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3,686,124

CARBOXYMETHYLATED DERIVATIVES OF DI- AND TRI-SACCHARIDE COMPOUNDS AND DETERGENT COMPOSITIONS CONTAINING THEM

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4 Claims

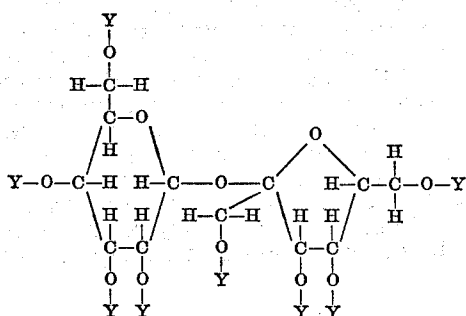
ABSTRACT OF THE DISCLOSURE

Carboxymethylated derivatives of disaccharide compounds such as sucrose and lactose and trisaccharide compounds such as raffinose are provided. These compounds are useful as sequestering agents, e.g., water softeners, and also as detergency builders in detergent compositions. Built detergent compositions are also provided.

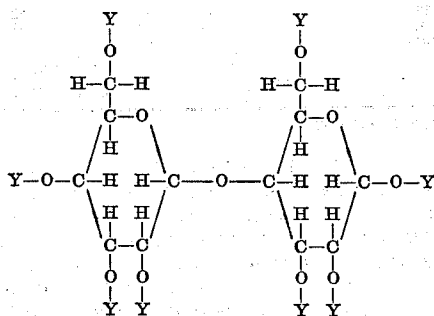
This is a division of application Ser. No. 811,605, filed Mar. 28, 1969 now Pat. No. 3,634,392.

This invention relates to carboxymethylated di- and tri-saccharides which are useful as sequestering agents and also as detergency builders for organic water-soluble synthetic detergents.

The compounds of the present invention have a formula selected from the group consisting of:

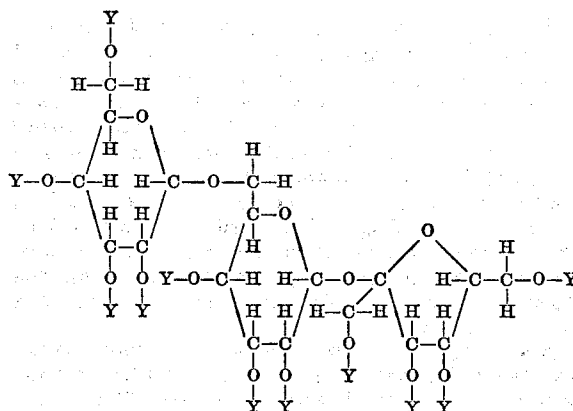


Formula A



Formula B

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Formula C

in which each Y represents H or $-\text{CH}_2\text{COOH}$, at least one Y being $-\text{CH}_2\text{COOH}$.

Compounds depicted by Formula A are derivatives of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, molecular weight, 342.2. Sucrose is a disaccharide having monoclinic crystalline form. It hydrolyzes to fructose and glucose. It is widely found free in juice of all land plants, in particular sugarcane, sugar beet, and sugar maple.

Compounds depicted by Formula B are derivatives of lactose, $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$, molecular weight, 360.2. Lactose is a disaccharide found free in milk of all mammals and also in pollen from Forsythia. It hydrolyzes to glucose and galactose.

Compounds depicted by Formula C are derivatives of raffinose, $\text{C}_{18}\text{H}_{32}\text{O}_{16} \cdot 5\text{H}_2\text{O}$, molecular weight, 594.4. Raffinose is a trisaccharide derived from sugar beets, cottonseed, eucalyptus, and other plants. It hydrolyzes to fructose, glucose, and galactose. It has colorless monoclinic needles, d-1.465, M. PT. 119.

Further description of the parent materials is found in volume 13, Encyclopedia of Chemical Technology, Kirk and Othmer, Copyright 1954 by the Interscience Encyclopedia, Inc.

