REACTIONS OF GLYCOSYLAMINES WITH β -DIKETONES AND WITH BENZOYLACETALDEHYDE*

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ABSTRACT

The glycosylamines of the common aldohexoses react with β -diketones and with benzoylacetaldehyde yielding N-glycosyl derivatives of β -amino α,β -unsaturated ketones. The structures of these substances are discussed on the basis of their chemical and spectroscopic properties.

INTRODUCTION

Previous work¹ has shown that glycosylamines react with ethyl acetoacetate to yield ethyl 3-(glycosylamino)crotonates (1). Because the *N*-glycosyl derivatives of β -amino α,β -unsaturated ketones and esters (2) may be of interest as intermediates in the synthesis of nucleosides and related substances, we have investigated their properties and methods of preparation. In this paper, we describe several ketones of the type 2 obtained by reaction of β -diketones and benzoylacetaldehyde with aldosylamines. The reaction of 2,4-pentanedione with glycosylamines has been previously studied², and, under the conditions used, resulted in the formation of (tetrahydroxybutyl)pyrroles (e.g., compound 3), presumably *via* intermediates of



^{*}Presented in part at the 12th Biennial Meeting of the Real Sociedad Española de Física y Química, Salamanca, June 1965; A. Gómez Sánchez, J. Velasco del Pino, and U. Scheidegger, *Anales Real Soc. Españ. Fis. Quím.* (Madrid), 62-B (1966) 487.

