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## FOOD PROTEIN PRODUCTS FROM MILK

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### SUMMARY

The protein content and composition of New Zealand milk, together with the nutritional and functional properties of casein and related milk protein products, is discussed. Attention is drawn to the rapid change from industrial to edible uses of casein and to the expanding range of milk protein products which are now being manufactured in New Zealand to meet the requirements of a wide variety of food formulators. The manufacture of some of these products involves processes completely new to the dairy industry, and some of these, such as membrane separation techniques, open up the possibility of producing an ever-increasing range of protein products.

It is pointed out that the milk protein picture is a little confused at the present stage, owing to the tremendous shortage of all dairy products and the tendency for most manufacturers to concentrate on milk powders, which are currently returning a greater yield than milk proteins. It is suggested that this is to some extent an artificial situation, and that, from past experience, it may be assumed that the pendulum will swing in the opposite direction and that the emphasis will return to protein products. When it does, traditional casein as known for so many years, and as developed for industrial markets, is likely to be of less importance, and the New Zealand dairy industry will be involved in the manufacture of a wide variety of specialty products to meet the requirements of food formulators in different parts of the world. Despite competition from possibly lower-priced but certainly less acceptable alternative protein sources, the prospects in the edible market for casein, caseinates, lactalbumins and related products are regarded as extremely good.

MILK is the natural food of the young of all mammals, which are dependent on it for their energy, protein, mineral and vitamin requirements during their early stages of development. It is not surprising, therefore, that the amino acid composition of milk proteins fairly precisely parallels the requirements of the young of the particular species for which nature intended it, and that the nutritional value of milk of domestic animals should have been recognized early in the history of mankind, not only as a food for infants, but throughout later life. In this respect, it is perhaps relevant to recognize that humans, and those of Caucasian origin in particular, are abnormal in this

respect in that they are the only species which continues to drink and to use milk beyond infancy. Thus, from early times through to the present, considerable quantities of milk protein have been consumed as liquid milk, and this is an important edible usage of milk proteins which is frequently overlooked.

As time went on, man learnt to develop from milk, products of longer storage life. The first of these was cheese, discovered, we are told, by accident, through an Arab taking his goat's milk out into the desert with him in a container made from the dried stomach of a young animal. The warm sun and the rennin from the stomach gave him a new product.

Over the past half-century or more, with advancing milk processing technology, there have emerged a variety of milk powders many of which are used in human foods of one form or another, and more recently there has been a rapid upsurge of interest in specially formulated milk protein products, which are used either for their functional or nutritional properties.

The nutritional value of milk proteins is well recognized and requires no elaboration here beyond occasional reference to particular uses where nutritional considerations have been of some importance.

#### CASEIN AND RELATED PRODUCTS

Casein is generally taken as the reference protein in most nutritional studies. There are certain differences in the amino acid composition between casein and the other proteins of milk. These latter contain more sulphur, whereas casein is distinguished by a remarkably high phosphorus content of about 0.8% in the form of phosphoric acid which esterifies the hydroxyl groups of the serine and threonine. However, in general, no significant difference has been found between the nutritive value of casein and the other whey proteins.

Because of our predominantly Jersey breed, the protein content of New Zealand milk is on average considerably higher than that produced in most parts of the world. Standard texts quote protein content of milk in the order of 3.0 to 3.3%, whereas New Zealand milk of average fat test (4.7%) contains about 3.75% protein with a standard variation of about  $\pm 0.2\%$ . The protein content of milks of higher fat content is 4.0% or more. As a consequence, the protein content of many of our dairy products, particularly milk powders, is much higher than in comparable products produced elsewhere, a point which

may be of considerable importance in the marketing of our products, particularly to developing areas where nutritional considerations are of great importance.

Round threequarters of the protein in milk consists of casein, a fairly complex mixture of various components which differ quite markedly in their composition and physical characteristics, but which are not separated commercially and therefore need not be of concern in a discussion of the uses of casein. The remainder of the protein in milk is made up of the so-called whey protein complex, which consists mainly of  $\beta$ -lactoglobulin and  $\alpha$ -lactalbumin. The striking differences between these proteins are that casein is precipitated at its iso-electric point of pH 4.6 and is coagulated by the enzyme rennin, whereas whey proteins are not. In contrast the whey proteins are coagulated by heat, but the caseins are not.

Casein was the first milk protein to be produced commercially in significant quantities and, until the dramatic switch this season from casein to powder production because of the higher prices for the latter, manufacture increased steadily in New Zealand, reaching just under 70,000 tons, or roughly half the world's production. Casein is produced by acidulating skim milk to a pH of about 4.6, either by the addition of mineral acids, generally hydrochloric or sulphuric, or by the development of lactic acid by suitable starter bacteria. The casein coagulates, is mechanically separated from the whey, washed, pressed, dried, ground and sifted, usually to 30-mesh fineness.

