

**Title: A process for the Preparation of methionine
alpha-hydroxy analogues from sugars and derivatives thereof.**

Description:

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A process for the preparation of methionine α -hydroxy analogue and derivatives thereof from sugars in the presence of zeotype compounds.

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Background:

Carbohydrates represent the largest fraction of biomass and various strategies for their efficient use as a feedstock for the preparation of commercial chemicals are being established. Biomass is of particular interest due to its potential for supplementing, and ultimately replacing, petroleum as a feedstock for such purposes. Carbohydrates obtainable from biomass comprise C2 to C6 sugars and are of particular interest industrially as they are a potential source of highly functionalised short chain carbon compounds.

This invention is directed towards the preparation of methionine α -hydroxy analogue and derivatives thereof from sugars in the presence of zeotype compounds. Methionine α -hydroxy analogue is 2-hydroxy-4-(methylthio) butanoic acid. Methionine α -hydroxy analogue and derivatives thereof may be used as a food/nutritional supplement in animal feed compositions/formulations.

It is known that C2-C6 sugars may be converted to methyl lactate and methyl vinylglycolate (MVG) in the presence of zeotype materials such as Sn-BEA. EP 2 184 270 B1 and Science (2010) 328, pp 602 - 605 report average yields of methyl lac-

tate of 64%, 43% and 44% at 160 °C, in the presence of Sn-BEA and methanol from sucrose, glucose and fructose, respectively. Methyl vinylglycolate (MVG) is the major by-product with a reported yield of 3-11%. MVG may be produced in yields of up to 56% from the C4 sugar D-erythrose.

WO 98/32735 discloses a process for the preparation of methionine α -hydroxy analogue methyl ester, 2-hydroxy-4-(methylthio) butanoic acid methyl ester, , in an 85% yield via a free radical addition of methylthiol to a non-conjugated olefinic substrate, i.e. methyl vinylglycolate (MVG). Although high yielding, radical reactions have the potential to form region-isomeric by-products.

WO 98/32735 also discloses an alternative, multi-step, commercially feasible process for preparing methionine α -hydroxy analogue, 2-hydroxy-4-(methylthio)butanoic acid. The process comprises a Michael addition of methyl mercaptan to acrolein (a conjugated olefinic substrate) in the presence of an organic amine catalyst to produce 3-(methylthio)-propanal, followed by nitrile addition and hydrolysis to the acid. Although the process is industrially feasible, the use of toxic and expensive reagents such as HCN and acrolein should be avoided.

ChemCatChem (2013) 5, pp 569-575 discloses the conversion of tetroses (C4 sugars) to MVG and MMHB under homogenous catalytic conditions. MMHB is selectively produced from erythrose (C4 sugar) in the presence of a homogenous tin chloride catalyst.

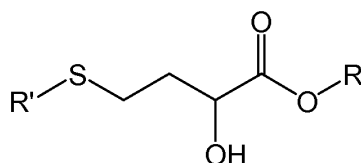
Accordingly, it is desirable to provide an alternative process for the preparation of methionine α -hydroxy analogue and derivatives thereof. In particular, it is desirable to provide a process that is industrially feasible, it is therefore desirable that the process is high yielding, direct and selective. It is desirable that the process is carried out under conditions that are industrially feasible, with reagents or catalysts that enable ease of production and reduced toxic waste, such as the use of heterogeneous catalysts that may be regenerated. Additionally, the provision of a process wherein the substrates are derived from renewable sources such as C2-C6 sugars, is desirable. In particular because the sugar substrates are much less toxic and much cheaper than, for example acrolein and the HCN reagent, consequently the use of sugar substrates significantly lowers the costs of production.

Disclosure of the Invention

It has surprisingly been found that a methionine α -hydroxy analogue and derivatives thereof is obtainable by contacting one or more sugars with a metallo-silicate composition in the presence of a compound comprising sulphur and a solvent.

The methionine α -hydroxy analogue and derivatives thereof may be represented by the formula
$$R'-S-CH_2-CH_2-CHOH-COO-R \text{ (I)},$$
wherein R is selected from the group consisting of H, C₁-C₈ alkyl or alkaline or alkaline-earth metals; and R' is selected from the group consisting of H and methyl.