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LE 1 YCCONT. DERIVATIVES OF β -AMINO $\alpha_i \beta$ -UNSATURATED KETONES 73-166 AND THEIR O -ACETYL DERIVATIVES 71-166 THE $M_{P_i}^{*}^{*}(Crystallization solvent) [e]_{501}(degrees) Yield (%) Formula Calc. For M_{P_i}^{*}(Crystallization solvent) [e]_{501}(degrees) Yield (%) Formula Calc. For 202-195 (propan-2-01) -100.2 (gryridine) 34 CubH2nO10 57.85 5.7 2.9 58.177-179 (ethanol) -100.2 (gryridine) 34 CubH2nO10 57.85 5.7 2.9 58.177-179$ (ethanol) -103.3 (gryridine) 38 CubH2nO10 57.85 5.7 2.9 57. 177-179 (ethanol) -103.3 (gryridine) 38 CubH2nO10 57.85 5.7 2.9 57. 177-179 (ethanol) -103.6 (gryridine) 38 CubH2nO10 57.85 5.7 2.9 57. 177-179 (ethanol) -103.6 (chanol) 54 CubH2nO10 53.1 6.3 3.5 4.3 55. $124-136$ (ethanol) -150.30 (chanol) 54 CuH12nO10 53.1 6.3 3.5 5.8 5.3 5.8 5.3 1.00-105 (ethanol) -150.30 (chanol) 54 CuH12nO10 58.65 5.95 2.85 5.8 5.3 2.9 5.1 1.44-145 (anbol terachloride) -203.7 (chanol) 54 CuH12nO10 58.65 5.95 2.85 5.8 5.3 2.8 5.3 1.2 1.42-1215 (ethanol-water) -16.0^{0} (ethanol) 54 CuH12nO10 58.65 5.95 2.85 5.95 2.85 5.8 5.3 2.85 5.8 5.3 5.1 2.9 5.1 1.12-1215 (ethanol-water) -16.0^{0} (ethanol) 54 CuH12nO10 58.65 5.95 2.85 5.95 2.85 5.8 5.95 2.85 5.8 5.95 2.85 5.95	LE I	, derivatives of eta -amino $lpha,eta$ -uns	SATURATED KETONES 7a	HL UND BYL-	PIB O.ACETVI. DBDIVA	i	-16h				
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a b $C_{aB}H_{ar}NO_{10}$ ST_{aB}	26	M.p., ° (crystallization solvent)	[\alpha]_{5401} (degrees)	Yield (%)	Formula	Calc.			Found		
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$ \begin{array}{rcrcrc} 175-177 \mbox{ (ethanol-ethyl acetate)} & -100.2 \mbox{ (pridine)} & 34 & C_{16}H_{21}NO_{0} & 59.4 & 6.55 & 4.3 & 59. \\ 177-179 \mbox{ (ethanol)} & - 28.5 \mbox{ (ethanol)} & - 28.5 \mbox{ (ethanol)} & - 28.5 \mbox{ (ethanol)} & - 105.8 \mbox{ (pridine)} & 80 & C_{15}H_{10}NO_{0} & 58.6 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.284 & 5.55 & 4.43 & 5.55 & 5.95 & 5.85 & 5.95 & 2.284 & 5.55 & 5.95 & 2.285 & 5.95 & 2.285 & 5.95 & 2.244 & 5.55 & 4.43 & 5.55 & 5.95 & 5.85 & 5.95 & 2.142 & 1.040 & 1.11 & C_{17}H_{25}NO_{10} & 57.16 & 5.95 & 2.85 & 5.35 & 2.142 & 5.17 & 2.43 & 5.55 & 2.13 & 2.142 & 1.79 & (propan-2-01) & -164.0^{10} (ethanol) & 71 & C_{17}H_{25}NO_{10} & 57.16 & 5.8 & 3.28 & 5.55 & 2.85 & 5.85 & 2.85 & 5.85 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.95 & 2.85 & 5.17 & 2.43 & 5.55 & 2.13 & 2.142 & 1.79 & 1.72 & 4.3 & 5.54 & 1.79 & 1.72 & 4.3 & 5.24 & 1.74 & 1.72 & 4.3 & 5.95 & 1.94 & 1.76 & 1.96 & (propan-2-01) & -7$		192-195 (propan-2-ol)	- 41.6 (chloroform)		C23H27NO10	57.85	5.7	2.9	58.2	5.8	2.7
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		175-177 (ethanol-ethyl acetate)	 – 100.2 (pyridine) 	34	C ₁₆ H ₂₁ NO ₆	59.4	6.55	4.3	59.2	6.4	4.7
$ \begin{array}{rcrcrc} 177-179 \ (ethanol) & - 105.8 \ (pyridine) & 80 & C_{13}H_{10}NO_{0} & 58.2 & 6.2 & 4.5 & 58. \\ 124-126 \ (ether-light petroleum) & 0.0 \ (chloroform) & 44 & C_{23}H_{20}NO_{10} & 57.85 & 5.7 & 2.9 & 57. \\ 195-196 \ (ethanol) & - 179.3 \ (pyridine) & 38 & C_{10}H_{20}NO_{10} & 58.65 & 5.95 & 2.85 & 58. \\ 106-108 \ (ethanol) & - 11.1 \ (chloroform) & 45 & C_{24}H_{20}NO_{10} & 58.65 & 5.95 & 2.85 & 58. \\ 223-225 \ (ethanol) & - 158.0^{b} \ (ethanol) & 5 & C_{11}H_{10}NO_{6} & 59.4 \ 6.55 & 4.3 & 55. \\ 104-105 \ (ethanol-water) & - 16.0^{b} \ (ethanol) & 64 & C_{19}H_{27}NO_{10} & 53.1 \ 6.3 & 3.5 & 55.3 & 53. \\ 104-105 \ (ethanol-water) & - 203.7 \ (ethanol) & 82 & C_{16}H_{10}NO_{6} & 58.2 \ 6.2 & 4.5 & 53. \\ 144-145 \ (carbon \ tetrachloride) & - 32.0 \ (chloroform) & 85 & C_{24}H_{29}NO_{10} & 58.2 \ 6.2 & 4.5 & 53. \\ 144-145 \ (carbon \ tetrachloride) & - 32.0 \ (chloroform) & 85 & C_{24}H_{29}NO_{10} & 58.2 \ 6.2 & 4.5 & 53. \\ 144-145 \ (carbon \ tetrachloride) & - 32.0 \ (chloroform) & 85 & C_{24}H_{29}NO_{10} & 58.65 \ 5.95 \ 2.45 & 5.7 & 2.9 & 57. \\ 144-145 \ (carbon \ tetrachloride) & - 32.0 \ (chloroform) & 75 & C_{24}H_{29}NO_{10} & 58.65 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.95 \ 2.85 \ 5.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.95 \ 2.9$		177–178 (propan-2-ol)	 28.5 (chloroform) 	78	C24H20NO10	58.65	5.95	2.85	58.8	6.0	2.9