In the preceding formulae, as noted, each Y represents hydrogen or a carboxymethyl group. Such carboxymethylated compounds have been discovered to possess useful sequestering properties and detergency builder properties. Both of these properties are improved with an increase in the number of carboxymethyl groups present in each compound. The maximum degree of substitution, D.S. (number of carboxymethyl groups) for sucrose and lactose is 8 and for raffinose is 11. In practicing this invention in a sequestering application, it is preferred to use compounds having a degree of substitution greater than 3. For optimum detergency builder properties, a degree of substitution of greater than 50% in each instance is preferred, e.g., greater than 4 in the case of sucrose and lactose and greater than about 6 in the case of raffinose.

The carboxymethylated derivatives of sucrose, lactose, and raffinose provided by the present invention can be prepared by many carboxymethylating procedures. A typical preparative method, and one which is exemplified hereinafter, comprises a reaction between sucrose, lactose, or raffinose with an alkaline material such as sodium hydroxide to form an alkoxide of the polyhydric alcohol. The reaction product of this reaction is then reacted with a compound such as sodium chloroacetate and the mixture is allowed to digest. An ordinary work-up follows these reactions in order to recover the desired carboxymethylated sucrose, carboxymethylated lactose, or carboxymethylated raffinose, depending on whatever the starting material was.

The following examples are given by way of specific illustration for preparing the compounds of this invention:

EXAMPLE I

Preparation of carboxymethylated sucrose

A solution of 4.3 g. (0.10 equivalent) of sucrose in 19.6 ml. of water was mixed with 7.2 g. (0.18 mole) of ground sodium hydroxide and this mixture was blended for ten minutes. To this was added 21.4 g. (0.18 mole) of sodium chloroacetate and blending was again carried out for ten minutes. The mixture was then allowed to stand and digest with occasional blending, for three days until all of the sodium chloroacetate had reacted. This procedure of adding sodium hydroxide and sodium chloroacetate in equivalent amounts, followed by a digestion step, was reported six times to arrive at a completed reaction. Water was added, as needed, to maintain a pasty consistency.

After completion of the reaction, the reaction mixture was dissolved in water and the product was then precipitated by the addition of excess of methanol. The precipitate was collected by filtration, redissolved in water, and then the precipitation-isolation procedure was repeated. There was obtained 5.4 g. of product. Final purification was effected by gel filtration using Sephadex® G-10 resin.

The product was analyzed by dissolving a weighed amount of it in water, passing this solution over a column of a strongly acidic ion exchange resin, and then titrating the resulting eluant with standardized sodium hydroxide solution. Analysis indicated an equivalent weight of 120 for the carboxymethylated sucrose product which corresponds to a degree of substitution of 8.

EXAMPLE II

Preparation of carboxymethylated lactose

A solution of 4.3 g. (0.10) equivalent of lactose in 19.6 ml. of water was mixed with 7.2 g. (0.18 mole) of ground sodium hydroxide and this mixture was blended for ten minutes. To this was added 21.4 g. (0.18 mole) of sodium chloroacetate and blending was again carried out for ten minutes. The rest of the procedure of Example I was followed and the product recovered was carboxymethylated lactose having a degree of substitution of 8. Carboxymethylated lactose with degrees of substitution of 6, 5, 4, 2, or 1 are prepared by decreasing the amount of sodium hydroxide and sodium chloroacetate added to the reaction and also by using shorter digestion times.

EXAMPLE III

Preparation of carboxymethylated raffinose

Following the procedure described in Example I, 5.4 g. of raffinose pentahydrate (0.1 equivalent of raffinose) and 31.9 ml. of water were reacted. Sodium chloroacetate was added as noted in Example I followed by digestion for about three days.

