Celtic Colloids Inc.

Celtic Colloids Inc.
13 Garnet Drive
Topsham, ME 04086
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USDA-AMS-NOP
1400 Independence Ave. SW
Room 2648-So.
Mail Stop 0268
Washington, DC 20250-0268

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Subject:

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Comments: Sunset – Carrageenan

Technical Evaluation Report (October 3, 2011)

Background

Celtic Colloids Inc. is an independent consultancy company providing technical assistance on hydrocolloid technology. The author of this submission has been active in carrageenan technology since 1962, and has participated directly with several *in vivo* feeding studies (for example, reference Weiner *et al*).

Carrageenan is a natural seaweed extract, and all by-products and wastes from its processing are biodegradable and environmentally friendly. The seaweeds used for carrageenan manufacturing are predominantly cultivated species, and the related farming industries have had significant positive economical and sociological impacts in many tropical and sub-tropical countries in several continents.

Carrageenan has been subjected to numerous *in vivo* mammalian toxicological studies over its 80 years of use in foods. Carrageenan continues to be recognized as a safe and suitable food additive by US Food and Drug Administration, the European Food Safety Authority, and the Joint FAO/WHO Expert Committee on Food Additives when meeting the specifications in the monographs established by these respective authorities.

Carrageenan is a natural key ingredient in many food applications due to its well-documented unique stabilizing, thickening, gelling, and texturizing properties, not only in aqueous systems, but in combination with structural interactions with all proteins.

Carrageenan is the preferred stabilizer in essentially all dairy chocolate milk products, where its unique interaction with casein proteins maintains homogeneity by prevention of cocoa particle settling and fat separation. Carrageenan has served this industry well since about 1930, with no evidence of a cost-effective alternative in sight. This unique functional synergy with milk protein makes carrageenan a logical ingredient choice for other dairy foods such as ice-cream, fortified milks, evaporated milks, sterilized milks, nutritional beverages, frozen desserts, dairy beverages, cultured products, custards, puddings, flans, and cheese products. Over the last decade, the commercial trends towards more healthy foods with lower fat and alternate proteins has heightened the functional value of carrageenan for texture and mouth feel balance to restore consumer acceptability. Carrageenan has made significant contributions to the growth and expansion of commercial soy products, and will continue to do so as the soy market continues to be developed. Carrageenan has a future role to play in the commercial development of food proteins in addition to casein and soy.

Carrageenan is the preferred ingredient in processed meats such as organic ham or turkey, where carrageenan's strong water binding properties prevent moisture loss on cooking, retaining juiciness and avoiding dry-out. Carrageenan is particularly effective for the retention of moisture and texture in natural meat products when other ingredients such as phosphates, salt, and modified starches are reduced. The need for low salt organic meat products continues to expand.

The above dairy and meat product examples are two of many food application segments where carrageenan has the functionalities to be the sole stabilizing ingredient. However, carrageenan is compatible with many other natural ingredient gums, these combinations of gum ingredients further enhancing the attributes and acceptability of commercial food products.

An example of typical gum combinations with carrageenan would be with galactomannans, such as guar gum and locust bean gum, and glucomannans, such as konjac gum, these natural seed and yam gums being synergistic with carrageenan. Food products based on these combinations would include sour creams, ice creams, cheese products, gelled desserts, dressings, and formed food products.

Another example of typical gum combinations with carrageenan would be with various natural food starches from, for example, potato, tapioca, and corn. Food products based on this combination would include seafood products, such as surimi and kamaboko, tomato sauces, syrups and variegates, pie fillings, puddings and desserts, and thickened protein beverages.

National List – Sections 7 **CFR** 205.605 and 7 **CFR** 205.606

Review of the NOSB agricultural, non-agricultural, nonsynthetics allowed, and synthetic listings and placement of hydrocolloid gums within these categories concludes that such assignments have been done on a completely arbitrary, capricious, and disorganized basis, and with little consideration of the technology of these gums, their manufacture, and composition.

Starting with pectin, we have high methoxyl pectin (HMP) listed as “agricultural product”, and low methoxyl pectin (LMP) listed as “allowed synthetic”. Looking at this in more detail, all native / natural pectins in fruit solids are copolymers comprising two primary components, methylgalacturonic acid (MGA) and galacturonic acid (GA), the ratio of these being approximately 80% MGA to 20% GA (reference Brejnholt).

Commercial pectins are extracted from fruit solids such as apple pommace or citrus peels using strong mineral acid (e.g. nitric acid at pH 1.5), which changes the ratio of these two primary structures to yield a range of HMP products with the ratio of 55-75% MGA and 25-45% GA. As indicated above, HMP is listed as “agricultural product”.

