FLAVOUR ENHANCED CHOCOLATE CRUMB

The present invention relates to a process for the preparation of chocolate crumb.

The manufacture of chocolate crumb includes several steps of evaporation, heating and vacuum drying of milk solids, sugar and cocoa liquor to obtain a stable crumb powder. The resulting chocolate crumb is used as an intermediary product in the manufacture of chocolate. Chocolate production using chocolate crumb involves mixing crumb with cocoa butter followed by refining, conching and tempering. Chocolate crumb generally forms a large proportion of the ingredients (around 70%) in finished milk chocolate.

Chocolate crumb flavour develops from flavour precursors in Maillard reactions during preparation of the crumb powder. This reaction gives the chocolate crumb a taste and colour which is desired for confectionary products. Lactose reacts in Maillard reactions with free amino acids/peptides and with milk protein-bound lysine residues. It is recognized that the lactose come from the milk, whereas the amino acids and peptides come from cocoa liquor and milk. There is a low level of free amino acids in standard crumb ingredients. This low amount of free amino acids in the reaction mixture and the consumption of these free amino acids during crumb processing is a limiting factor during the generation of crumb powders with strong flavour intensity

Attempts have thus been made to increase the level of flavour precursors in chocolate manufacture. However, these studies have been performed by incorporating artificial flavours directly into chocolate. For example in US 2,887,388 and US 2,835, 592 there is disclosed a process for the production of artificial chocolate flavour by reacting reducing sugars and

protein hydrolysates of corn, wheat, hemp, soy, rye, oats, peanut, barley, animal and fish proteins, such as casein, lactalbumin, egg albumin, serum albumin, fish albumin, gelatin, elastin, collagen and keratin. In a similar way DDR 205 815 and DD 239 942 describe the production of artificial chocolate flavour by reacting reducing sugars and protein hydrolysates, e.g. gelatin and wheat gluten, in the presence of 1-30% water at 115-160°C. US 2,835,590 is also directed to a process of producing an artificial chocolate flavour using a wide range of hydrolysed peptides.

Another approach, to enhance cocoa flavour was to increase the free amino acid pool. US 5, 676,993 discloses a process for producing cocoa flavour by roasting a combination of amino acids and reducing sugars and treating the cocoa nibs (soaking) and unroasted liquor with the amino acid/sugar mixture.

US 3,900,578 and US 4,346,121 disclose a process for the manufacturing of crumb products by preparing a first raw material flow containing liquid milk and one or more flows which contain, sugar raw materials, dry protein raw materials, amino acids, fats or emulsifiers. This document discloses that the lactose present in the milk products can be partly or completely hydrolysed so that lactose is transferred to corresponding amounts of glucose and galactose since the presence of these sugars is advantageous for the desired Maillard reaction. This teaching is limited to the use of hydrolysed lactose.

Thus, an object of the present invention is to manipulate the raw materials used in crumb processing or to use other raw materials to increase the consumption of amine flavour precursors in chocolate crumb processing and to result in an alteration of flavour intensity and profile in the resultant crumb.

According to one aspect of the present invention there is provided a process for the production of a chocolate crumb comprising mixing and heating from about 15 to about 70% by weight of milk solids, with about 10 to about 75% by weight of sugar and about 0.1 to about 10% by weight of milk or vegetable protein hydrolysates, the percentages being based on the weight of the mixture.

This process involves the use of milk and vegetable protein hydrolysates to generate a pool of free amino acids and peptides for Maillard reactions in chocolate flavour reactions. Normally there is a large excess of lactose which is not significantly reduced during crumb processing, however, when free amino acid/peptide consumption is increased by the addition of milk or vegetable protein with a high degree of hydrolysis (DH), a greater consumption of lactose is also observed. Such an increase in the consumption of free amino acid and peptides alters the flavour profile in the resultant chocolate crumb.

The process may further comprise the addition of cocoa solids. Preferably, the ratio of protein hydrolysates to cocoa solids to sugar to milk solids is 1:2:3:9. The milk or vegetable protein hydrolysates may be prepared from milk powder, casein, whey, soy, wheat, cotton, peanut, rice or pea protein. Preferably from about 2 to about 7% by weight of milk or vegetable protein hydrolysates may be used. The milk powder is skimmed milk powder or caramelised milk powder.