The compounds of this invention possess a useful sequestering property which makes them valuable for treating aqueous solutions containing polyvalent metal ions (iron, calcium, magnesium, and the like) by adding to a solution an effective amount of one of the compounds described herein, or a mixture of such compounds. Ordinarily the amount employed ranges from .25 part per million to 10,000 parts per million of the aqueous solution. This embodiment of the present invention is based on the discovery of the sequestering properties of the carboxymethylated compounds described herein. The optimum amount for any given water treatment application can be readily determined by merely adding a sufficient amount of sequestrant to accomplish the desired objective. The useful sequestering properties of the compounds of the present invention are demonstrated by a swatch-dip procedure which measures the relative sequestering ability of a compound. The procedure involves the use of a fabric swatch impregnated with soap and an aqueous solution containing a predetermined level of calcium hardness minerals. Briefly, the procedure first calls for preparing an aqueous solution containing the hardness minerals, at a pH of 10, and then dipping into it or immersing in it a fabric swatch which has been impregnated with a measured amount of soap. The swatch is allowed to remain in the solution for a predetermined amount of time. During this immersed period, free calcium in the solution is being absorbed by the fabric swatch. The amount of free calcium absorbed is then measured. The identical procedure is then repeated but with a predetermined concentration of a sequestrant compound added to the aqueous solution containing the calcium ions. The amount of calcium absorbed in this second instance is also measured. Comparisons are then made between the two results, i.e., those obtained without the use of a sequestrant against those results obtained with the use of a sequestrant. Differences between the amounts of calcium absorbed in demonstrations with and without sequestrants is attributed to the capability of the sequestrant to sequester or complex the calcium ions and, thereby, reduce the amount of free calcium ion available for absorption upon the immersed fabric swatch. A percentage is calculated which is called "percent hardness retained by sequestrant."

Several demonstrations were conducted in this manner and comparisons were drawn between the performance of compounds of the present invention and sodium tripolyphosphate (STP), sodium citrate, and sodium pyrophosphate. These latter compounds are three known sequestering agents. The data obtained from these demonstrations are tabulated below in Table I and indicate the useful sequestering properties of representative compounds of the present invention, i.e., carboxymethylated sucrose of Example I, carboxymethylated lactose of Example II, and carboxymethylated raffinose of Example III.

TABLE I

Sequestrant (sodium salts)	Degree of substitution	Percent hardness retained			
		.02% ¹	.03% ¹	.04% ¹	.06% ¹
1. Carboxymethylated sucrose.....	8	43	44	53	57
2. Carboxymethylated lactose.....	8	50	58	63	-----
3. Carboxymethylated raffinose.....	10.7	43	49	50	74
4. Sodium citrate.....			51.4	-----	58.6
5. Sodium pyrophosphate.....			81.4	81.4	82.9
6. Sodium tripolyphosphate.....			81.4	84.4	91.4

¹ Concentration of sequestrant in solution.

The same work-up procedure was practiced to recover the desired carboxymethylated raffinose. The recovered product was analyzed for an equivalent weight of 130 which corresponds to a degree of substitution of about 10.8 out of a maximum of 11. Routine adjustments in both reaction time and digestion time result in the preparation of carboxymethylated raffinose having lesser degrees of substitution.

In addition to the useful sequestering properties which the carboxymethylated derivatives of sucrose, lactose, and raffinose of this invention possess, they are also useful as detergency builders. In practicing this builder embodiment, the carboxymethylated builder compounds described and illustrated above are used in conjunction with organic synthetic detergents to provide built laundering and detergent compositions.

The organic water-soluble synthetic detergents useful in the present invention include the anionic, nonionic, zwitterionic, and ampholytic detergents which are illustrated and exemplified in detail in U.S. Pat. 3,159,581 issued on Dec. 1, 1964, to Francis L. Diehl and assigned to the Procter & Gamble Company. The patent is hereby incorporated herein by reference and especially the disclosure beginning at column 3, line 74, and extending to column 5, line 59. There are numerous other detergents which fall within the named classes of detergents and they can also be usefully employed herein. Olefin sulfonate detergents such as those described in U.S. Pat. 3,332,880 (also incorporated herein by reference) are especially useful in combination with the builder compounds of this invention.