$ \begin{array}{rcrcrc} 124-126 \ (ether-light petroleum) & 0.0 \ (chloroform) & 44 & C_{23}H_{27}NO_{10} & 57,85 & 5.7 & 2.9 & 57. \\ 195-196 \ (ethanol) & -179.3 \ (pyridine) & 38 & C_{10}H_{21}NO_{10} & 58.65 & 5.95 & 2.85 & 5.8 \\ 106-108 \ (ether-light petroleum) & -11.1 \ (chloroform) & 45 & C_{24}H_{20}NO_{10} & 58.65 & 5.95 & 2.85 & 5.8 \\ 223-225 \ (ethanol) & -158.0^{b} \ (ethanol) & 5 & C_{10}H_{19}NO_{10} & 58.65 & 5.95 & 2.85 & 5.9 \\ 104-105 \ (ethanol-water) & -16.0^{b} \ (ethanol) & 82 & C_{10}H_{21}NO_{10} & 53.1 \ 6.3 & 3.5 & 5.3 \\ 144-145 \ (carbon tetrachloride) & -32.0 \ (chloroform) & 85 & C_{24}H_{20}NO_{10} & 58.2 & 6.2 & 4.5 & 5.9 \\ 144-145 \ (carbon tetrachloride) & -32.0 \ (chloroform) & 85 & C_{24}H_{20}NO_{10} & 58.8 & 5.7 & 2.9 & 57.1 \\ 144-145 \ (carbon tetrachloride) & -32.0 \ (chloroform) & 85 & C_{24}H_{20}NO_{10} & 58.6 & 5.95 & 2.85 & 5.9 \\ 144-145 \ (carbon tetrachloride) & -32.0 \ (chloroform) & 71 & C_{14}H_{21}NO_{10} & 58.65 & 5.95 & 2.85 & 5.9 \\ 144-145 \ (carbon) & -164.0^{b} \ (ethanol) & 11 & C_{11}H_{19}NO_{5} & 53.8 & 7.8 & 5.7 & 2.9 & 57.1 \\ 180-182 \ (ethanol) & -164.0^{b} \ (ethanol) & 71 & C_{17}H_{25}NO_{8} & 55.0 & 6.8 & 3.8 & 55.1 \\ 188-189 \ (ethanol) & -164.0^{b} \ (ethanol) & 53 & C_{13}H_{21}NO_{5} & 5.36 & 5.95 & 2.85 & 5.8 \\ 178-179 \ (propan-2-0l) & -163.2 \ (carbon & 89 & C_{21}H_{25}NO_{8} & 60.1 & 6.0 & 3.3 & 60. \\ 178-179 \ (propan-2-0l) & -103.2 \ (carbon & 93 & C_{21}H_{25}NO_{8} & 60.1 & 6.0 & 3.3 & 60. \\ 194-196 \ (propan-2-0l) & -78.4 \ (carbon & 93 & C_{21}H_{21}NO_{5} & 6.95 & 6.3 & 3.2 & 60. \\ 194-196 \ (propan-2-0l) & -78.4 \ (carbon & 93 & C_{24}H_{21}NO_{6} & 6.95 & 6.3 & 3.2 & 60. \\ \end{array}$		177-179 (ethanol)	- 105.8 (pyridine)	80	C ₁₅ H ₁₀ NO ₆	58.2	6.2	4.5	58.3	6.2	4.1
$\begin{array}{llllllllllllllllllllllllllllllllllll$		124-126 (ether-light petroleum)) 0.0 (chloroform)	44	C23H27NO10	57.85	5.7	2.9	57.9	5.5	3.0
$ \begin{array}{rcrcrc} 106-108 \ (ether-light petroleum) & - 11.1 \ (chloroform) & 45 \ C_{24}H_{20}NO_{10} & 58.65 & 5.95 & 2.85 & 53. \\ 223-225 \ (ethanol) & - 158.0^{b} \ (ethanol) & 5 \ C_{19}H_{27}NO_{10} & 53.1 & 6.3 & 3.5 & 53. \\ 104-105 \ (ethanol-water) & - 16.0^{b} \ (ethanol) & 64 \ C_{19}H_{27}NO_{10} & 53.1 & 6.3 & 3.5 & 53. \\ 188-190 \ (ethanol-water) & - 203.7 \ (ethanol) & 82 \ C_{26}H_{27}NO_{10} & 53.1 \ 6.3 & 3.5 & 53. \\ 144-145 \ (carbon tetrachloride) & - 32.0 \ (chloroform) & 85 \ C_{26}H_{29}NO_{10} & 57.85 & 5.7 & 2.9 & 57. \\ 144-145 \ (carbon tetrachloride) & - 32.0 \ (chloroform) & 85 \ C_{26}H_{29}NO_{10} & 57.85 & 5.7 & 2.9 & 57. \\ 144-145 \ (carbon tetrachloride) & - 194.2 \ (pyridine) & 9 \ C_{10}H_{21}NO_{6} & 59.4 \ 6.55 \ 4.3 & 55. & 53. \\ 168-169 \ (propan-2-01) & 0.0 \ (chloroform) & 75 \ C_{24}H_{29}NO_{10} & 58.65 & 5.95 \ 2.85 & 5.85 \\ 213-214 \ (methanol) & -164.0^{b} \ (ethanol) & 11 \ C_{17}H_{29}NO_{6} \ 55.6 \ 5.95 \ 2.85 & 5.85 \\ 213-214 \ (methanol) & -164.0^{b} \ (ethanol) & 71 \ C_{17}H_{25}NO_{8} & 55.6 \ 6.8 \ 3.8 \ 5.8$		195-196 (ethanol)	-179.3 (pyridine)	38	C16H21NO6	59.4	6.55	4.3	59.4	6.7	4.3
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		106-108 (ether-light petroleum)) - 11.1 (chloroform)	45	C24H20NO10	58.65	5.95	2.85	58.5	6.0	2.9
