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A Simple Procedure for the One Pot Synthesis of Ascorbic Acid As Efficiency And Recyclable Media

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ABSTRACT

A method for producing L-ascorbic acid which compromise forming substantially anhydrous slurry of 2-keto-l-gulonic acid, and reacting said slurry with a substantially hydrous acid catalyst to convert said 2-keto-l-gulonic acid to l-ascorbic acid. L-ascorbic acid is produced in a high yield and no efficiency by converting 2-keto-l-gulonic acid to L-ascorbic acid by acid catalyst as anhydrous condition.

Keywords : L-Ascorbic Acid, HCl, Isopropanol

I. INTRODUCTION

Ascorbic Acid is a naturally occurring organic compound. Ascorbic acid one form of Vitamin C. Vitamin C is an essential micronutrient with several important biological functions. It reduces the symptoms of Cold & Flu, accelerating the recovery process. Conventional method for organic synthesis usually needs reacting said slurry with sub surfactant anhydrous, Hydrogen Chloride gas as an acid catalyst. Which result in the excessive use HCl Gas generation in environmental pollution. In these new process no gas generation, and not environmental pollution. If want to preparation of ascorbic Acid from 2-keto-hexnoic acid using alkaline earth silicate catalyst. But in these process used acidic media. The process carried out in water, alcohol or in a variety of polar or moderately polar solvent or solvent mixture & proved for simple workup purification of ascorbic acid The new process were developed by considering important parameter and minimum by-products formation leading to maximum yield of the pure product with desired quality.

The invention relates to a process for the preparation of L-ascorbic acid, in which a melt of C3—C1O-alkyl Z-keto -L gulonate is lactonization under acidic conditions. In the past, a large number of process variants for the preparation of L-ascorbic acid have been published. Are view is found, inter alia, in Crawford et al., Adv. Carbohydrate Chem. 37, 79 (1980) and in Ullmann's Encyclopaedia of Industrial Chemistry, Vol. A27, 551—557 (1996).A number of processes for the preparation of ascorbic acid by 15 reaction of 2-keto-L-gulonic acid With an acid are known. Thus, US. Pat. No. 2,185,383 describes the reaction of 2-keto-L-gulonic acid with concentrated hydrochloric acid and acetic acid as a solvent.

US. Pat. No. 5,391,770 describes the esterification of 2-keto-L-gulonic acid with subsequent base-catalyzed lactonization of the esters formed to give salts of L-ascorbic acid and liberation of the ascorbic acid by the addition of a strong acid.

Japanese published patent specification 22113/75 describes the esterification of 2-keto-L-gulonic acid with butanol and the subsequent acid-catalyzed lactonization in benzene as a solvent. EP-A-0 671 405 discloses a process for the preparation of methyl or ethyl 2-keto-L-gulonate by esterification of 2-keto-L-gulonic acid with methanol or ethanol in the presence of an acidic ion exchanger.

The above mentioned embodiments of the acid-catalyzed, single-stage process variant exhibit serious Weaknesses. Thus, as a rule the use of an inert solvent is unavoidable in order to suppress the secondary reactions of the ascorbic acid with aqueous hydrochloric acid. At the same time, the 2-keto-L-gulonic acid is always present undissolved and the form of a suspension at the start and in the course of their action and reaction only takes place on the crystal surface. The addition of surface-active substances alters the course of the reaction only slightly. What is more, this auxiliary can only be removed from the crude product with difficulty

and means additional Working-up steps in order to obtain the desired purity of the L-ascorbic acid.

It was therefore the object to make available a process for the preparation of L-ascorbic acid which does not have the above mentioned disadvantages.

This object was achieved by a process for the preparation of L-ascorbic acid which comprises lactonizing a melt of C3—C1O-alkyl 2-keto-L-gulonate under acidic conditions. In a preferred embodiment, the process according to the invention further more comprises

a) esterifying 2-keto-L-gulonic acid or 2,3:4,6-di-Oisopropylidene-2-keto-L-gulonic acid in the presence of an acidic catalyst using a C3—C10-alcohol,
b) Distilling off the excess C3—C1O-alcohol together With the Water of reaction formed and
c) Then lactonizing the C3—C1O-alkyl 2-keto-L-gulonate formed in the form of an anhydrous melt under acidic conditions.

In the course of the process according to the invention,2-keto-L-gulonic acid or 2,3:4,6-di-O-isopropylidene-2 keto-L-gulonic acid is first reacted to give the alkyl ester in a single-stage esterification step in the presence of an acidic catalyst. The esterification is carried out in a temperature range from —10 to 160° C., preferably from 20 to 100° C., particularly preferably in a temperature range from 40 to 106° C.

As a rule, the monohydrate of 2-keto-L-gulonic acid is obtained an crystallization from Water or Water-containing, solvents. By centrifuging off the crystal magma, organic moist monohydrate is accessible. This can be employed directly in the subsequent esterification reaction as a centrifuge-moist product or dried under mild conditions .It is also possible to employ a concentrated aqueous solution of the 2-keto-L-gulonic acid directly in the esterification reaction. The excess solvent is removed before or during the esterification reaction, Ex. by extraction and phase separation or azeotropic distillation.