In practicing the present invention, a detergent and laundering composition comprises an organic water-soluble synthetic detergent and a carboxymethylated sucrose, lactose, or raffinose builder in a proportion by weight, respectively, of 5:1 to 1:10 and preferably 2:1 to 1:5. The built composition can be formulated as a liquid or solid form. Built liquid compositions having an aqueous or alcoholic (ethanol) base are especially useful. Solid formulations such as tablets, granules, powders, flakes, and the like find widespread application.

In a detergent formulation of this invention, minor amounts of other materials can be present which make the product more effective or more aesthetically attractive. The following are mentioned by way of example. A soluble sodium carboxymethylcellulose or starch can be added in minor amounts (.2-2%) to inhibit soil redeposition. A tarnish inhibitor such as benzotriazole or ethylene-thiourea may also be added in amounts up to about 2%. Fluorescers, perfume, and color while not essential in the compositions of the invention, can also be added in amounts up to about 3%. An alkaline material such as sodium hydroxide or potassium hydroxide can be added in minor amounts as supplementary pH adjusters. Other suitable additives include water, brightening agents, enzymes, sodium sulfate, and sodium carbonate, buffers, fillers and the like.

In addition, corrosion inhibitors can also be present. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium silicates having a weight ratio of $\text{SiO}_2\text{M}_2\text{O}$ of from 1.0:1 to 2.8:1 can be used. M in this ratio refers to sodium and potassium. A sodium silicate having a ratio of $\text{SiO}_2\text{:Na}_2\text{O}$ of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotrope can at times be found desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. The preferred hydrotropes are potassium or sodium toluenesulfonates. The hydrotrope salt may be added, if desired, at levels from 0% to about 12%. While a hydrotrope is not ordinarily found necessary, it can be added if so desired for any reason such as to produce a product which retains its homogeneity at a low temperature.

The built detergent and laundering compositions of this invention provide best cleaning results when used in aqueous solutions having a pH of 9 to 12, preferably 9.5 to 11.5. This point can be taken into account in formulating the complete built composition by including alkaline ingredients to satisfy the pH requirement. Alternatively, alkaline materials can be added directly to the washing solution to bring the pH into the 9-12 range.

The compositions of this invention provide best cleaning results when used at a sufficient level to provide in solution a concentration of builder in the range of .02% to .5% by weight, and preferably .03% to .3%.

The following built detergent compositions illustrate this embodiment of the present invention:

EXAMPLE IV

A granular built detergent composition having the following composition provides effective laundering results in aqueous solutions having a pH of about 9:

- 20% sodium dodecylbenzene sulfonate, dodecyl being a linear straight-chain radical
- 50% sodium carboxymethylated sucrose builder (D.S.=8) of Example I
- 14% sodium sulfate
- 6% sodium silicate
- 10% water

In this example, the sucrose builder can be replaced by a sodium carboxymethylated lactose of Example II (D.S.=8) or sodium carboxymethylated raffinose (D.S.=11) without any loss in cleaning properties.

EXAMPLE V

An effective granular built detergent composition comprises:

- 17.5% sodium olefin sulfonate (having 12-16 carbon atoms)
- 20.0% sodium tripolyphosphate
- 20.0% sodium pyrophosphate
- 10.0% sodium carboxymethylated sucrose (D.S.=7)
- 16.0% sodium sulfate
- 10.0% sodium silicate
- 4.0% water

In this example, the sodium pyrophosphate can be replaced on an equal weight basis by sodium carboxymethylated lactose (D.S.=5), sodium carboxymethylated (D.S.=3), sodium carboxymethylated sucrose (D.S.=6), sodium carboxymethylated raffinose (D.S.=8), or sodium carboxymethylated raffinose (D.S.=4).

In addition, the sodium olefin sulfonate detergent can be replaced by sodium tallow alkyl sulfate or sodium coconut alkyl sulfate.