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		223-225 (ethanol)	-158.0 ^b (ethanol)	ŝ	C11H19NO6	50.6	7.3	5.4	50.8	7.0	5.2
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		104-105 (ethanof-water)	 16.0^b (ethanol) 	64	C19H27NO10	53.1	6.3	3.5	53.1	6.4	3.7
$ \begin{array}{rclcrcl} 144-145 \ (carbon \ tetrachloride) & -32.0 \ (chloroform) \ 85 & C_{28}H_{27}NO_{10} & 57.85 \ 5.7 & 2.9 & 57. \\ 214-215 \ (ethanol) & -194.2 \ (pyridine) & 9 & C_{16}H_{21}NO_{6} & 59.4 & 6.55 \ 4.3 & 59. \\ 168-169 \ (propan-2-ol) & 0.0 \ (chloroform) \ 75 & C_{24}H_{26}NO_{10} & 58.65 \ 5.95 \ 2.85 & 53. \\ 213-214 \ (methanol) & -164.0^{b} \ (ethanol) & 11 & C_{11}H_{19}NO_{5} & 53.8 \ 7.8 & 5.7 & 54. \\ 213-214 \ (methanol) & -164.0^{b} \ (ethanol) & 71 & C_{17}H_{25}NO_{8} & 55.0 \ 6.8 & 3.8 & 55. \\ 213-214 \ (methanol) & -164.0^{b} \ (ethanol) & 53 & C_{15}H_{10}NO_{5} \ H_{20} & 57.9 \ 6.8 & 3.8 & 55. \\ 180-182 \ (ethanol-water) & -40.0^{b} \ (ethanol) & 53 & C_{15}H_{10}NO_{5} \ H_{20} & 57.9 \ 6.8 & 3.8 & 55. \\ 178-179 \ (propan-2-ol) & -163.2 \ (earbon) & 89 & C_{21}H_{25}NO_{8} \ 60.1 \ 6.0 & 3.3 & 60. \\ 178-179 \ (propan-2-ol) & -140.3 \ (pyridine) & 36 & C_{16}H_{21}NO_{5} \ H_{20} & 59.1 \ 7.2 \ 4.3 & 59. \\ 220-221 \ (ethanol) & -78.4 \ (earbon & 93 & C_{26}H_{21}NO_{5} \ H_{20} & 59.1 \ 7.2 \ 4.3 & 59. \\ 194-196 \ (propan-2-ol) & -78.4 \ (earbon & 93 & C_{26}H_{21}NO_{8} \ 60.95 \ 6.3 \ 3.2 & 60. \\ \end{array}$		188-190 (ethanol-water)	-203.7 (ethanol)	82	C ₁₅ H ₁₉ NO ₆	58.2	6.2	4.5	58.4	6.4	4.35
$\begin{array}{llllllllllllllllllllllllllllllllllll$		144-145 (carbon tetrachloride)	- 32.0 (chloroform)	85	C23H27NO10	57.85	5.7	2.9	57.6	5.9	3.2
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		214-215 (ethanol)	- 194.2 (pyridine)	6	C ₁₆ H ₂₁ NO ₆	59.4	6.55	4.3	59.6	6.7	4.4
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		168-169 (propan-2-ol)	0.0 (chloroform)	75	C24H29NO10	58.65	5.95	2.85	58.5	5.7	3.0
180-182 (ethanol-water) - 40.0 ^b (ethanol) 71 $C_{15}H_{16}NO_{6}$ 55.0 6.8 3.8 55.1 188-189 (ethanol) - - 153.0 (ethanol) 53 $C_{15}H_{16}NO_{6}$ 4.5 58 58 178-179 (propan-2-ol) - 103.2 (carbon 89 $C_{21}H_{25}NO_{8}$ 60.1 6.0 3.3 60. 220-221 (ethanol) - - 140.3 (pyridine) 36 $C_{26}H_{21}NO_{5}$ H_{20}O 59.1 7.2 4.3 59. 194-196 (propan-2-ol) - 78.4 (carbon) 93 C $_{22}H_{27}NO_{8}$ 60.95 6.3 3.2 60.		213-214 (methanol)	-164.0 ^b (ethanol)	11	C11H19N05	53.8	7.8	5.7	54.0	6.7	5.7
188-189 (ethanol) -153.0 (ethanol) 53 $C_{15}H_{16}NO_{5}$. $H_{2}O$ 57.9 6.8 4.5 $58.$ 178-179 (propan-2-ol) -103.2 (carbon 89 $C_{21}H_{25}NO_{8}$ 60.1 6.0 3.3 $60.$ 220-221 (ethanol) -140.3 (pyridine) 36 $C_{26}H_{21}NO_{5}$. $H_{2}O$ 59.1 7.2 4.3 $59.$ 194-196 (propan-2-ol) -78.4 (carbon 93 $C_{22}H_{27}NO_{8}$ 60.95 6.3 3.2 $60.$		180-182 (ethanol-water)	 40.0^b (ethanol) 	71	C17H25NO8	55.0	6.8	3.8	55.3	6.8	3.7
178-179 (propan-2-ol) -103.2 (carbon 89 $C_{21}H_{25}NO_8$ 60.1 6.0 3.3 60. tetrachloride) tetrachloride) tetrachloride) 136 $C_{16}H_{21}NO_5$. H_2O 59.1 7.2 4.3 59.1 220-221 (ethanol) -140.3 (pyridine) 36 $C_{16}H_{21}NO_5$. H_2O 59.1 7.2 4.3 59.1 194-196 (propan-2-ol) -78.4 (carbon 93 $C_{22}H_{27}NO_8$ 60.95 6.3 3.2 $60.$		188-189 (ethanol)	– 153.0 (ethanol)	53	C15H10NO5. H2O	57.9	6.8	4.5	58.15	6.65	4.6
220-221 (ethanol) -140.3 (pyridine) 36 $C_{16}H_{21}NO_5$, H_2O 59.1 7.2 4.3 59. 194-196 (propan-2-ol) -78.4 (carbon 93 $C_{22}H_{27}NO_8$ 60.95 6.3 3.2 60.		178-179 (propan-2-ol)	— 103.2 (carbon tetrachloride)	89	C ₂₁ H ₂₅ NO ₈	60.1	6.0	3.3	60.1	5.8	3.6
194-196 (propan-2-ol) – 78.4 (carbon 93 C22H27NO8 60.95 6.3 3.2 60.		220-221 (cthanol)	-140.3 (pyridine)	36	C16H21NO5. H2O	59.1	7.2	4.3	59.2	7.4	4.3
		194-196 (propan-2-ol)	- 78.4 (carbon	93	C22H27NO8	60.95	6.3	3.2	60.9	6.3	3.2