The methionine α -hydroxy analogue and derivatives thereof may alternatively be represented as follows:



5 It has surprisingly been found that a high yield of the methionine α -hydroxy analogue and derivatives thereof is obtainable according to the process of the present invention.

10 The compound comprising sulphur is preferably a compound of the formula RSR' , wherein R and R' are selected from the group consisting of H, C₁-C₅ alkyl or alkaline or alkaline-earth metals. The compound comprising sulphur is preferably selected from the group consisting of C₁-C₅ alkyl thiol, C₁-C₅ alkyl thiol salts, dimethylmercaptan, dimethyl disulphide and
15 hydrogen sulphide. C₁-C₅ alkyl thiol is in the present context meant to refer to mono- and di-substituted thiols with a substituent comprising a straight or branched chain saturated aliphatic alkyl group comprising one, two, three, four or five carbons. C₁-C₅ alkyl thiol is in the present context
20 meant to refer to an alkyl thiol selected from the group consisting of methane thiol, ethane thiol, straight or branched chain propane thiol, straight or branched chain butane thiol and straight or branched chain pentane thiol.

25 C₁-C₅ alkyl thiol salt is in the present context meant to refer to the alkali or alkaline earth metal salt of a C₁-C₅ alkyl thiol. Specifically, C₁-C₅ alkyl thiol salt is in the present context meant to refer to a C₁-C₅ alkyl thiol in the salt form wherein the cation is selected from the group con-

sisting of sodium, potassium, lithium, magnesium and calcium. Specifically, C₁-C₅ alkyl thiol salt is in the present context meant to refer to a C₁-C₅ alkyl thiol selected from one or more of the group consisting of NaSCH₃, KSCH₃, Ca(SCH₃)₂ and Mg(SCH₃)₂.

Hydrogen sulphide can be used as sulphur compound to produce 2-hydroxy-4-mercapto-butanoic acid or esters thereof, which can be further converted to the methionine α -hydroxy analogues by reaction with methanol. Alternatively, hydrogen sulphide can be used to form a C₁-C₅ alkyl thiol in the presence of the sugar, an alcohol and an acidic catalyst, as described in Roberts, J. S. 2000. Thiols, Kirk-Othmer Encyclopedia of Chemical Technology.

The methionine α -hydroxy analogue and derivatives thereof are selected from the group consisting of 2-hydroxy-4-(C₁₋₅ alkylthio)butanoic acid, salts and esters thereof. C₁₋₅ alkylthio corresponds to the C₁₋₅ alkyl thio compound comprising sulphur present in the process. Preferably, the methionine α -hydroxy analogue and derivatives thereof are selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid, salts and esters thereof. Preferably, the methionine α -hydroxy analogue and derivatives thereof are selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid, alkali and alkaline earth metal salts and C₁₋₈ alkyl esters thereof. Preferably, the methionine α -hydroxy analogue and derivatives thereof are selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid, alkali and alkaline earth metal salts and C₁₋₈ alkyl esters thereof.

C₁₋₈ alkyl esters is in the present context meant to refer to esters comprising the alkyl group selected from the group consisting of methyl, ethyl, propyl, butyl, isopropyl, isobutyl, pentyl, hexyl, heptyl, octyl and 2-ethylhexyl. Alkali and alkaline earth metal salts mean salts of the acid wherein the salt cation is selected from the group I and group II metals.

In one embodiment of the invention the methionine α -hydroxy analogue and derivatives thereof is 2-hydroxy-4-(methylthio)butanoic acid.

In a another embodiment of the invention the methionine α -hydroxy analogue and derivatives thereof is selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid methyl ester, 2-hydroxy-4-(methylthio)butanoic acid ethyl ester, 2-hydroxy-4-(methylthio)butanoic acid propyl ester, 2-hydroxy-4-(methylthio)butanoic acid butyl ester, 2-hydroxy-4-(methylthio)butanoic acid isopropyl ester, 2-hydroxy-4-(methylthio)butanoic acid pentyl ester, 2-hydroxy-4-(methylthio)butanoic acid hexyl ester, 2-hydroxy-4-(methylthio)butanoic acid heptyl ester, 2-hydroxy-4-(methylthio)butanoic acid octyl ester and 2-hydroxy-4-(methylthio)butanoic acid 2-ethylhexyl ester.

