in EtOH. The EtOH-insoluble material was collected by filtration, and the recrystallization from hot water yielded 2.7 g. of colorless needles, m.p. 242~244.5°, not depressed by mixture with the authentic sample synthesized from cyanuric chloride. *Anal.* Calcd. for $C_7H_{12}ON_6$: C, 42.85; H, 6.12; N, 42.85. Found: C, 42.43; H, 6.32; N, 43.01.

Synthesis of 2-Morpholino-4,6-diamino-*s*-triazine

2-Chloro-4,6-diamino-*s*-triazine——To 70 ml. of 12% NH_3-H_2O, 9.2 g. of cyanuric chloride suspended in hot Me_2CO was added with agitation. The reaction mixture was warmed at 40~45° for 4 hr. under stirring. After reacting, the precipitate was collected, washed with cold H_2O until no more Cl^- ion appeared, recrystallized from hot H_2O, and submitted to the next reaction without further purification.

2-Morpholino-4,6-diamino-*s*-triazine——To 1.7 g. of morpholine in 10 ml. of H_2O, 1.5 g. of 2-chloro-4,6-diamino-*s*-triazine was added and refluxed at 130~140° in an oil bath during 3 hr. The product was collected by filtration, and recrystallized from hot H_2O to give colorless needles, melted at 243~245°. *Anal.* Calcd. for $C_7H_{12}ON_6$: N, 42.85. Found: N, 42.95.

Summary

Thermal reaction of equimolar amounts of 1,1-(2,2'-oxydiethyl)biguanide with dicyanodiamide afforded a compound (I) other than the both reactants. The analytical data, infrared spectra, and chemical properties of I agreeded closely with those of 2-morpholino-4,6-diamino-*s*-triazine, synthesized by conventional manner from cyanuric chloride, ammonia, and morpholine. Consequently, I was verified to be 2-morpholino-4,6-diamino-*s*-triazine.

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Teiichiro Ito: Reactions of Trifluoroacetic Acid with N-Benzyloxycarbonyl-tetra-O-acetyl-D-glucosamine.

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In the field of aminosugar chemistry, the carbobenzyloxy group has often been used to protect the amino group and it is usually removed by catalytic hydrogenation.[1] In our studies on sulfur-containing aminosugars,[2] some of the catalytic hydrogenation of carbobenzyloxy to remove the protective group was unsuccessful, and other methods were studied.

In 1959, F.Weygand and W. Steglich[3] described that the benzyloxycarbonyl groups of amino acids or peptides could be cleaved by refluxing in trifluoroacetic acid in good yield. Therefore this reaction was chosen in the decarbobenzyloxylation of 2-benzyloxycarbonylamino-2-deoxy-1,3,4,6-tetra-O-acetyl-β-D-glucopyranose (N-benzyloxycarbonyl-1,3,4,6-tetra-O-acetyl-β-D-glucosamine) (I), as a model compound.

By the treatment of the compound (I) with trifluoroacetic acid at 70° for 15 minutes, the reaction product was isolated as needle crystals, which, however, was not the expected

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1) cf. *a*) C. G. Greig, D. H. Leaback, P. G. Walker: J. Chem. Soc., **1961**, 879. *b*) C. L. Stevens, K. Nagarajan: J. Med. Pharm. Chem., **5**, 1124 (1962). *c*) J. D. Dutcher, D. R. Walters, O. Wintersteiner: J. Org. Chem., **28**, 995 (1963).
2) The previous report. T. Ito, T. Ishii: Agr. Biol. Chem., **27**, 423 (1963).
3) F. Weygand, W. Steglich; Z. Naturforsch., **14b**, 472 (1959).

substance, 2-amino-2-deoxy-1,3,4,6-tetra-O-acetyl-β-D-glucopyranose (Ⅲ),[4] but was 2-amino-2-deoxy-1,2-O,N-carbonyl-3,4,6,-tri-O-acetyl-D-glucopyrane (Ⅱ).

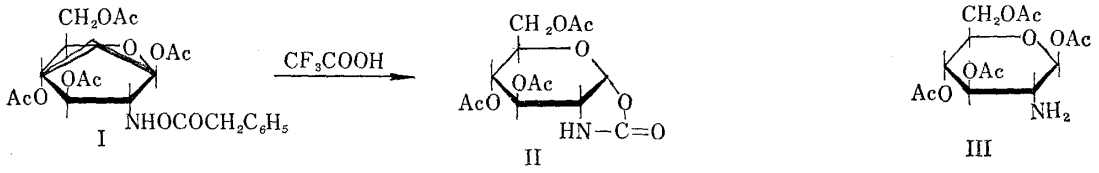

Chart 1.

The synthesis of the compound (Ⅱ) was already described by S. Konstas, I. Photaki and L. Zervas[5] from the compound (I) by the treatment either with titanium tetrachloride or a mixture of phosphorus pentachloride and aluminum chloride. The compound (I) was assumed to be converted to the intermediate (Ⅳ) and finally to the compound (Ⅱ), eliminating $C_6H_5CH_2Cl$.

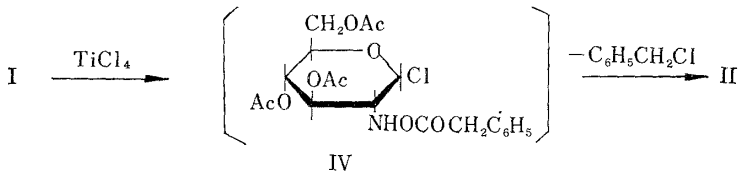

Chart 2.

