COMMUNICATION TO THE EDITOR

THE STRUCTURES OF THE ACETONE DERIVATIVES OF GALACTOSE-, GLUCOSE- AND MANNOSEDIBENZYLMERCAPTALS

Sir:

In 1929 Brigl and Schinle [*Ber.*, **62,** 1716 (1929)] found that their 2-methylglucose was capable of osazone formation with the loss of the methyl group. This striking discovery cast doubt on the structure of those partially methylated sugars whose formulas had previously been assigned on the assumption, till then unquestioned, that a 2-methyl sugar could not possibly form an osazone. Among those partially methylated sugars affected by this discovery were 4-methylglucose [Pacsu, *ibid.*, **58,** 1455 (1925)], 4-methylmannose [Pacsu and v. Kary, *ibid.*, **62,** 2811 (1929)], and 4-methylgalactose [Pacsu and Löb, *ibid.*, **62,** 3104 (1929)]. Levene and co-workers [Levene, Meyer and Raymund, *Science*, **73,** 291 (1931); *J. Biol. Chem.*, **91,** 497 (1931)] were the first to notice that the supposed 4-methylglucose was identical with 2-methylglucose. In a later publication [Pacsu, *Ber.*, **65,** 51 (1932)] this fact has been confirmed. In the same place it has also been stated that in the light of Brigl's discovery it appears certain that the supposed 4-methylmannose is likewise a 2-methyl derivative, whereas nothing definite could be said as to the structure of the supposed 4-methylgalactose until the necessary revision of the entire problem has been concluded. For the past year this reinvestigation has been in progress in this Laboratory. In a recent publication, Munro and Percival [*J. Chem. Soc.*, 640 (1936)] apparently undertook "A Revision of the Constitutions of the Supposed 4-Methyl Galactose and 4-Methyl Mannose of Pacsu. . ." and stated "The structures of the acetone compounds of the dibenzylmercaptals of glucose, galactose, and mannose, assigned by Pacsu, require revision in the light of the facts now known and this problem is under investigation." This was precisely the conclusion arrived at in my publication (*loc. cit.*), which Munro and Percival doubtless overlooked. Therefore, it is deemed advisable briefly to communicate the results so far obtained with John W. Green during the course of our reinvestigation. We have found that the formerly described crystalline "2,3-monoacetone galactosedibenzylmercaptal" with m. p. 102–103° and $[\alpha]^{18}_{D}$ 8.8° ($C_2H_2Cl_4$), in spite of its apparent uniformity, is not a chemical individual. By repeated fractional crystallization from different solvents we have succeeded in separating this mixture into two monoacetone mercaptals, one with m. p. 112.5° and $[\alpha]^{20}_{D}$ 17.4° ($CHCl_3$), and the other with m. p. 101.5° and $[\alpha]^{20}_{D}$ 30.5° ($CHCl_3$). Neither compound reacts with triphenylmethyl chloride in pyridine solution. Therefore, the OH-group at carbon atom 6 must be occupied in each substance. We have tentatively assigned to them the structure of 5,6- and 4,6-monoacetone galactosedibenzylmercaptal, respectively. By removing the mercaptan residues from one of these compounds in methyl alcoholic solution according to our method which yields glycofuranosides [Pacsu and Green, This Journal, **58,** 1723 (1936)], a crystalline, non-reducing substance has been obtained which still contains the acetone residue. The structure of this key compound is being investigated. If the formation of the diacetone mercaptal in the presence of concd. sulfuric acid will prove to have passed through the monoacetone stage, then neither the sirupy diacetone mercaptal, always used as a starting material, nor any of its sirupy derivatives could represent uniform substances. A detailed account of the revisionary work on these derivatives of galactose as well as glucose and mannose will be published as soon as it has been completed.

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