Additional treatment with mineral acid further reduces the ratio further to 30-40% MGA and 60-70% GA. This is LMP which is listed as “allowed synthetic”.

Thus, the two primary components of all commercial pectins, whether HMP or LMP, are the same as present in the fresh natural fruits, the ratio of these being changed during extraction with strong acid. No new components have been introduced.

Turning to carrageenan, we have three primary types, kappa, iota, and lambda. Native / natural kappa carrageenan is a copolymer of two primary ideal random repeating components, kappa carrageenan and mu carrageenan, the ratio being approximately 70:30. So, in the natural state, “kappa carrageenan” is actually only 70% ideal kappa carrageenan.

Extraction of commercial kappa-carrageenan for gelation and protein reactivity is carried out using strong alkali, which results in a change of the ratio of kappa : mu carrageenan from 70:30 to approximately 90:10. This enhances and broadens the functional qualities of commercial kappa carrageenan, making it more attractive for food product usage.

Thus, the two primary components of commercial kappa carrageenan are the same as present in the fresh natural seaweed, the ratio of these being changed during extraction with strong alkali. No new components have been introduced.

The above overview of commercial kappa carrageenan can be directly applied to iota carrageenan, in this case the natural iota carrageenan in the seaweed being a copolymer of ideal iota carrageenan and ideal nu carrageenan, and with the same 70:30 ratio. Also, as above, extraction with strong alkali changes this ratio to approximately 90:10 and for the same reasons with respect to improved functional qualities.

Thus, the two primary components of commercial iota carrageenan are the same as present in the fresh natural seaweed, the ratio of these being changed during extraction with strong alkali. No new components have been introduced.

Extractions of lambda carrageenan do not use strong alkali as no change in structural components is necessary or desired. In fact the use of strong alkali will lessen functional qualities. These extractions use very mild alkali (pH 8). Native / natural extract components have not been changed, and no new components have been introduced (reference Blakemore & Harpell).

Carrageenans are currently listed as “allowed nonsynthetic”.

Comparing commercial pectins and carrageenans, the only difference is that pectin extraction uses strong acid, and kappa / iota carrageenans use strong alkali. The primary components in both hydrocolloids are identical to those in the fresh raw material, with just the ratio being changed for improved performance in foods. No new components have been introduced.

Therefore, why does the NOSB have pectin and carrageenan in different lists?

From this technical comparison of carrageenans and pectins, and based on the current listings for pectins, it would appear to be more appropriate to consider “carrageenan” as “agricultural product” rather than proposing its movement to “synthetic”.

The primary native component of agar-agar in the fresh seaweed is agarose, which, like kappa and iota carrageenans, is a copolymer of two primary ideal structures, one sulphated and one without sulphation in a ratio of about 15:85. Extraction with strong alkali converts this ratio to 5:95 for improved functional qualities (reference Imeson). Native / natural extract components have not been changed, and no new components have been introduced. Agar-agar is currently listed as “allowed nonsynthetic”, same as carrageenan.

The extraction process to produce gelatin from animal skins and bones involves treatments with both strong alkali and strong mineral acid. Commercial gelatins comprise specific amino acid sequences, which are not altered during processing, but the insoluble collagen molecules are significantly reduced in molecular weight to yield soluble gelatin. Gelatins are currently listed as "agricultural product".

Looking at other listings, the use of strong alkali is accepted as "natural" by the NOSB for the production of , for example, cocoa, pretzels, and soap.

These examples demonstrate the previously mentioned arbitrary, capricious, and disorganized listings of hydrocolloid gums by the NOSB, and it is strongly recommended that the criteria for their placement in these listings be reviewed, preferably from a sound technical perspective, before making more arbitrary "sunset" decisions that will further compound the situation.

Toxicology / Bioactivity

I have four items to be addressed with respect to some of the publications cited in submissions to the NOSB regarding the toxicity or bioactivity of carrageenan.

First, we have the ongoing confusion between "carrageenan" and "poligeenan", the latter being the current correct name for "degraded carrageenan' which was commonly used in the earlier publications dating back to the 1960s.

Poligeenan uses carrageenan as a raw material for deliberate molecular degradation using strong mineral acid taking the average molecular weight (Mw) down from 500-700,000 Daltons to 10-20,000 Daltons. Poligeenan is currently only used clinically for barium enemas. Poligeenan is not an approved additive for food carrageenan specifications. Poligeenan has zero functionally in food products and costs at least twice to manufacture, so there is absolutely no incentive for poligeenan to be associated with any carrageenan used in food.