Advantageously, higher alkyl esters of saturated, branched or unbranched alkyl alcohols having a hydrocarbon number of greater than or equal to 3, preferably having an alkyl radical of 3 to 10 carbon atoms, are suitable for the esterification, such as, for example, n- propanol , isopropanol,1butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2 propanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol,2-hexanol, 1-heptanol,2heptanol, 1-octanol, 2-octanol,3-octanol, 1-nonanol, 2-nonanol, 1-decanol, 2-decanol,4-decanol.Those alcohols in Which L-ascorbic acid is poorly soluble are preferably employed for the esterification. Those particularly preferably suitable are C4—C8 alcohols, selected from the group consisting of n-propanol, isopropanol,1-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol,1-pentanol, 1-hexanol and 1-octanol and 1-butanol and1-pentanol.

2-Keto-L-gulonic acid is preferably employed for the synthesis as a starting material. The acid monohydrate can be employed here either in crystalline form, for example as a dried or centrifuge-moist or as an anhydrous compound or as an aqueous solution, for example as a concentrated fermentation solution.

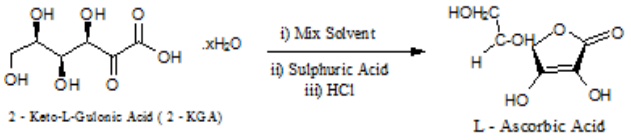
As a rule, the monohydrate of 2-keto-L-gulonic acid is obtained an crystallization from Water or Water-containing, organic solvents. By centrifuging off the crystal magma, moist monohydrate is accessible. This can be employed directly in the subsequent esterification reaction as a centrifuge-moist product or dried under mild conditions.

It is also possible to employ a concentrated aqueous solution of the 2-keto-L-gulonic acid directly in the esterification reaction. The excess solvent is removed before or during the esterification reaction, eg by extraction and phase separation or azeotropic distillation. This procedure is particularly suitable for a ketogulonic acid solution from a fermentative preparation process. After removal of the biomass by standard processes known per se, the fermentation solution, Which is usually colored, can preferably be employed directly Without further purification after liquid liquid extraction. The excess solvent is then removed, asdescribed above, before or during the esterification reaction, e.g. by phase separation or azeotropic distillation.

The drying or dehydration of the monohydrate of 2-ketoL-gulonic acid can advantageously be dispensed

With in the process according to the invention, as in the subsequent activation reaction according to the invention an azeotropic dehydration is carried out any Way.

SCHEME:



II. EXPERIMENTAL SCHEME

212g (1 mol) of hydrous 2-keto-L-gulonic acid Were suspended in 400 ml mix solvent n-butanol : toluene (37.5:62.5) and, after addition dehydrate reaction mass at 85 to88° C ,for quantity of water 18 ml .add 2 g of concentrated sulphuric acid, the mixture Was dehydrate to 410-435 mbar. After heating to 85° C. for 5-6 hr, for quantity of water 18 ml .

The viscous, brown coloured mass was cool up to 70-75 for 17 hr after addition of 22 ml conc. hydrochloric acid. After reaction completion dehydrated reaction mass at 70-75 at 460-475 mbar, for quantity of water 22 ml. Then cool reaction mass at room temp. stir well .

The precipitated L-ascorbic acid Was filtered off With suction, Washed With mix solvent n- butanol: toluene (37.5:62.5) and dried invacuo. 180 g (90%) of a pale gray crude product having a purity of 98.5% Were obtained. The crude product dissolved in Water. After clarifying filtration, a colourless solution was obtained from which it was possible to isolate L-ascorbic acid in a manner known from the literature. The residue (0.9%) consisted mainly of carbon. Purification of L- ascorbic acid by using n-butanol as solvent.

Reaction monitor by TLC (Acetonitrile : MeOH : Butanol : Acetic Acid) assay by HPLC(99%), SOR,

III. RESULT

The L-Ascorbic acid is a white crystalline powder, becoming freely soluble in water and sparingly soluble ethanol (95%). PH between 2.2 -2.5, specific optical rotation between + 20 – +21.5. The absorbance at 244 nm is about 0.56. Assay by titration 99.5% -100.5%.
IR (cm^{-1}): 3412 (s), 3317 (s), 3221 (s) OH , 3032 CH , 1753 C=O , 1668 C=C , 1500 CH, 1273 C-O-C, 1220 and 1197 C-C(=O)-O, 1026 C-O-H, 985 (s) C-H & O-H.

IV. DISCUTION

In previous patent describe the process preparation of ascorbic acid by dry HCl thus leading to charring of ascorbic acid. In previous patent describe the process preparation of ascorbic acid by dry HCl thus leading to poor yield and purity. Due to draw back associated with the process known in the literature for the preparation of ascorbic acid by using conc. HCl as catalyst. The present literatures have developed industrially advantages for the preparation of ascorbic acid of high purity and better yield. Which circumvent the drawback associated with process known in the prior art .After removal of desire quantity of water in first part dehydration do not heat more time at reflux. If we addition of Conc. HCl at 70-75°C, because the high temperature addition for Conc. HCl the charring the material. Give proper washing to Ascorbic acid by mixture of solvent dry under vacuum.

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