Some off flavours, such as cheesy, bitter or savoury may be generated by the hydrolysis of the protein. However a majority of off-flavours come from the protein mixture itself, when protein mixtures have not been purified. Thus, it is important to start with flavour-neutral starting materials or to purify the proteins prior to use. Such flavour-neutral starting materials

include soy isolates and casein. In particular when casein and soy hydrolysates are used with different degree of hydrolysis (DH) up to a 50-fold increase in free amino acid consumption can be achieved. However, other protein hydrolysates may also be used such as milk powder, whey, wheat, cotton, peanut, rice or pea protein hydrolysates. To introduce a caramelised note and strong flavour enhancement, protein hydrolysates can be used in combination with caramelised milk powders.

According to a further aspect of the present invention there is provided a chocolate crumb having enhanced flavour characteristics obtainable by the process according to the present invention. Preferably the chocolate crumb comprises from 1:1.5 to 1:3 milk solids to sugar and from 0 to about 25% by weight, preferably from about 10 to about 15% by weight, of mixture of cocoa solids.

According to another aspect of the present invention there is provided a process for the preparation of chocolate which comprises processing chocolate crumb together with other chocolate ingredients to form chocolate wherein the chocolate crumb is prepared by the process according to the present invention.

According to yet further aspect of the present invention there is provided a chocolate product with modified flavour characteristics obtainable by a process according to the present invention.

The milk solids may comprise for example, whole milk powder, whey proteins or low fat milk solids. The low fat milk solids preferably contain less than 5% by weight of fats, more preferably less than 2% by weight of fats and is most preferably skimmed milk powder, or

ingredients thereof or recombined solids. The amount of milk may be from about 20 to about 70% and preferably from about 30 to about 65% by weight based on the total weight of the mixture.

The sugar used is preferably in the form of a dry powder which may be crystalline or in the form of a slurry. The sugar used may be, for example, sucrose, glucose, dextrose, lactose, maltose, maltose syrup, malt extract, fructose, invert sugar, corn syrup solids, rhamnose, fucose or sugar replacers such as polyols eg soribtol, mannitol, xylitol, maltitol, lactitol, polydextrose, etc or mixtures thereof. Preferably, the sugar used is sucrose alone, but if desired, one or more other sugars may be used together with sucrose in an amount up to 25% by weight based on the total weight of the sugar. If desired a low calorie sweetening agent may be used as part of the sugar. The amount of sugar may be from about 10 to about 75% and preferably from about 20 to about 60% by weight based on the total weight of the mixture.

When the process is carried out in the absence of cocoa solids, a white crumb is obtained. When the process is carried out in the presence of cocoa solids, the cocoa solids may be in the form of cocoa liquor, cocoa powder, cocoa butter or cocoa butter alternatives which are vegetable fats such as cocoa butter equivalents or substitutes. The amount of cocoa solids used in the process of the present invention may be from about 3 to about 20% by weight based on the total weight of the mixture, preferably from about 5 to about 15% by weight based on the total weight of the mixture. The amount of water used in the process of the present invention is preferably from 1.5 to 8% by weight based on the total weight of the mixture.

Consumption of flavour precursors and subsequent flavour changes can be increased by using high degree of hydrolysis hydrolysates and/or by increasing the reaction time. The invention is not limited to the above recipes and processes, but covers also the use of protein hydrolysates in crumb processing under other conditions such as different temperature, different moisture content, different fat content, different pH and different processing equipment (e.g. shear force, extrusion).

The invention will now be described in more detail with reference to the following non-limiting examples:

Preparative Example 1:

Preparation of Protein Hydrolysates:

Protein hydrolysates based on milk powder, casein, whey, soy, wheat, cotton, peanut, rice and pea protein were prepared by standard techniques using Flavourzyme 1000 L (fungal protease/peptidase mixture from Novo Nordisk, Denmark. Hydrolysis was performed at 50°C using 1% enzyme by weight of protein content)

A first set of hydrolysates were produced by 3, 6 and 24 h of incubation, resulting hydrolysates with varying degrees of hydrolysis (DH), in the range of approximately 24-56% DH. Primary amino groups were determined by fluorescence using standard fluorescamine derivatization method. Degree of hydrolysis was defined as the ratio between the primary amino groups for the sample and the total amino groups following 6N HCl hydrolysis. Free amino groups were determined by standard HPLC method using PITC derivatization. Table 1 shows the results obtained for various different protein hydrolysates.

