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SYNTHESIS OF 2-AMINO-2-DEOXYALDONIC ACIDS BY THE USE OF THE BASE-CATALYZED CONDENSATION REACTION OF N-PYRUVYLIDENEGLYCINATOAQUOCOPPER(II) WITH D- AND L-GLYCERALDEHYDE

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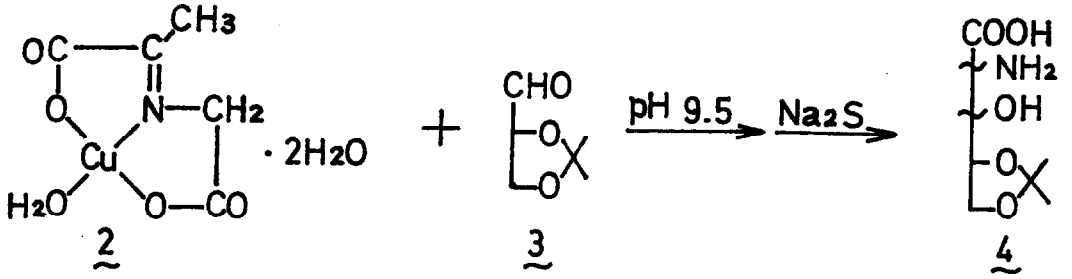
Although the Akabori reaction,[1] which involves the base-catalyzed condensation reaction of bis(glycinato)copper(II)(1) with aldehydes to give the corresponding β-hydroxy amino acids, has been placed a limit upon aldehydes applicable to the reaction because of the strongly alkaline condition, and high molar ratio of aldehydes to 1, the limit was fortunately overstepped by our recent investigation[2] on the application of N-pyruvylideneglycinatoaquocopper(II)(2) to the reaction in place of 1. Namely: 1) The reaction condition was considerably moderated enough to proceed at pH 8.0 — 9.5. 2) The mole equivalent ratio of aldehydes to the copper complex was reduced from 2 — 5 to 1.5 — 3.0.

In consideration of these situations, the authors explored the possibility for the synthesis of 2-amino-2-deoxyaldonic acids by the above improved procedure involving an elongation of the backborn of sugars by two carbon atoms.

An aqueous solution of 2(10 mmol) and 2,3-O-isopropylidene-D-glyceraldehyde(3)(11 mmol), which was prepared by the method of Horton et al.,[3] was stirred at pH 9.5 for 1 hour at room temperature. Then, the mixture was treated with 1.3 equivalent of sodium sulfide followed by filtration to remove the precipitated copper sulfide. The filtrate was treated on a column of Amberlite IR-120B(NH_4-type) and successively on that of Amberlite IRC-50. As occasion demands, this treatment was repeatedly carried out. The combined effluent was evaporated in vacuo to a volume of 10 ml, and methanol(10 ml) was added to the residue to stand overnight for crystallization. By repeating the crystallization procedure, the raw crystals of five crops were collected, and were

recrystallized from a small amount of water to give 2-amino-2-deoxy-4,5-O-isopropylidene-aldopentonic acid(4)[mp 198°(dec.), and $[\alpha]_D$ +0.2°(c 1.0, H_2O)] in 70% yield.[4)]



Similar treatment of 2,3-O-isopropylidene-L-glyceraldehyde, 2,4-O-ethylidene-D-erythrose[5)] and 2,3;4,5-di-O-isopropylidene-D-arabinose[6)] with 2 gave the corresponding 2-amino-2-deoxyaldonic acids[36%, mp 209°C(dec.); 70%, mp 198 – 199°C(dec.), and 26%, mp 212°C(dec.), respectively]. The possibility mentioned above was thus confirmed for the first time in the field of cabohydrate chemistry by these experiments.

The detailed results of this communication will be published elswhere along with those of an investigation which is now in progress in our laboratory by the utilization of carbohydrates with free aldehyde group. Moreover, the stereochemistry of the 2-amino-2-deoxyaldonic acids is also under investigation deriving them into the corresponding α-aminolactones and 2-aminosugar derivatives.

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