a Substance obtained as a syrup. $b[\alpha]_D$ value.

structure 2 (R = R' = Me). It is also known³ that 2-amino-2-deoxy-D-glucose reacts with 2,4-pentanedione, 1-phenyl-1,3-butanedione, and benzoylacetaldehyde, yielding derivatives 4-6.

RESULTS AND DISCUSSION

The reactions of the glycosylamines of the common aldohexoses (D-glucose, D-galactose, D-mannose, and L-rhamnose) with β -diketones (2,4-pentanedione, 1-phenyl-1,3-butanedione) and with benzoylacetaldehyde took place in methanol at room temperature yielding N-glycosyl derivatives of β -amino α , β -unsaturated ketones 7a-16a. Reactions with 1-phenyl-1,3-butanedione were better carried out in methanol containing acetic acid, as otherwise the corresponding products were obtained in admixture with other unidentified substances. The physical constants and yields of the products are indicated in Table I. The reactions of β -D-glucopyranosylamine and β -D-galactopyranosylamine with 2,4-pentanedione gave syrups which could neither be crystallized nor converted into crystalline derivatives. The condensate 7a of β -D-glucopyranosylamine and benzoylacetaldehyde was also obtained as a syrup which was easily transformed into a crystalline tetra-O-acetyl derivative 7b. Compound 14a was identical with that obtained directly in the reaction of L-rhamnose with 2,4-pentanedione and ammonia⁴.