This type of casein was used mainly for industrial purposes, particularly as an adhesive in papercoating, and it is only recently that real interest has developed in the use of casein and other milk proteins for edible purposes. Traditional 30-mesh casein met the requirements of industrial users, but its granular form, relative insolubility in water, non-functionality and gritty characteristics made it an unpromising choice for direct use as an ingredient for food preparations to be consumed in liquid form. More finely ground forms of traditional casein—usually 80-mesh or finer in particle size—found some early applications in food formulations such as bread and breakfast cereals, but here the application was totally nutritional and not functional.

Rennet casein is manufactured in a somewhat similar manner to acid casein, except that the casein is coagulated at the natural pH of milk by the addition of rennet, rather than by adjusting the pH to the iso-electric point. It is used mainly for the manufacture of plastics, particularly

small articles such as buttons, and for food uses has the same general disadvantages as traditional acid casein.

Small quantities of lactalbumin have been produced commercially for a number of years in a denatured form by heating acid casein or cheese whey with suitable pH adjustment. The light flocculant curd so produced is washed, dried, ground, and milled to a fine powder. This type of lactalbumin, like casein, is non-functional in its properties, and its uses in foods are entirely nutritional.

Thus in the mid-1950s, when for a variety of reasons interest started to swing from industrial to edible uses for milk proteins, food formulators had available to them basically three commercial protein products—acid casein, rennet casein and lactalbumin—all of high nutritive value but lacking the functional versatility of the natural milk proteins, and the caseins having the additional disadvantages that they were in forms developed primarily for industrial usage.

Over the past 15 or more years, and particularly over the last half-decade, a wide variety of alternative milk protein products has been produced, designed specifically to meet the requirements of food formulators, and retaining the functional as well as the nutritional properties of the proteins as they occur in milk. These include a variety of caseins differing in their physical properties, particularly dispersibility, and particle size and structure, caseinates which are prepared by reacting casein with suitable alkalis, co-precipitates which are produced by the simultaneous coagulation of casein and whey protein in skim milk, solubilized protein products of various types, improved denatured lactalbumin, and soluble lactalbumin.

It is difficult to obtain accurate information about food usage of these milk protein products, but recent estimates suggest that some 60,000 tons, or a little more than one-third of total world production of casein and related milk proteins, is being utilized in the food industry. About half of this is used in United States, 15,000 to 20,000 tons in Japan, and up to 15,000 tons in the rest of the world. The decline in casein usage, as a consequence of high price and general world shortage, has been in the industrial rather than the edible field.

Historically, the first milk protein product used to any extent in the edible field was sodium caseinate, but because of the rather poor flavour of the caseinate originally available, its use was limited to fairly highly flavoured products where spices etc. could mask the off-flavours. Manufacturers of processed meats were quick to realize the

advantages of the functional properties of caseinates where they could act as fat emulsifiers and water binders, and caseinates are now widely used by the meat trade to the extent of about 2% in sausages, meat loaves, and related products.

Sodium caseinate is probably the most versatile of the milk proteins currently available, and as its flavour improved, its use extended to more bland formulations, particularly coffee whiteners and powdered toppings, and these probably represent the major food use of caseinates at present. Here the caseinate is used not so much for its nutritional value, but because of its protective and whipping function, the protein film which forms around the emulsified fat particles preventing clumping of the fat and resultant loss of stability. In whiteners the sodium caseinate is critical to fat stability and plays an important role in the development of maximum whitening effect. Convenience foods of this type are rapidly replacing more traditional products, such as cream in the case of coffee whiteners, and usage is expanding rapidly.

The functional properties of caseinates have also been put to good effect in frozen desserts, ice creams, filled and imitation milks, cake and pie mixes, milkshakes and other specialty foods, including slimming preparations, instant breakfast formulations, dry shortenings for confectionery, bread and other baked goods, instant desserts, and texturizing agents in starch-reduced bakery goods.

Co-precipitates have attracted a great deal of interest and techniques have been developed for the manufacture of a range differing in their functional properties such as solubility, viscosity and water-binding capacity. It might be anticipated that such products could be of considerable interest to food formulators, but to date the demand has been extremely limited. A partial explanation for this may lie in the tendency for manufacturers, particularly in Australia, to attempt to define a small range of co-precipitate products and to hope that these meet food formulators' requirements, rather than taking a more flexible attitude to manufacture and attempting to produce products tailor-made to particular processors' requirements. This is extremely important in the development of milk protein products, and one may assume that the future of milk proteins lies in a very wide range of products, each formulated to the precise requirements of some user, rather than, as in the past, large tonnages of a small range of standard products.