The one or more sugars or derivatives thereof are selected from the group consisting of C2-C6 sugars or derivatives thereof. C2-C6 sugars or derivatives thereof is in the present context meant to refer to carbohydrates commonly found in biomass selected from the group consisting of glucose, fructose, galactose, mannose, sucrose, xylose, erythrose, erythrulose, threose, glycolaldehyde and 2-hydroxy- γ -

butyrolactone. The one or more sugars or derivatives thereof may be used in solution or it may be a sugar syrup. Such a solution and syrup may be referred to as a sugar composition. The sugar composition may contain the solvent. Accordingly, 5 the one or more sugars and derivatives thereof may be mixed with the solvent and/or the compound comprising sulphur. before it is contacted with the metallo-silicate composition. It may be referred to as a reaction mixture.

10 The process is preferably a one step process wherein the methionine α -hydroxy analogue and derivatives thereof are obtainable directly from the sugar substrate by contacting one or more sugars with a metallo-silicate composition in the presence of a compound comprising sulphur and a solvent.

15 In a further embodiment of the invention the sugars can be used in the presence of other C₁-C₃ oxygenates such as, acetol, pyruvaldehyde, formaldehyde and glyoxal. Glycolaldehyde (C₂ sugar) can be produced together with minor amounts of 20 other C₁-C₃ oxygenates by hydrous thermolysis of sugars according to the procedure described in US 7,094,932 B2 and PCT/EP2014/053587.

The methionine α -hydroxy analogue and derivatives thereof 25 are also obtainable by subjecting the one or more sugars or derivatives thereof to a pyrolysis step to obtain a pyrolysis product and subsequently contacting the pyrolysis product with the metallo-silicate composition in the presence of the compound comprising sulphur and the solvent.

30 Metallo-silicate composition refers to one or more solid materials comprising silicon oxide and metal and/or metal oxide

components, wherein the metal and/or metal oxide components are incorporated into and/or grafted onto the surface of the silicon oxide structure (i.e. the silicon oxide structure comprises M-O-Si bonds). The silicon oxide structure is also
5 known as a silicate. Metallo-silicate compositions may be crystalline or non-crystalline. Non-crystalline metallo-silicates include ordered mesoporous amorphous or other mesoporous amorphous forms. The metallo-silicate composition is selected from one or more of the group consisting of zeotype
10 materials and ordered mesoporous amorphous silicates.

Preferably the active metal of the metal and/or metal oxide component is selected from one or more of the group consisting of Ge, Sn, Pb, Ti, Zr and Hf. The genus of zeotype materials encompasses the zeolite material genus. Preferably the
15 zeotype material has a framework structure selected from the group consisting of BEA, MFI, FAU, MOR and FER. Preferably the ordered mesoporous amorphous silicate has a structure selected from the group consisting of MCM-41 and SBA-15. In a preferred embodiment, the metallo-silicate composition is a
20 zeotype material. More preferably the metallo-silicate composition is a zeotype material and is selected from the group consisting of Sn-BEA, Sn-MFI, Sn-FAU, Sn-MCM-41 and Sn-SBA-15.

25 The solvent is preferably selected from one or more of the group consisting of methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-butanol, DMSO and water.

30 WO 2015/024875 discloses that in certain conditions, the presence of a metal ion in the reaction solution is beneficial to the yield. WO 2015/024875 provides experimental de-

tails describing the origin and addition of the metal ion to the process either via the catalyst itself or independently of the catalyst.

5 A further embodiment of the present invention is a basic reaction solution. The basic solution may be obtainable by the addition of one or more basic components. The basic component may be selected from one or more of the reagents selected from a metal salt and a basic polymer resin. Basic polymer
10 resin may be for example a basic amberlyst resin.