Hydrolysates based on casein and soy protein were then prepared using short hydrolysis times, of 30 min, 1 and 2 hours, to produce a set of samples with medium degree of hydrolysis (20-30%). Table 2 shows the results obtained using soy and caesin protein hydrolysates.

Protein material	Total NH_2 (μmol/g)	Free NH_2 (μmol/g)	DH(%)	Total N (%)
Cotton	6012	160	2.7	9.2
Cotton 3h	3490	1017	29.1	8.5
Cotton 6h	4387	1343	30.6	8.5
Cotton 24h	4093	1842	45.0	9.3
Soy	7032	281	4.0	14.0
Soy 3h	7003	2205	31.5	14.1
Soy 6h	6998	2324	33.2	13.9
Soy 24h	7155	2847	39.8	14.0
Casein	6816	599	8.8	13.4
Casein 3h	6819	2908	42.7	12.9
Casein 6h	6866	3557	51.8	12.9
Casein 24h	6949	3921	56.4	13.1
Whey	7255	614	8.5	12.2
Whey 3h	7180	1730	24.1	12.0
Whey 6h	7165	2122	29.6	11.9
Whey 24h	7038	3009	42.8	11.5
Peanut	4068	88	2.2	9.0
Peanut 3h	3309	1054	31.9	8.3
Peanut 6h	3258	1282	39.4	8.6
Peanut 24h	3587	1704	47.5	9.4
Wheat	4896	24	0.5	12.5
Wheat 3h	6587	1711	26.0	14.0
Wheat 6h	6804	2497	36.7	14.0
Wheat 24h	6525	3335	51.1	13.8
SMP	3051	103	3.4	5.8
SMP 3h	1358	448	33.0	2.9
SMP 6h	1568	674	43.0	3.5
SMP 24h	2228	1060	47.6	4.6
Pea	7441	238	3.2	15.4
Pea 6h	7627	3218	42.2	15.2
Pea 24h	7723	3449	44.7	15.3
Rice	5609	137	2.5	10.6
Rice 6h	5957	1769	29.7	10.6
Rice 24h	5679	2112	37.2	10.5

Table 1 - Protein Hydrolysates

Protein Material	Total NH_2 (μmol/g)	Free NH_2 (μmol/g)	DH (%)
Casein	6816	599	8.8
Casein 30 min	5528	1556	28.1
Casein 1h	5804	1672	28.8
Casein 2h	5850	1838	31.4
Soy	7032	281	4.0
Soy 30 min	5764	1251	21.7
Soy 1h	6012	1384	23.0
Soy 2h	5701	1587	27.8

Table 2 - Hydrolysates of casein and soy protein

The strongly hydrolysed protein samples (24 h) of table 1 contained up to 50% free amino acids compared to total free amino groups. Substantial amounts of free hydrophobic amino acids were liberated, showing that these hydrolysates can be used as a rich source of chocolate amine flavour precursors, for example the 24 hour casein hydrolysate contains 18% Leu, 6% Ile, 8% Phe, 8% Val.

A reference cocoa reaction flavour (E2) was prepared by reacting 0.8% Leu, 1.45% Phe, 0.8% Val, 1.5% Fructose, 1.5% water (4 drops of NaOH in 20ml water) and 90% propylene glycol at 125°C for 60 min under reflux. Reaction flavours, prepared with protein hydrolysates by replacing the amino acids with 1% lyophilised hydrolysate. Tasting was performed on a 0.1% solution in 1% sucrose. The reaction flavours produced with protein hydrolysates were tasted and compared against reference E2.

