DESCRIPTION

TITLE: Method for producing methionine

The invention relates to an improvement of a method for producing methionine or its “seleniated” analogue (selenomethionine), from the precursors 2-amino-4-methylthiobutyronitrile or 2-hydroxy-4-methylthiobutyronitrile for methionine, or 2-amino-4-methylselenobutyronitrile or 2-hydroxy-4-methylselenobutyronitrile for selenomethionine.

The size of the methionine market no longer needs to be presented, particularly in animal nutrition, and its production methods are still the subject of numerous developments. The seleniated derivatives of methionine are also constituents of major interest in animal nutrition.

The preparation of methionine may be practiced by different methods involving various synthesis intermediates, and in particular 2-amino-4-methylthiobutyronitrile (AMTBN), 2-amino-4-methylthiobutyramide (AMTBM) and 2-hydroxy -4-methylthiobutyronitrile (HMTBN).

The document WO01/60790A1 describes a synthesis of methionine from 2-hydroxy-4-methylthiobutyronitrile (HMTBN). Upon reaction with ammonia, HMTBN is transformed into AMTBN which, in turn, is reacted with acetone in a basic medium to form AMTBM. A catalytic hydrolysis of AMTBM, in the presence of a titanium compound having a determined porosity, results in ammonium methioninate from which the methionine is recovered.

According to the document WO2004/089863A1, a method for producing the ammonium salt of HMTBA from the nitrile precursor of HMTBA is known, HMTBN, according to which HMTBN in aqueous solution, placed in the presence of a titanium-based catalyst, is converted in a single step into ammonium salt of HMTBA. This synthesis also leads to the formation of methionine and HMTBM, and the reported ammonium salt yields of HMTBA are in the range of 10%. They are too insufficient to consider an application of this method on an industrial scale.

The present ~~invention~~ disclosure provides an alternative to the existing methods making it possible to dispense with at least one step, while leading to methionine or its seleniated derivative, in high yields.

It has been discovered according to the disclosure ~~invention~~ that the amino-nitrile (AMTBN or its seleniated equivalent) and hydroxy-nitrile (HMTBN or its seleniated equivalent) intermediates could be converted into methionine (or into seleno-methionine) in a

single step, in presence of water and a catalyst and, where appropriate, ammonia or an ammonium salt. The accessibility and performances of this conversion are such that its transposition to an industrial production of methionine is conceivable. Compared to the known synthetic methods and their improvements which remain insufficiently beneficial for conventional industrial methods to be modified, the present disclosure ~~invention~~ represents a real advance. Significant yields are obtained in very short times.

Thus, in one aspect, the disclosure ~~invention~~ provides a method for preparing a compound of formula (I),

[Chem 1]

$CH_3XCH_2CH_2C(NH_2)COOH$ (I)

where X represents S or Se,

by catalytic conversion of a compound of formula II

[Chem 2]

$CH_3XCH_2CH_2C(Y)CN$ (II)

where X represents S or Se and Y represents NH_2 or OH,

characterized in that,

when Y represents NH_2, the conversion is carried out in the presence of water and at least one catalyst comprising at least alumina, titanium dioxide or a mixture thereof, and

when Y represents OH, the conversion is carried out in the presence of water, of at least one catalyst comprising at least alumina, titanium dioxide, zirconia or a mixture thereof, and NH_3 or an ammonium salt.

in one example, the disclosure provides a method for preparing a compound of formula (I),

[Chem 1]

$CH_3XCH_2CH_2C(NH_2)COOH$ (I)

where X represents S or Se,

by catalytic conversion of a compound of formula (II)

[Chem 2]

$CH_3XCH_2CH_2C(Y)CN$ (II)

where X represents S or Se and Y represents NH_2 or OH,

when Y represents NH_2, the conversion being carried out in the presence of water and of at least one catalyst comprising at least alumina, titanium dioxide or a mixture thereof, and where appropriate NH_3 or an ammonium salt, and

when Y represents OH, the conversion being carried out in the presence of water, of at least one catalyst comprising at least alumina, titanium dioxide, zirconia or a mixture thereof, and NH_3 or an ammonium salt.

By “where appropriate”, it should be understood according to the invention that, when the method involves the hydroxy-nitrile precursor which is the compound of formula (II) in which Y represents OH, the presence of NH_3 or of an ammonium salt is necessary, while it is not necessary when the method involves the amino-nitrile precursor which is the compound of formula II in which Y represents NH_2. However, this definition does not exclude the presence of NH_3 when the method engages the amino-nitrile precursor, this variant constituting a particular implementation of the invention, described later on.

An ammonium salt according to the invention comprises any salt having the formula $(NH_4)_nA$ where A is in particular selected from halogens, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates, sulfates, hydrogen sulfates, acetate, the citrate, formate, hydroxide and n is an integer varying from 1 to 5. As an illustration, it can be selected from $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$, $(NH_4)HSO_4$, $(NH_4)_2SO_4$, $(NH_4)HCO_3$ or $(NH_4)_2CO_3$.