The metal salt comprises a metal ion. Preferably the metal ion is selected from the group consisting of potassium, sodium, lithium, rubidium and caesium. Preferably the metal salt
15 is a salt of an alkaline earth metal or alkali metal and anion is selected from the group consisting of carbonate, nitrate, acetate, lactate, chloride, bromide and hydroxide. Even more preferably the metal ion originates from one or more salts of the alkaline earth metal or alkali metal and is
20 selected from the group consisting of K_2CO_3 , KNO_3 , KCl , potassium acetate (CH_3CO_2K), potassium lactate ($CH_3CH(OH)CO_2K$), Na_2CO_3 , Li_2CO_3 and Rb_2CO_3 .

The reaction vessel/solution that is used in the process is
25 heated to a temperature of less than 250 °C. Preferably the vessel is heated to from 50 °C to 180 °C, from 60 °C to 170 °C, from 80 °C to 150 °C; more preferably from 60 °C to 140 °C.

30 According to the process of the present invention the inventors have surprisingly found that the yield of the methionine α -hydroxy analogue and derivatives thereof is greater than

than the yield of MVG. If a C4 saccharide is the substrate, the yield of MVG is less than 5%, 4%, 3%, 2%, 1%.

Also, the inventors have surprisingly found that the yield of
5 the methionine α -hydroxy analogue and derivatives thereof prepared according to the process of the present invention is greater than 15%.

The process for the preparation of methionine α -hydroxy ana-
10 logue and derivatives thereof may be carried out in a batch scale reaction or a continuous flow reaction.

The one or more sugars or derivatives thereof are contacted with the metallo-silicate composition in the presence of the
15 compound comprising sulphur and the solvent in a reactor. Sugars or derivatives thereof are gradually converted into the methionine α -hydroxy analogue and derivatives thereof. Preferably the reactor is stirred such as by a mixer or by the flow through the reactor. The conversion is preferably
20 carried out under heating and for a period of time sufficient to achieve a high conversion of the sugars and derivatives thereof. Preferably for a period of from 10 minutes to 12 hours, more preferred of from 20 to 300 minutes. The methio-
nine α -hydroxy analogue and derivatives thereof may be re-
25 covered as it is or it may be purified such as by distillation.

Products obtained from bio materials such as sugars, will have a significantly higher content of ^{14}C carbon than the same products obtained from petrochemical sources. Previous-
30 ly, methionine and its derivatives for use as nutritional supplements have been obtained from fossil fuels.

Accordingly a product is provided according to the present invention, which is obtainable by the process for the preparation of a methionine α -hydroxy analogue and derivatives thereof from sugars described above. Such a product is characteristic by having a ^{14}C content above 0.5 parts per trillion of the total carbon content. The methionine α -hydroxy analogue and derivatives thereof may be 2-hydroxy-4-(methylthio)butanoic acid, salts and esters thereof and at least 70% of the initial carbon may be recovered in that form.

Legends to the Figures

Figure 1. Yield of methyl ester of methionine α -hydroxy analogue (2-hydroxy-4-(methylthio)butanoic acid methyl ester) with Sn-Beta as catalyst using glycolaldehyde as sugar in continuous flow reaction. Feed composition: 9 g/L glycolaldehyde in methanol as solvent, 10.7 wt% of water, 0.9 g/L methanethiol.

Figure 2. Yield of methyl ester of methionine α -hydroxy analogue (2-hydroxy-4-(methylthio)butanoic acid methyl ester) with Sn-Beta as catalyst using glycolaldehyde in the presence of C_1 - C_3 oxygenate compounds in continuous flow reaction. Feed composition: 10.9 g/L glycolaldehyde in methanol as solvent, 8 wt% of water, 0.7 g/L methanethiol.