Evidence for the structures of these substances is presented in the following discussion of their properties. They gave positive Fehling's and ferric chloride tests,



presumably because of their hydrolysis to the parent β -dicarbonyl compound and sugar. Hydrolysis also took place during the chromatography, on paper, of analytically

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pure samples of the 2,4-pentanedione derivatives 11a and 14a, and of the condensate of 1-phenyl-1,3-butanedione with β -D-glucopyranosylamine (8a), since spots appeared corresponding to the parent glycoses and glycosylamines in addition to those of the condensates (see Table II). Similar observations have been made^{1a} on ethyl 3-(glycosylamino)crotonates (1) and on simpler glycosylamines⁵. Further evidence of the formation of free glycoses and β -dicarbonyl compounds in the hydrolysis of the substances under discussion was obtained for 3-(β -D-glucopyranosylamino)-1-phenyl-2-buten-1-one (8a); treatment of this compound with 0.2N hydrochloric acid gave 1-phenyl-1,3-butanedione and D-glucose (characterized as N-p-nitrophenyl- β -D-glucopyranosylamine). However, the N-glycosyl derivatives of β -amino α,β -unsaturated ketones seemed to be more resistant to hydrolytic cleavage than ethyl 3-(glycosylamino)crotonates; for example, the optical rotation of an aqueous solution of 4-(β -D-mannopyranosylamino)-3-penten-2-one (11a) changed from $+251 \rightarrow +120^{\circ}$ in two months without having reached equilibrium; paper chromatography then showed the presence of D-mannose and unchanged compound 11a. Under the same conditions, ethyl 3-(β -D-mannopyranosylamino)-protonate was completely hydrolyzed in five days.

TABLE II

CHROMATOGRAPHIC MOBILITIES^a OF COMPOUNDS 7a-16a and reference substances

Substance (formula)	R _F			
3-(β -D-Glucopyranosylamino)-1-phenyl-2-buten-1-one (8a)	0.06,	0.12,	0.15,	0.67
β -D-Glucopyranosylamine	0.07,	0.13,	0.16	
D-Glucose			0.16	
3-(β-D-Galactopyranosylamino)-1-phenyl-2-propen-1-one (9a)				0.59
3- $(\beta$ -D-Galactopyranosylamino)-1-phenyl-2-buten-1-one (10a)				0.68
4-(β-D-Mannopyranosylamino)-3-penten-2-one (11a)			0.21,	0.40
3-(β -D-Mannopyranosylamino)-1-phenyl-2-propen-1-one (12a)				0.60
3-(β-D-Mannopyranosylamino)-1-phenyl-2-buten-1-one (13a)				0.66
D-Mannose			0.21	
4-(β-L-Rhamnopyranosylamino)-3-penten-2-one (14a)			0.30	0.60
3-(β-L-Rhamnopyranosylamino)-1-phenyl-2-propen-1-one (15a)				0.73
3-(β-L-Rhamnopyranosylamino)-1-phenyl-2-buten-1-one (16a)				0.73
L-Rhamnose			0.30	

^aOn Whatman No. 1 paper with butyl alcohol-water-ammonia (40:10:49:1, organic phase) as solvent; R_F measured at 20°.

Treatment of compounds 7a-16a with acetic anhydride in pyridine at 0° gave the corresponding acetates 7b-16b. The physical constants of these substances have been included in Table I. Catalytic (sodium methoxide) deacetylation of 1-phenyl-3-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylamino)-2-buten-1-one (8b) regenerated the parent compound 8a; hydrolysis of 8b with dilute formic acid⁶ gave 1-phenyl-1,3butanedione and 2,3,4,6-tetra-O-acetyl-D-glucose.

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The u.v. spectra of compounds **8a-16a** (Table III) were similar to those³ of the 2-amino-2-deoxy-D-glucose derivatives³ **4-6**. The i.r. spectra of compounds **8a-16a** and those of the acetates **7b-16b** (Table III) showed bands at 1640-1600 (ketone C=O), 1585-1575, and 1560-1530 cm⁻¹ typical of intramolecularly bonded β -amino α,β -unsaturated ketones^{3b,c7}. The large shift to low frequencies of the carbonyl band of these compounds is considered to be a consequence of the highly pronounced mesomeric character of the enamino ketone system and of the strong, intramolecular hydrogen bond. For the same reasons, the N-H stretching bands of the acetates were very broad and displaced to low frequencies. It was then concluded that, in the solvents used, compounds **7-16** were completely, or to a large extent, in the chelated form **17**.