Protein hydrolysates resulted in similar sensory scores as compared to hydrophobic amino acids (reference E2 of Table 3), for key attributes such as cocoa and chocolate as well as other predominant attributes in the E2 reference. The protein hydrolysates produced a richer and more complex flavour profile than the hydrophobic amino acids alone. Other attributes might

be recognised using protein hydrolysates such as cotton, peanut, wheat and rice hydrolysates. Lowest level of other attributes were found in the hydrolysates of casein, whey, skimmed milk protein, soy and pea protein. Thus, it is preferable to use flavour neutral protein substrates or a purified protein material. Sensory evaluation was carried out by a panel of six persons and a scale from 1 (low) to 10 (high) was defined for attributes such as cocoa, milk, malt, biscuit, caramel, sweet and bitter.

Attribute	Ref. E2	Casein hydrolysate	Soy hydrolysate	Cotton hydrolysate	Whey hydrolysate	Peanut hydrolysate	SMP hydrolysate	Wheat hydrolysate	Pea hydrolys-ate	Rice hydrolys-ate
Cocoa	5	5	4	5	5	4	7	3	6	5
Choco-late	3	3	3	3	3	3	4	2	3	3
Coffee	4	5	2	4	4	4	4	4	2	4
Burnt	2	3	2	2	2	2	2	2	2	2
Roasted	3	4	2	3	3	3	3	3	2	3
Caramel	2	2	2	2	2	2	2	2	2	2
Malt	2	2	2	2	2	2	2	2	2	2
Wheat	2	2	2	2	2	2	2	2	2	2
Peanut	2	2	2	2	2	2	2	2	2	2
Honey	1	1	1	1	1	1	3	1	1	1
Off-flavour	2	2	2	3	2	3	2	6	2	6

Table 3 - Sensory scores of reaction flavours produced from protein hydrolysates and fructose in propylene glycol.

Preparative Example 2:

Preparation of Chocolate Crumb:

Chocolate crumb was prepared using the following ingredients, 130.8 g of skimmed milk powder, 43.6g sucrose and 25.5g of cocoa liquor. The cocoa liquor was melted at 50 °C. The sugar and the skimmed milk powder were added and the incubation mix was mixed in a Winkworth Z-blade mixer at 100 rpm to 90 °C. Water (5%) was added dropwise during 2 min, and the reaction of the ingredients to form the typical crumb flavour was performed for

15 min at 90 °C. After reaction, the crumb powder was removed from the mixer and let cool to room temperature. Moisture was analysed with a halogen moisture analyser working on the thermo-gravimetric principle.

Sensory evaluation of the crumb powder was performed by adding water heated to 65 °C and mixing with 30 g of crumb powder. The paste mixture in a beaker was covered and the paste was tasted after 30 min at ambient temperature. A panel with the same 6 persons tested all the samples and the results are shown in Table 4 (reference crumb).

Preparative Example 3:

Preparation of White Chocolate

A white model chocolate was prepared to evaluate flavour changes introduced by the crumb powder. The white chocolate was prepared by standard chocolate processing methods according to the following general formula and procedure. Deodorized cocoa butter was used to have a minimum of flavour in the resultant chocolate. The general formula of the recipe comprised crystal sugar (46.4%), cocoa butter (34.6%), skimmed milk powder (18.9%) and soya lecithin (0.2%).

To evaluate the flavour delivered by the crumb powders when introduced into chocolate, the crumb powders were incorporated at a 10% level into 90 % of the white chocolate base. The mixture was refined on a 3 roll refiner (roll temp of 25 °C). The mass was treated in an Electrolux mixer for 1 hour at 50 °C. The mass was tempered on a marble desk and moulded.

A panel of 6 persons tasted the white chocolate samples, using a scale from 1 (low) to 10 (high) for the attributes cocoa, milk, malt, biscuit, caramel, sweet and bitter. The white model chocolate without crumb addition was given the following scores (in parentheses): cocoa (0), milk (5), malt (0), biscuit/baked (0), caramel (0), burnt (0), sweet (5), bitter (0), carton (0) and butter (3). Incorporation of the crumb prepared in accordance with preparative example 2 resulted in slight increase in caramel and cocoa note (Table 5).

Example 1:

Preparation of Chocolate Crumb using Casein Hydrolysates:

Chocolate crumb was prepared by replacing 10% of the skimmed milk powder of preparative example 2 with casein hydrolysates with different degrees of hydrolysis from 28% to 56.9%, see table 4. Sensory evaluation of the resultant crumb was then undertaken.