Examples

Preparation of catalyst

Sn-BEA (Si/Sn = 125) is prepared according to a modification of the procedure described in US 4,933,161. Commercial zeolite Beta (Zeolyst, Si/Al 12.5, ammonium form) is calcined (550°C for 6 h) to obtain the H form (de-aluminated form) and
5 treated with 10 grams of concentrated nitric acid (Sigma-Aldrich, 65%) per gram of zeolite beta powder for 12 h at 80°C. The resulting solid is filtered, washed with ample water and calcined (550°C for 6 h) to obtain the de-aluminated Beta. This solid is impregnated by incipient wetness methodology with a Sn/Si ratio of 125. For this purpose, tin (II)
10 chloride (0.128 g, Sigma-Aldrich, 98%) is dissolved in water (5.75 mL) and added to the de-aluminated Beta (5 g). After the impregnation process, the samples are dried 12 h at 110 °C and calcined again (550°C for 6 h)

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Example 1: Catalytic reaction in batch reaction

A stainless steel pressure vessel (40 cc, Swagelok) is charged with 15.0 g of methanol (Sigma-Aldrich, >99.8%),
20 0.450 g of sucrose (Fluka, >99.0%) and 0.150 g of catalyst. The reactor is then filled with 75 mL of methanethiol at 1.7 bar, pressurized at 11 bar with N₂ and closed. The reactor is heated in an oil bath at 170 °C under stirring (700 rpm). The reaction is continued for the desired time and after this pe-
25 riod, the reaction is quenched by submerging the vessel in cold water. Samples from the reaction vessel are filtered and analysed by HPLC (Agilent 1200, Biorad Aminex HPX-87H column at 65 °C, 0.05 M H₂SO₄, 0.6 ml min⁻¹) to quantify unconverted hexoses and dihydroxyacetone (DHA), glyceraldehyde (GLA); and
30 GC (Agilent 7890 with a Phenomenex Solgelwax column) was used to quantify: methyl lactate (ML), methyl vinylglycolate (MVG, methyl 2-hydroxy-3-butenate), glycolaldehyde dimethylacetal

(GADMA) and MHA (Methionine α -hydroxy analogue and derivatives thereof).

The methionine α -hydroxy analogue esters prepared according to Example 1 may be reacted in a basic aqueous solution, such as aqueous NaOH or KOH or an acidic aqueous solution, such as aqueous HCl, or solid acid catalyst to produce the salts and the acid derivatives of the methionine α -hydroxy analogue ester.

Table 1: Conversion of sugars to methionine α -hydroxy analogue and derivatives thereof in the Presence of a Metallo-silicate composition and sulfur compound. MHA means methionine α -hydroxy analogue and derivatives thereof. In the case of solvents A, B and C, MHA means 2-hydroxy-4-(methylthio)butanoic acid methyl ester. In the case of H₂O as solvent, MHA means 2-hydroxy-4-(methylthio)butanoic acid. In the case of IPA, MHA means 2-hydroxy-4-(methylthio)butanoic acid isopropyl ester. In the case of ethanol, MHA means 2-hydroxy-4-(methylthio)butanoic acid ethyl ester.

Ex	Sugar	Catalyst	Sol-vent	CH3SH / mL	MHA Yield	MVG Yield	Conver-sion	Temp	Time
1	Erythrulose	Sn-BEA	A	25	20.7	0	68.1	60	16
2	Erythrulose	Sn-BEA	A	25	6.8	0	43.8	60	4
3	Erythrulose	Sn-BEA	A	50	3.5	0	14.0	60	4
4	Erythrulose	Sn-BEA	A	25	24.3	0	77.7	100	4
5	Erythrulose	Sn-BEA	A	25	11.4	0	86.6	60	4
6	Erythrulose	Sn-BEA	A	25	12.7	17.4	93.8	170	16
7	Erythrulose	Sn-MFI	A	25	29.1	0	81.3	100	4
8	Erythrulose	Sn-FAU	A	25	0	0	54.0	100	4
9	Erythrulose	Sn-MOR	A	25	0	-	97.2	100	4
10	Erythrulose	Sn-BEA	IPA	25	0	0	66.7	100	4
11	Erythrulose	Sn-BEA	EtOH	25	15.6	0	68.7	100	4
12	Erythrulose	Sn-BEA	H2O	25	0	0	0	80	4
13	Erythrulose	Sn-BEA	A	25	21.2	0	76.6	140	4
14	Erythrulose	Sn-BEA	A	50	19.7	8.3	85.7	170	4
15	Erythrulose	Sn-BEA	A	25	6.7	0	27.4	60	4
16	Erythrulose	Sn-BEA	A	25	14.8	0	84.6	170	4
17	Erythrulose	Sn-BEA	B	25	23.7	0	73.0	100	4
18	Erythrulose	Sn-BEA	C	25	22.1	0	76.9	100	4
19	Glucose	Sn-BEA	A	25	3.6	<<1	0	160	3
20	Glucose	Sn-BEA	A	25	8.3	0	100	160	4
21	Glucose	Sn-BEA	A	25	5.0	5.8	96.8	170	16
22	GA	Sn-BEA	A	25	12.7	0	44.3	120	4
23	GA	Sn-BEA	A	25	17.4	0	41.9	120	16
24	GA	Sn-BEA	A	25	14.9	5.4	30.7	140	16
25	GA	Sn-BEA	A	10	7.5	0	48.0	60	4
26	GA	Sn-BEA	A	25	5.0	0	8.4	60	4
27	GA	Sn-BEA	A	25	17.7	4	28.9	60	3
28	GA	Sn-BEA	H2O	25	0	0	51.3	80	4