The p.m.r. spectra of compounds 7-16 confirmed their structures and gave an indication of their anomeric configurations. Data from the spectra of the acetates of the condensates of benzovlacetaldehyde, namely, compounds 7b, 9b, 12b, and 15b, are indicated in Table IV. The absorptions of the enamine portion of these substances were very similar to those of the intramolecularly bonded *cis* forms of the enamines derived from benzoylacetaldehyde and simple amines⁸ and to that^{3c} of the tetra-Oacetyl derivative of compound 5. The chelated *cis* structures were derived from the positions of the N-H signals at very low field and the magnitude of the vicinal coupling constants, $J_{2',3'}$, between the two olefinic protons. The protons of the sugar moiety of these substances, as well as those of compounds discussed later, were identified by double-resonance experiments and/or by consideration of the chemical shifts and the coupling constants. All of these chemical shifts and coupling constants observed were consistent with the compounds, having pyranose rings. The assignment of the β -D-anomeric configuration was straightforward in the D-glucose and D-galactose derivatives, compounds 7b and 9b, by considering the values of $J_{1,2}$. In the case of the D-mannose and L-rhamnose derivatives (12b) and (15b), respectively, the assignment of the anomeric configuration was tentatively made by comparing the chemical shifts for H-1 with those for the same proton in compounds 7a and 9b having the D-gluco and p-galacto configuration. The paramagnetic shift of 0.20-0.29 p.p.m. observed thereby was ascribed to the deshielding effect produced on an axial H-1 by the change of the acetoxyl group on C-2 from the equatorial to the axial position. Similar paramagnetic shifts have been observed before in acetylated aldopyranoses ^{9a,b} in penta-acetylglycopyranosylamines⁹, and in the O-acetyl derivatives of ethyl 3-(glycosvlamino)crotonates^{1b}. Substances 12b and 15b would then have H-l in an axial position and, therefore, β -D and β -L configurations, respectively.

The p.m.r. spectra of 3-(glycosylamino-1-phenyl-2-propen-1-ones (9a, 12a, and 15a) (Table V) were taken in methyl sulphoxide- d_6 in order to prevent effects due to hydrolysis and/or mutarotation^{1b,10}. Under these conditions, the D-galactose

Substanc	e U.v.a	bsorption ^b	I.r. absor	ption (cm ⁻¹)	
	Amax II	m log e	Phase	0-H and/or N-II	H-N-C=C-C=0
7b			C	3250w,b	1636, 1585, 1559m
8a	245	3.86	Z	3320b	1595bc, 1576, 1538b
8b			ũ	3200vw,b	1620, 1587, 1559
9a	747	3.84	Z	3550, 3280b, 3198b	1622, 1580, 1530
9b			ರ	3240vw,b	1638, 1585, 1559m
10a	244	3.88	Z	3401, 3172b	1600bc, 1580, 1532
10b			ŭ	3200w,b	1618, 1583, 1556
Ila	303	4.28	z	3448m,b, 3133m	1613, 1547b
11b			с С	3200w,b	1629, 1590, 1502m
12a	248	3.83	z	3540m, 3430, 3305b, 3250b	1630b, 1578, 1543b
12b			ರ	3250vw,b	1639b, 1588, 1560m
13a	244	3.84	Z	3350b, 3281b	1600b°, 1574, 1525b
13b			c	3180w,b	1619, 1583, 1559b
14a	303	4.37	z	3440b, 3180m	1614, 1550, 1530m
14b			с С	3185w,b	1623, 1577, 1502m
15a	248	3.85	Z	3350b, 3274b, 3180b	1632, 1580, 1532b
15b			ರ	3240vw,b	1636, 1584, 1556
1 6a	244	3.84	Z	3344b, 3170b	1601b°, 1576, 1533b
16b			cſ	3090vw,b	1608b, 1584, 1558m

benzene ring.