Attribute:	Reference crumb	Casein Non-hydrolysed	Casein Hydrolysate 30m DH 28	Casein Hydrolysate 1h DH 29	Casein Hydrolysate 2h DH 31	Casein Hydrolysate 3h DH43
Cocoa	3.0	2.8	3.3	3.0	4.0	3.5
Milk	3.0	3.0	2.3	3.0	2.5	2.7
Malt	3.0	2.3	3.3	3.7	4.2	4.7
Biscuit	5.0	4.7	3.7	3.8	4.0	4.3
Caramel	5.0	4.3	3.7	4.3	5.2	5.0
Burnt	2.0	1.7	2.5	2.8	2.8	2.7
Sweet	5.0	3.7	3.3	3.8	3.7	3.7
Bitter	2.0	1.7	2.0	3.8	4.0	3.0

Attribute:	Reference crumb	Casein Hydrolysate 6h DH 52	Casein Hydrolysate 6h DH 52	Casein Hydrolysate 24h DH 56	Casein Hydrolysate 24h DH 56
Cocoa	3.0	3.2	3.5	3.0	3.3
Milk	3.0	2.8	2.7	3.1	2.2
Malt	3.0	4.0	3.8	5.8	5.8
Biscuit	5.0	4.2	4.0	4.3	3.3
Caramel	5.0	3.9	4.3	3.6	3.7
Burnt	2.0	2.4	2.7	3.0	4.2
Sweet	5.0	3.9	4.2	3.7	3.3
Bitter	2.0	3.4	2.8	2.8	4.2

Table 4 - Sensory evaluation of crumb samples prepared by replacing 10% of the skimmed milk powder of preparative example 2 with casein hydrolysates

The casein hydrolysates resulted in increased malt flavour attribute in crumb. This increase was most pronounced in the hydrolysate with highest DH (56%), with an increase in aroma intensity from 3.0 in the reference crumb to 5.8 in two replicate crumb samples. The casein hydrolysates obtained by shorter hydrolysis, resulted in lower enhancement of the malt flavour attribute. Thus, only a major increase in the free amino acid pool results in strong malt flavour enhancement. No increase in malt flavour was obtained in a control sample prepared with non-hydrolysed casein.

Cocoa and caramel notes were enhanced in some of the crumb samples, and an increase in bitter and cheesy notes were detected in several of the samples produced with casein hydrolysates.

Example 2:

Preparation of Chocolate Crumb using Soy Hydrolysates

Chocolate crumb was prepared by replacing approximately 10% of the skimmed milk protein used in preparative example 2 with soy hydrolysates. Soy hydrolysates (30 min, 1 h and 2 h) resulted in only minor modification of flavour profiles, whereas crumb prepared from the 24 h hydrolysate showed increased malt flavour as well as other flavours such as acid, spicy, rancid and cheesy.

Volatile analysis of Chocolate Crumb Produced using Milk or Vegetable Protein Hydrolysates according to Examples 1 to 2 was then carried out. Crumb prepared by 10% replacement of skimmed milk protein (SMP) by milk or protein hydrolysates were subjected to solid-phase micro-extraction (SPME) volatile analysis. It was found that there was a significant increase in Strecker aldehydes. For example, up to 10-fold increase was found in the levels of 2-methylpropanal, 2-methylbutanal and 3-methylbutanal from val, ile and leu, respectively.

Volatile analyses were also performed on crumb prepared with soy and casein/SMP hydrolysates. In particular, the sample prepared with SMP hydrolysate contained high level of isovaleric acid. This could explain the strong "sweaty" flavour observed in this sample. The samples prepared with casein hydrolysate, however, contained low levels of isobutyric as well

as isovaleric acid. The low level of such flavours in these crumb samples might therefore be related to relatively low levels of these compounds.

Thus, casein and soy hydrolysates showed the lowest off-flavour intensity and the strongest enhancement of malt flavour. The use of protein hydrolysates in crumb reactions strongly increases the consumption of amine flavour precursors. By using casein and soy hydrolysates with different degree of hydrolysis (DH) and increasing crumb reaction time (Figure 1), up to a 50-fold increase in free amino acid consumption can be achieved. Thus, increasing reaction time may also alter the flavour profile of the resultant crumb.