Ex	Sugar	Catalyst	Sol-vent	CH3SH / mL	MHA Yield	MVG Yield	Conver-sion	Temp	Time
29	GA	Sn-BEA	A	25	0	0	39.4	60	4
30	GA	Sn-BEA	A	25	0	0	52.3	60	4
31	GA	Sn-BEA	A	10	0	0	51.1	60	4
32	GA	Sn-BEA	B	25	0	0	46.5	60	4
33	GA	Sn-BEA	C	25	5.0	0	88.9	120	4
34	GA	Sn-BEA	A	25	8.3	0	62.1	120	4
35	Sucrose	Sn-BEA	A	25	2.0	4.2	96	170	16
36	Sucrose	Sn-BEA	A	25	0.9	0	72.8	160	3
37	MVG	Sn-BEA	A	25	0		0	100	4
38	MVG	Sn-BEA	A	25	0		100	100	4
39	MVG	Sn-BEA	A	25	0.2		12.7	170	16
40	Erythrose	Sn-BEA	A	25	0	0	0	60	4
41	Erythrose	Sn-BEA	A	25	20.0	0	80.0	100	4
42	Erythrose	Sn-BEA	A	25	19.3	0	94.0	170	4
43	GA	Sn-BEA	A	25	14.5	0	73.0	100	16
44	GA	Sn-BEA & Amberlyst	A	25	15.4	0	90.1	100	16
45	Glucose	Sn-BEA	A	85	8.3	-	79.4	120	4
46	Erythrulose	Sn-BEA	A	85	17.0	-	81.8	120	4

Solvent A: MeOH+0.13mmol K₂CO₃

Solvent B: MeOH+0.06mmol K₂CO₃

Solvent C: MeOH+0.3mmol K₂CO₃

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GA = glycolaldehyde

10 As observed in Table 1, C4 and C2 sugars (erythrulose and glycolaldehyde) provided the highest yields of methionine α -hydroxy analogue and derivatives thereof. Methanol and ethanol provided similar yields of the corresponding esters.

Example 2: Catalytic reaction in continuous flow reaction

Compositions comprising glycolaldehyde in the presence of C₁-C₃ oxygenate compounds may be prepared by pyrolysis of biomass or C₅-C₆ sugars such as glucose, sucrose, fructose or xylose. Exemplary pyrolysis reactions are provided in US 7,094,932 B2 and PCT/EP2014/053587.

A composition comprising glycolaldehyde or C₁-C₃ oxygenate compounds with 814 g/L glycolaldehyde was dissolved in methanol (Sigma-Aldrich, 99.9%) at room temperature to reach a concentration of 10.9 g/l. Additionally, methanethiol (Sigma, 1.7 bar) and if necessary water, were added to the feed solution. Catalyst Sn-Beta (Si:Sn 125) prepared according to the above preparation was fractionized (0.25 g, 300-600 µm.) and loaded into a stainless steel 0.25 inch reactor. Glass wool was used to hold the catalyst in place. The reactor was introduced into an oven and the temperature of the reactor increased to 160 °C. When the temperature was over 140°C, the pump was started with a flow of 0.05 ml/min.