EXAMPLE VI

An excellent built liquid detergent composition according to this invention comprises:

- 6% sodium dodecylbenzene sulfonate (the dodecyl radical being polypropylene predominantly tetrapropylene averaging 12 carbons).
- 6% dimethyldodecylamine oxide
- 20% sodium carboxymethylated lactose (D.S.=6)
- 8% potassium toluenesulfonate
- 3.8% sodium silicate (ratio $\text{SiO}_2\text{:Na}_2\text{O}$ of 2.45:1)
- 0.8% carboxymethyl hydroxyethyl cellulose
- Balance water

In practicing the built detergent composition embodiment of the present invention, the carboxymethylated sucrose, lactose, and raffinose builders described herein can be used separately or in combination either with each other, or in combination with any inorganic alkaline detergency builders or organic alkaline sequestering builders such as sodium nitrilotriacetate, sodium ethylenediaminetetraacetate, sodium ethane-1-hydroxy-1,1-diphosphonic acid, sodium polyitaconate, or sodium polymaleate.

As detergency builders, the carboxymethylated sucrose, lactose, and raffinose are in a class with such builders as citrate and pyrophosphate salts. This can be demonstrated by the following evaluation:

White dress shirts, cotton T-shirts and other fabrics are distributed among various individuals. Each dress shirt and T-shirt is worn for one normal working day under uniform conditions and the other articles are used for their generally intended purposes. The soiled items are then washed in an automatic agitating type washer, for a period of ten minutes, with detergent solutions at 130° F. temperature, a pH of 10, and a hardness of 7 grains per gallon. After washing, the clothes are rinsed and then dried. (No fluorescers or bleaches were used.)

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Direct comparisons are made by a panel of five graders between pairs of shirts and fabrics worn and soiled by the same individual. The dress shirts, T-shirts and other fabrics used are graded on the degree of whiteness and the degree of cleaning obtained, paying particular attention on this latter feature to the dress shirt collars and cuffs. The term "cleaning" or "cleanliness" denotes the ability of a washing composition to remove actual soil lines or deposits such as the crease lines of collars and cuffs where the soil is deeply embedded. Whiteness, on the other hand, denotes a more general concept which measures the ability of a cleaning composition to whiten areas which are only slightly or moderately soiled. Clean washcloth size swatches of cotton terry cloth and muslin are washed along with the soiled clothes to arrive at an independent evaluation of the whiteness maintenance or whiteness compositions. The relative cleaning effectiveness of each detergent composition in each area is graded on a raw score under U.V.-free artificial light, averaged, and then translated onto a 0-10 scale wherein the highest grade of 10 is assigned to the relatively best performance obtained.

A sample detergent composition employed during the tests contains 20% sodium tallow alkyl sulfate as the detergent active, (the alkyl chain length distribution of tallow alkyl sulfate was approximately 66% C₁₈, 30% C₁₆ and 4% others), 50% of a builder such as sodium citrate, sodium pyrophosphate, or the carboxymethylated sucrose, lactose, or raffinose builders described herein, 6% sodium silicate and 24% sodium sulfate. The pH of the washing solution is 10.

By practicing this demonstration, it is seen that the builders of this invention are substantially equal in builder properties and effectiveness in areas of cleaning and whiteness to sodium citrate and alkali metal salts of pyrophosphoric acid, e.g., sodium pyrophosphate.

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The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. A detergent composition comprising an organic synthetic detergent selected from the group consisting of anionic, nonionic, zwitterionic or ampholytic detergents or mixture of these detergents and a detergency builder selected from the group consisting of carboxymethylated sucrose, carboxymethylated lactose, or carboxymethylated raffinose, the proportion by weight of detergent to builder being from 5:1 to 1:10.

2. A detergent composition according to claim 1 in which the builder is a carboxymethylated sucrose having a degree of substitution greater than four.

3. A detergent composition according to claim 1 in which the builder is a carboxymethylated lactose having a degree of substitution greater than four.

4. A detergent composition according to claim 1 in which the builder is a carboxymethylated raffinose having a degree of substitution greater than five.

References Cited

UNITED STATES PATENTS

2,893,990	7/1959	Hass et al.	252-89
2,970,962	2/1961	Hass et al.	252-135
3,159,581	12/1964	Diehl	252-526

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