In addition, some publications on carrageenan bioactivity state that "carrageenan" contains some "poligeenan". This is absolutely not the case.

Carrageenan in the native / natural growing seaweed does not all magically appear as high Mw molecules. Carrageenan molecules are built enzymatically one sugar unit at a time. Consequently, carrageenans extracted from these seaweeds will comprise some level of native / natural lower molecular weight molecules. We call this the "low molecular weight tail" or LMT. Accurate measurement of the LMT is not yet feasible (reference Marinalg).

However, assuming we have a carrageenan with Mw of 500,000 Daltons, the percentage below 50,000 Daltons should be less than 5%. Assuming we have 5% below 50,000 Daltons, the LMT would have a profile of approximately 2.5% below 40,000 Daltons, 1% below 30,000 Daltons, 0.5% below 20,000 Daltons, and less than 0.1% below 15,000 Daltons.

The typical profile of poligeenan would have 100% below 50,000 Daltons, 90% below 40,000 Daltons, 80% below 30,000 Daltons, 70% below 20,000 Daltons, 50% below 10,000 Daltons, and 20% below 5,000 Daltons.

In summary, carrageenan has less than 0.1% below 20,000 Daltons where poligeenan has 70%, confirming that the terms “poligeenan” or “degraded carrageenan” must not be considered as being part of “carrageenan” or interchangeable with “LMT”. An example of this improper use and the earlier-mentioned confusion would be the Tobacman reference.

Consequently, all literature references citing “poligeenan” or “degraded carrageenan” should be discarded as being irrelevant to any discussion on carrageenan toxicology or bioactivity.

In addition, it should be noted that all *in vivo* toxicology or bioactive studies using carrageenan must have had the natural LMT as an integral component of that carrageenan. This means that the carrageenan LMT has already been extensively investigated as part of all carrageenan toxicological studies.

The second issue with carrageenan toxicology or bioactivity studies is the lack of a clear definition by the authors of the “carrageenan”, “poligeenan”, or “degraded carrageenan” used in their studies. These researchers do complicated screenings and assays and report complex theories and draw often damaging conclusions, and they don’t have a clue about what they are working with. Quite commonly, the authors declare, for example, “lambda carrageenan”, sometimes with a mention of Sigma as the source, but with no other details, such as molecular weight, seaweed species used (each seaweed species produces a different lambda carrageenan), viscosity, ester sulphate, impurities, etc. (one reference by Borthakur *et al*, and six references Bhattacharyya, *et al*). Sigma does not list this information, as they also have no clue as to the carrageenans they promote.

Competent researchers would analyze the basic components of their study. Competent peer reviewers would send these proposed publications back to the authors for completion.

Consequently, all literature references where the carrageenan being used has not been reasonably well defined should be considered incomplete and discarded as questionable for any discussion on carrageenan toxicology or bioactivity.

The third issue relates to the necessary weightings of "*in vivo*" versus "*in vitro*" studies related to carrageenan toxicology or bioactivity. Too many times, referenced publications draw multiple, often damaging, theories about carrageenan bioactivity from "*in vitro*" experiments, where isolated cells are immersed in a carrageenan solution (often unidentified carrageenan) and the effects measured. Conclusions are drawn and suggested metabolic pathways created, without any thought as to the exposure or mode of contact between these cells and orally consumed carrageenan in an "*in vivo*" environment (one reference by Borthakur *et al*, and six references Bhattacharyya, *et al*).

Consequently, all literature references based on "*in vitro*" research on carrageenan toxicology or bioactivity should be treated as questionable until thoroughly reviewed. Note that many of these questionable "*in vitro*" studies also fall into the previous issue. In addition, all "*in vivo*" publications on carrageenan toxicology or bioactivity should be given much greater weighting for consideration, and certainly well ahead of all "in vitro" references. Also, *in vivo* research carried out under GLP should be given the highest level of consideration (reference Weiner *et al*).

The fourth issue covers several submitted statements that claim that carrageenan is significantly degraded in the gastrointestinal tract. This is simply not the case (reference Uno *et al*). When carrageenans are used in foods they are either bound to proteins or in their gel mode conformation, both structures being stable in the acidic stomach and alkaline intestine. In addition, enzymatic and microbial breakdown of the carrageenan molecules in the intestine is essentially zero as the required organisms are not present.

Consequently, all references to carrageenans being degraded in the gastrointestinal tract should be given no consideration.

I appreciate this opportunity to contribute to this review.

William R. Blakemore

William R. Blakemore

President / Principal

Hydrocolloid Technology

Celtic Colloids Inc.

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