As observed from figures 1 and 2, stable yields of 2-hydroxy-4-(methylthio)butanoic acid methyl ester (over 30%) were obtained from glycolaldehyde in water and methanol using Sn-Beta as catalyst. The presence of other C₁-C₃ oxygenates (Figure 2) did not affect the reaction of production of the methionine α -hydroxy analogue methyl ester.

Embodiments

The present invention may also be described according to the following embodiments:

Embodiment 1. A process for the preparation of methionine α -hydroxy analogues comprising contacting one or more sugars or derivatives thereof with a metallo-silicate composition in the presence of a compound comprising sulphur and a solvent.

Embodiment 2. The process according to embodiment 1, wherein the compound comprising sulphur is selected from the group consisting of C₁-C₅ alkyl thiol, C₁-C₅ alkyl thiol salt, dimethylmercaptan, dimethyl disulphide and hydrogen sulphide.

Embodiment 3. The process according to any one of embodiments 1 and 2, wherein the compound comprising sulphur is selected from the group consisting of methane thiol, dimethylmercaptan, dimethyl disulphide and hydrogen sulphide.

Embodiment 4. A process according to any one of embodiments 1 to 3, wherein the one or more sugars or derivatives thereof is selected from the group consisting of glucose, fructose, galactose, mannose, sucrose, xylose, erythrose, erythrulose, threose, glycolaldehyde and 2-hydroxy- γ -butyrolactone.

Embodiment 5. A process according to any one of embodiments 1 to 3, wherein the one or more sugars or derivatives thereof are derivatives obtained by subjecting one or more sugars selected from the group consisting of glucose, fructose, galactose, mannose, sucrose, xylose, erythrose, erythrulose, threose; to a pyrolysis step to obtain a pyrolysis product and subsequently contacting the pyrolysis product with the metallo-silicate composition in the presence of the compound comprising sulphur and the solvent

Embodiment 6. The process according to any one of embodiments 1 to 5, wherein the metallo-silicate composition is a zeotype material.

5 Embodiment 7. The process according to embodiment 6, wherein the zeotype material is one or more materials selected from the group consisting of Sn-BEA, Sn-MFI, Sn-FAU, Sn-MCM-41 and Sn-SBA-15.

10 Embodiment 8. The process according to any one of embodiments 1 to 7, wherein the solvent is selected from one or more of the group consisting of methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-butanol, DMSO and water.

15 Embodiment 9. The process according to any one of embodiments 1 to 8, wherein the methionine α -hydroxy analogues is selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid, salts and esters thereof.

20 Embodiment 10. The process according to any one of embodiments 1 to 9, wherein the methionine α -hydroxy analogues is selected from the group consisting of 2-hydroxy-4-(methylthio)butanoic acid, 2-hydroxy-4-(methylthio)butanoic acid methyl ester and 2-hydroxy-4-(methylthio)butanoic acid ethyl ester

25 Embodiment 11. The process according to any one of embodiments 1 to 10, wherein the temperature of the process is less than 200°C, preferably within the range of from 50 to 200°C.

30 Embodiment 12. The process according to any one of embodiments 1 to 11, wherein the reaction solution comprises one or more basic components selected from the group consisting of a metal salt and a polymer resin.

Embodiment 13. The process according to any one of embodiments 1 to 12, wherein the yield of the methionine α -hydroxy analogues is greater than methyl vinylglycolate (MVG).

5 Embodiment 14. The process according to any one of embodiments 1 to 13, wherein the yield of the methionine α -hydroxy analogues is greater than 15%.

Embodiment 15. The process according to any one of embodiments 1 to 14, wherein the process is a continuous
10 process.

Embodiment 16. The process according to any one of embodiments 1 to 15, wherein the methionine α -hydroxy analogues are purified by distillation.

Embodiment 17. The process according to embodiment 9,
15 wherein the 2-hydroxy-4-(methylthio)butanoic esters are hydrolysed.

Embodiment 18. Use of 2-hydroxy-4-(methylthio)butanoic acid, salts and esters thereof prepared by the process of claims 9 to 17 for a nutritional supplement.

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