When 2-amino-2-deoxy-1,3,4,6-tetra-O-acetyl-β-D-glucopyranose (Ⅲ) was treated with trifluoroacetic acid for 15 minutes at 70°, the starting material (Ⅲ) was recovered unreacted, suggesting that trifluoroacetic acid did not react directly with 1-O-acetyl group. The reaction mechanism of treating I with trifluoroacetic acid is uncertain, but it might be considered that the -NHOCO group attacked the back face of the carbon atom 1 as the 1-O-acetyl group detached.

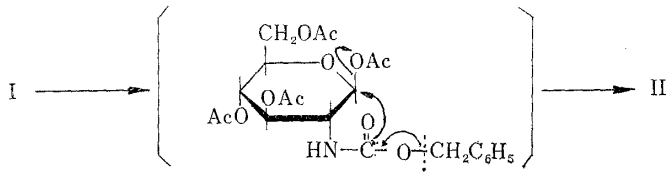

Chart 3.

Very recently, S. R. Kulkarni and H. K. Zimmerman Jr.[6] reported that, on treating propyl(or benzyl)-2-benzyloxycarbonylamino-2-deoxy-3,4,6-tri-O-benzoyl-β-D-glucopyranoside with sodium methoxide in chloroform, 2-amino-2-deoxy-1,2-O,N-carbonyl-3,4,6-tri-O-benzoyl-D-glucopyrane was produced.

Experimental*2

2-Benzyloxycarbonylamino-2-deoxy-1,3,4,6-tetra-O-acetyl-β-D-glucopyranose (I)——This compound was prepared as the method described by B. R. Baker, *et al.*[7] m.p. 147°, $[\alpha]_D^{26}$ +17° (c=1.4, $CHCl_3$). *Anal.* Calcd. for $C_{22}H_{27}NO_{11}$: C, 54.88; H, 5.65; N, 2.91. Found: C, 54.93; H, 5.67; N, 3.05.

*2 All melting points are uncorrected.

4) M. Bergmann, L. Zervas: Ber., **64**, 975 (1931).
5) S. Konstas, I. Photaki, L. Zervas: Chem. Ber., **92**, 1288 (1959).
6) S. R. Kulkarni, H. K. Zimmerman Jr.: Ann., **663**, 174 (1963).
7) B. R. Baker, J. P. Joseph, R. E. Schaub, J. H. Williams: J. Org. Chem., **19**, 1786 (1954).

2-Amino-2-deoxy-1,2-O,N-carbonyl-3,4,6-tri-O-acetyl- D-glucopyrane (II)——The compound (I) (500 mg.) was dissolved in trifluoroacetic acid (4 ml.) and the solution was refluxed for 15 min. at 70°. After the reaction, it was evaporated *in vacuo*, the resulting syrup was dissolved in $CHCl_3$, washed with cold $NaHCO_3$ aqueous solution and then cold H_2O successively. The $CHCl_3$ solution was dried and evaporated to syrup, which was crystallized gradually as needles, yielding 200 mg. (58%). It was recrystallized from Me_2CO-Et_2O, melted at 170°, $[\alpha]_D^{22}$ +33° (c=2, $CHCl_3$). *Anal.* Calcd. for $C_{13}H_{17}NO_9$: C, 47.11; H, 5.18; N, 4.23. Found: C, 47.23; H, 4.84; N, 4.24.

2-Amino-2-deoxy-1,2-O,N-carbonyl-3,4,6-tri-O-acetyl-D-glucopyrane was prepared from the compound (I) by the treatment with titanium tetrachloride[5] in $CHCl_3$, giving m.p. 170°,*3 $[\alpha]_D^{22}$ +33°*3 (c=1.5, $CHCl_3$). No melting point depression was observed on admixture of the above two crystals and their IR spectra[8] were identical.

The author is grateful to Dr. H. Ogawa of this laboratory for his kind advices and encouragements, and also to Miss K. Hibino for elemental analysis.

Summary

On treating with trifluoroacetic acid, 2-benzyloxycarbonylamino-2-deoxy-1,3,4,6-tetra-O-acetyl-β-D-glucopyranose afforded 2-amino-2-deoxy-1,2-O,N-carbonyl-3,4,6-tri-O-acetyl-D-glucopyrane.

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*3 m.p. 174~175°, $[\alpha]_D$+50.3°, were recorded by S. Konstas, I. Photaki and L. Zervas.

8) The infrared spectrum of the compound (II) showed the bands due to oxazolidone ring. cf. R. Mecke Jr., R. Mecke sen: Chem. Ber., **89**, 343 (1956).

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Masamichi Tsuboi, Shigesada Higuchi, Yoshimasa Kyogoku, Kimiko Matsuo,*1 and Akiyoshi Wada*2: Actinomycin Bound to Deoxyribonucleic Acid in Solution.

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Biological activity of actinomycin D is now correlated with its ability to bind deoxyribonucleic acid (DNA),[1~3] probably by complexing specifically to guanine residue.[4,5] The purpose of this note is to present a piece of information on the actinomycin D-DNA complex in solution, on the basis of the results of our recent two preliminary experiments.

First, the melting temperature (T_m) of DNA has been examined according to the method of Doty, Marmur and Sueoka,[6] in solutions with and without actinomycin D.

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1) J. M. Kirk: Biochim. Biophys. Acta, **42**, 167 (1960).
2) H. M. Rauen, H. Kersten, W. Kersten: Z. Physiol. Chem. Hoppe-Seyler, **321**, 139 (1960).
3) J. Kawamata, H. Imanishi: Biken's J., **4**, 13 (1961).
4) W. Kersten: Biochim. Biophys. Acta, **47**, 610 (1961).
5) I. H. Goldberg, M. Rabinowitz, E. Reich: Proc. U. S. Nat. Acad. Sci., **48**, 2094 (1962).
6) P. Doty, J. Marmur, N. Sueoka: Brookhaven Symp. Biol., **12**, 1 (1959).