Casein itself is now available in many forms besides the traditional granular product that met industrial requirements. The emphasis with the move to edible uses has been on improvement in flavour, and here quite spectacular success has been achieved, as also in the production of finer, more dispersible products. Casein fines were previously difficult to dispose of but have now become a premium product. Unfortunately, casein is fairly difficult to grind in conventional equipment, and this has led to attempts to produce finely powdered material by alternative means, such as spray or roller drying. Even the most finely ground or powdered caseins tend to be somewhat gritty on the palate, and therefore of limited usefulness in food formulations. Roller-drying, however, gives a flake rather than a granular particle, and this tends to lie flat on the palate and so avoid the problems associated with ground or spray-dried casein. Roller-dried products of this type are finding some use in breakfast cereal formulations and also in a number of convenience foods.

An extremely interesting possible use for casein involves its conversion into synthetic products such as artificial meats, and this is the subject of a number of recent patent specifications. In these processes the casein is spun into fibres which are bonded together to simulate the structure of meat, fish and other textured foods. The bonding agent currently used is a starch matrix, which also contains the meat or other flavour. The water binding capacity of casein is a great advantage, but with starch as the bonding agent, the casein meat cannot be baked or fried.

It is perhaps relevant to mention the quite substantial quantities of casein that are used in food and pharmaceutical preparations in the form of hydrolysates. This is unlikely to represent a large usage of casein as the cost of such products relative to alternative protein hydrolysates is relatively high. However, there is likely to be a place for casein hydrolysates as flavouring materials comparable to soy sauce, or in food formulations for people known to have allergic reactions against the intact protein. The pharmaceutical use of these materials is also likely to increase.

#### LACTALBUMIN

Lactalbumin is the other milk protein produced in commercial quantities. Although there have been recent improvements in its manufacture, it still remains an insoluble, non-functional product, although one of high

nutritive value. The functional properties which undenatured lactalbumin possesses, such as whipping and water binding, are substantially lost during the heat denaturing process that accompanies its heat precipitation from whey. Furthermore, for practical purposes lactalbumin, unlike casein, does not form soluble salts, so that it has no functional derivatives.

A demand has been known to exist for an undenatured water-soluble lactalbumin, but until recently the processes for extracting lactalbumin from whey without denaturation have been prohibitively expensive. With the advent of membrane separation techniques, however, the situation has changed dramatically, and it is now possible to produce a range of soluble lactalbumin products at relatively low cost. A considerable amount of pilot-scale investigational work in this field has been done at the New Zealand Dairy Research Institute, and a commercial ultrafiltration plant for recovering lactalbumin from whey is now in operation in New Zealand.

The most clearly defined market potential at present makes use of lactalbumin's functional property of solubility over the whole pH range, and it is clear that soluble lactalbumin fulfils a demand for a high nutritive value protein that can be used under pH conditions where the insolubility of protein such as casein would affect the consumer acceptance or other characteristics of the product. However, soluble lactalbumin has only just become available in commercial quantities, and food formulators have not had an opportunity to evaluate some of its other functional properties. It is clear that the ease with which it is denatured, and hence can be used to "fix" various food structures, opens up interesting possibilities. For example, it could to advantage be used in place of starch as a bonding agent in the textured foods referred to above. It is also an excellent egg-white substitute, and can be used to produce meringues and related products. There is considerable interest in its use in increasing the stability of foams in products like ice creams and related frozen desserts.

Unfortunately, the supplies of this very interesting milk protein will remain limited, since its source is casein or cheese whey, and it can only be recovered in quantities equivalent to about one-eighth or less of the amount of casein produced—a maximum of round 10,000 tons per annum in New Zealand, even if all the whey available from casein and cheese production were to be used.

## CONCLUSION

In the milk protein field a very rapid swing from industrial to edible uses is occurring. This began a number of years ago, and is accelerating rapidly.

The milk protein picture is a little confused at the present stage, owing to the tremendous shortage of all dairy products and the tendency for most manufacturers to concentrate on milk powders, which are currently returning a greater yield than milk proteins. This is, however, to some extent an artificial situation, and it is probable, in the light of past experience, that the emphasis will return to protein products: When it does the New Zealand manufacture of a wide variety of specialty products to meet the requirements for food formulators in different parts of the world seems likely.

Traditional casein as known for so many years, and as it was developed for industrial markets, is likely to become a thing of the past. Although industrial markets have been important ones, it has long been recognized that casein was too valuable a food product to use industrially, and except for certain specialty uses, mainly in the paper-coating field, it is probably now pricing itself off the industrial market. The prospects on the edible market for casein, caseinates, lactalbumins and related products, however, look extremely bright. Here again, of course, cost is an important consideration. Casein may be regarded as a relatively expensive raw material, but it has many unique functional and nutritional characteristics which cannot be duplicated by alternative proteins without a considerable amount of additional processing. This increases the cost of a seemingly cheap material, such as unprocessed soy protein, to be equivalent to or in many cases much higher than milk proteins.

Milk protein is also a prestige food, and it is being formulated into prestige products. These are the products that people in under-developed countries strive for—they are not interested in cheap substitutes of approximately the same nutritive value. They want the same food as the white man is eating, and this in the future will include a wide variety of products based on or containing milk proteins.