FORTIFICATION OF FOODSTUFFS WITH N-ACYL DERIVATIVES OF SULFUR-CONTAINING L-AMINO ACID ESTERS

BACKGROUND OF THE INVENTION

This invention relates to the fortification of proteinaceous foodstuffs, which are deficient in sulfur-containing amino acids with nutritionally available derivatives of those amino acids. The term 'proteinaceous foodstuff' is meant to encompass protein per se, whether derived from vegetable or animal sources, and additionally, to manufactured products intended for human or animal consumption containing such proteins as a significant component.

There is considerable impetus to satisfy the protein requirement in the diet of man with protein derived exclusively from vegetable sources. There are essentially two reasons which compel human populations to look to vegetable proteins for a substantial, if not an exclusive, source of dietary protein. The paramount reason is one of efficiency. That is, at least in certain parts of the world, it is no longer feasible, from the standpoint of consumption of energy, to grow a crop, to feed livestock, to obtain required dietary protein. The second reason is best couched in terms of nutrition and health. Manufactured foodstuffs based on vegetable proteins afford the possibility of ultimately achieving a perfect balance of nutrients with controlled exclusion of certain identified detrimental agents, such as cholesterol. And, there are subsidiary reasons involving the factor of convenience, and, to some, reasons of personal conviction.

There appears to be no question as to the capacity to obtain vegetable proteins in sufficient quantity. Success in the agriculture of, for example, the legumes (and in particular the soybean) have assured the ready procurement of vegetable protein in quantity. And this assurance of quantity is, in part, attributable to the development of associated technologies to exploit and make available this source of native vegetable protein. The principal concern is one of quality of that vegetable protein. If the vegetable protein is not nutritionally the equivalent of protein derived from animal sources, that is, of comparable quality, the fact that the vegetable protein is obtainable in quantity is of lessened significance. The fact is that proteins derived from a chosen plant species source are not of comparable nutritional quality to animal sources. This is evident, in part, by examination of the amino acid content, or profile, of a chosen plant protein. For example, wheat gluten is deficient in lysine; soybean protein is deficient in the sulfur-containing amino acids, such as methionine. Nutritionists have applied the term "limiting" to such amino acids, and have noticed that a protein characterized by a particular limiting essential amino acid is effectively levelled in nutritive value to the content of the first limiting amino acid. For example, if a certain vegetable protein was relied upon for the sole source of dietary protein, and if that protein was characterized by an amino acid profile revealing certain limiting amino acids, it would be necessary to consume in the diet an excessive amount of that protein in order to insure the nutritionally required intake of those limiting essential amino acids. Besides the sheer economic waste of such a diet, there is increasing evidence in the scientific literatue that excess dietary protein may have detrimental physiological effects.

Fortification of proteinaceous foodstuffs with sulfur-containing amino acids, and particularly with respect to methionine, has typically involved direct addition of DL-methionine as the free acid. The DL racemic mixture was employed even though only the L stereoisomeric form is found incorporated in human protein because it was thought that methionine ws one of the few α-amino acids in which the D form experienced the metabolic conversion to the L form. However, all attempts to fortify methionine deficient foodstuffs with free DL-methionine proved unfeasible because of a severely intractable flavor problem. It was discovered that foodstuffs so fortified with DL-methionine developed off-flavors and became discolored. This effect was particularly noticeable for foodstuffs that were either heated prior to eating, or were stored for an indefinite period in a hydrated condition, but the effect was also noticed after dry storage. The chemical basis for the generation of these off-flavors and unsightly discolorations was, in part, attributable to the well-known Strecker degradation — or more commonly, the Maillard reaction (chemical browning). The Maillard reaction comprises a set of reactions between amino containing compounds (here free α-amino acids) and carbonyl-containing compounds (for example, reducing sugars present in great abundance in the fortified foodstuff). The Maillard reaction is particularly distressing when sulfur-containing amino acids are involved because of the generation and liberation of noxious mercaptans and sulfides, e.g., methional is freely formed in foodstuffs fortified with methionine. Also, distinct from the Maillard reaction, degradative reactions, such as air oxidation of these sulfur-containing amino acids, adversely affect flavor. Needless to say, alternate means were sought to alleviate the sulfur amino acid deficiencies in vegetable derived proteins.

One means, of limited practical utility, involved blending proteins from different vegetable sources such that a particular amino acid deficiency of one protein was substantially cured by blending with it a precise amount of a distinct protein having that particular amino acid present in relative excess. By careful selection and precise blending, it is possible to achieve a reciprocal complementing effect. For example, sesame seed protein is rich in methionine but poor in lysine; soybean protein is poor in methionine but rich in lysine; consequently a precise blending of the two yields a more nutritionally balanced vegetable protein.

Other means available from the prior art are designed to defeat the Maillard reaction in the face of free addition of selected amino acids. Representative diverse means suggested by the prior art are: (1) encapsulation of the free amino acid; (2) simultaneous incorporation of certain alleged anti-browing agents, e.g., pyrocarbonic acid esters, and O-carboxy anhydrides of α-anhydroxy acids (U.S. Pat. No. 3,337,348 granted Aug. 22, 1967); and (3) utilization of the plastein reaction. This last mentioned means involves the bonding of the added amino acid by peptide linkage to protein molecules which constitute the bulk of the proteinaceous component of the foodstuff. All of the above-listed means are of limited practical utility. Consequently, the prior art continued the search for means in circumvention of the Maillard reaction. Among these means were suggested the utilization of tasteless derivatives of certain amino acids which were relatively inert to degradation yet nutritionally available on ingestion.