes and temperatures at the measuring points (8, 9), it serves as a good parameter for gelation of agar polysaccharides (8–11). Similar proton exchanges were considered to occur not only for agar in the water system but also for other dietary fiber systems, resulting in minor variations in proton relaxation behavior for sodium alginate-1, polydextrose, cellulose-3, alginic acid and so on.

Although agar had been classified as SDF (4), Tsuji (12, 13) recently claimed that agar should belong to IDF. Such a definition is also supported by the fact that agar swells in water with a sustaining multi-phase relaxation curve during incubation, but that the curve of H-SDF in water changes from multi-exponential into mono-phasedal (3). These phenomena may be intimately involved in the gel formation of agar via proton exchange between agar and water, even though the major portion of the water molecule in agar-water gel is unaffected (11). Such a proton exchange proceeds by heat treatment in the case of agar although it is done without heat treatment in other H-SDF. In other words, most dietary fibers change little in the spin-spin relaxation behavior before and after heat treatment. This may in-
dicate that proton exchange between dietary fiber and water is relatively constant, irrespective of absence or presence of heat treatment (e.g. 85°C, 30 min), although some of IDF convert to SDF after enzymatic digestion (14).

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