Example 3:

Crumb Preparation Using Caramelised Milk Powder and Casein Hydrolysate:

Crumb samples were prepared in accordance with preparative example 2 using caramelised milk powder (Milchkaramelpulver FK 30 from Felix Koch Offenbach, Germany), which strongly increased the caramel note from 2 to 7. Crumb prepared using both casein hydrolysate and caramelised milk powder resulted in a further enhanced malt note of the resultant crumb.

Example 4:

White Chocolate preparation

Crumb samples prepared in accordance with preparative example 2 and examples 1 to 3 were incorporated at 10% level into a white model chocolate for sensory evaluation.

The white chocolate without crumb incorporation was given the following reference attribute scores: sweet 5, milk 5, butter 3, other attributes 0. Incorporation of the reference crumb prepared in accordance with preparative example 2 resulted in slight increase in caramel and cocoa note. White chocolate with crumb prepared with casein hydrolysate resulted in a strong increase in the malt and caramel attribute. White chocolate with crumb prepared with caramelized milk powder strongly increased the caramel note, from 2 to 7. White chocolate with crumb prepared by both casein hydrolysate and caramelized milk powder resulted in a further enhanced malt note. Thus, protein hydrolysates can be used in combination with different raw materials to produce crumb powders which result in a wide range of different attributes when used in chocolate production.

Attribute:	White chocolate Reference	Reference Crumb 10% in white chocolate	Crumb using Casein 24hr hydrolysate 10% in white chocolate	Crumb using Caramelized milk FK30 10% in white chocolate	Crumb using Casein 24 hr hydrolysate and caramelised milk 10% in white chocolate
Sweet	5	3	5	4	3
Milk	5	4	2	3	2
Caramel	0	2	4	7	4
Biscuit/Baked	0	0	0	0	0
Cocoa	0	1	1	1	3
Malt	0	0	4	1	6
Burnt	0	0	0	0	0
Bitter	0	0	0	0	1
Carton	0	3	0	0	0
Butter	3	0	0	5	2
Comments	milk butter		Honey	caramel butter (toffee)	butter

Table 5 - Sensory evaluation of white chocolate with 10% crumb incorporation

The analytical and sensory data together, show that protein hydrolysates with high DH can be used to strongly increase the pool of free amino acids and peptides. This results in a strong increase in free amino acid and peptide consumption by Maillard reactions with a subsequent increase in certain volatile compounds and enhanced or modified flavour attributes in the crumb powders as well as in the final chocolate.

CLAIMS:

1. A process for the preparation of chocolate crumb comprising mixing and heating from 15 to 70% by weight of milk solids, with 10 to 75% by weight of sugar and 0.1 to 10% by weight of milk or vegetable protein hydrolysates, the percentages being based on the weight of the mixture.

2. A process for the preparation of chocolate crumb according to claim 1 further comprising cocoa solids.

3. A process for the preparation of chocolate crumb according to claim 2 wherein the weight ratio of protein hydrolysates to cocoa solids to sugar to milk solids is 1:2:3:9.

4. A process for the preparation of a chocolate crumb according to claims 1 to 3 wherein the milk or vegetable protein hydrolysates are prepared from milk powder, casein, whey, soy, wheat, cotton, peanut, rice or pea protein.

5. A process according to claim 4 wherein the milk powder is skimmed milk powder or caramelised milk powder.

6. A process according to any of the preceding claims wherein soy or casein protein hydrolysate are used.

7. A process for the preparation of a chocolate crumb according to claims 1 to 3 using caramelised milk powder and casein hydrolysate.

8. Chocolate crumb having enhanced flavour characteristics obtainable by process according to any of the preceding claims.

9. Chocolate crumb as claimed in claim 8 comprising from 1:1.5 to 1:3 milk solids to sugar and 0 to 25% by weight of mixture of cocoa solids.

10. A process for the preparation of chocolate which comprises processing chocolate crumb together with other chocolate ingredients to form chocolate, characterised in that the chocolate crumb is prepared by the process according to claims 1 to 8.

11. A process for the preparation of chocolate according to claim 10 wherein the chocolate is white chocolate.

12. A chocolate product with altered flavour characteristics obtainable by the process according to claims 10 and 11.