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TABLE III

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CHEMICAL	shifts (ô, p.I	p.m.) AND C	ONITANO	CONSTANTS (Hz) for <i>O</i>	АСЕТУЬ DER	UVATIVES OF	COMPOUND		.−c ₆ H ₅ AT I	00 MHz IN	CHLOROF	orm-d
Substance	H-N	H-2'	H-3′	Aromatic protons	I-H	Н-2	Н-3	Н-4	H-5	9-H	,9-Н	OAC	
J b	10.23q ^a Ј _{NH,} 3' 12.0 Ј _{NH,1} 9.1	5.87d J _{2',3'} 8.2	6.91q	∼7.4m ^b ~7.85m ^c	4.50t J _{1,2} 9.0	4.90)-5.40in		3.76m J _{4,5} 9.5 J _{5,6} 4.5	4.24q J _{6,6} , - 12.	4.10q .4	2.014	2.06
de	10.31q J _{NH,3} ' 12.0	5.89d J _{2',3'} 8.0	6.92q	\sim 7.4m ^b \sim 7.88m ^c	4.46t J _{1,2} 9.0	5.34q J _{2,3} 10.3	5.10q J _{3,4} 3.2	5.43 $J_{4,5} \simeq 1$	J _{5,6} , 2.5 3.90	-4.15m		1.98, 2.02°,	2.01 2.16
12b	JNH,1 9.0 10.43q JNH,8' 12.0	5.85d J _{2',3'} 8.0	6.92q	∼7.4m ^b ~7.85m°	4.75q J _{1,2} 1.6	5.49q J _{2,3} 3.2	5.10q J _{3,4} 10.0	5.25t J _{4,5} 9.0	3.72m J _{5,6} 5.3	4.26q J _{6,0} , -12	4.12q	1.99, 2.07,	2.04 2.34
15b	JNH,1 2.0 10.42q JNH,3' 11.8 JNH,1 9.3	5.83d <i>J</i> 2',8' 8.0	6.93q	∼7.4m ^b ∼7.85m ^c	4.70q J _{1,2} 1.5	5.47t J _{2,3} 2.5			J _{5,6} , 3.0 3.58m J _{5,6} 6.2		1.25d	2.33	2.05
^a Signal m was obser	ultiplicities al ved. ^b Comple:	re indicated x signal of it	as follov ntensity th	ving: d, dout hree. ^c Compl	blet; t, trip lex signal o	det; q, quar f intensity tv	tet; and m, vo. ^d Signal c	multiplet. ' of intensity	The absence nine. ^e Inten	of any ind sity six. / Si	lication imp gnal due to e	lies that C-5 meth	a sir yl gr

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ubstance	<i>N-H</i> cis	trans	<i>H-2'</i> cis	tranș	H.3' cis	trans	Aromatic protons	I-H	cis-trans ratio
et	10.29q ^a	ą	5.85d	6.14d	1.27գ	٩	<i>~</i> 7.47m ^e	4.31t	2:1
	JNH, 3' 12.5		J _{2',3'} 8.0	J ₂ r _{,3} , 12,4			∼7.85m ^d	J _{1,2} 8.0	
2a	10.37q	ą	5.82d	6.21d	7.24q	ą	~7.47m°	4.67a	4:1
	J _{NH,3} , 12.6		J _{2',3'} 8.0	J ₂ , ₃ , 11.6	ı		∼7.85m ^d	$J_{1,2} \simeq 1.0$	
Sa	JNH,1 7.4 10.37q		5.82		7.21q		~7.45m°	4.63q	
	J _{NH,3} , 13.0 J _{NH,1} 9.5		J _{2',3'} 8.0		ı		∼7.85m ^d	J1,2 س1.0	

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TABLE V

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and D-mannose derivatives, (9a) and (12a), existed as a mixture of the cis form (type 17) and the corresponding trans form (18 and 19, respectively). The existence of the two isomeric forms of the 3-(B-D-galactopyranosylamino)-1-phenyl-2-propen-1-one (9a) was deduced from the presence in the spectrum (Table V) of the two doublets at δ 5.85 (J_{2',3'} 8.0 Hz) and δ 6.14 (J_{2',3'} 12.4 Hz) which, based on the coupling constants, were assigned to H-2' of the cis and trans forms, respectively. The quartet at δ 7.27 ($\cdot_{\text{NH},3'}$ 12.5 Hz; $J_{2',3'}$ 8.0 Hz) was assigned to H-3' of the cis form; the corresponding signal of the trans form was not observed and must be hidden under the multiplet of the aromatic protons (δ 7.4–8.0). The quartet centered at & 10.29 (J_{NH,3}, 12.5 Hz; J_{NH,1} 8.5 Hz) was ascribed to the N-H of the cis form, and the triplet $(J_{\text{NH},1} 8.5 \text{ Hz}; J_{1,2} 8.0 \text{ Hz})$ at $\delta 4.31$ to H-1. These assignments were confirmed by irradiation of the N-H quartet, causing the collapse of the H-1 and cis H-3' signals. Furthermore, treatment of the sample with deuterium oxide changed the cis H-3' quartet into a doublet $(J_{2',3})$ and the H-1 triplet into a doublet $(J_{1,2})$. The cis-trans ratio (2:1) for compound 9a was obtained from the integral values of the H-2' doublets, and the magnitude of $J_{1,2}$ proved the β -D-anomeric configuration. Similar observations were made in the spectrum of 3-(β -D-mannopyranosylamino)-1-phenyl-2-propen-1-one (12a) (Table V) which was a mixture of the cis and trans forms in the approximate ratio of 4:1. A different picture, however, was shown by the p.m.r. spectrum of the L-rhamnose analogue (15a) which, under the conditions observed, existed in the cis form only. The anomeric configurations of the two last compounds were tentatively assigned by considering again the δ -values of the H-1 protons; they showed paramagnetic shifts of approximately 0.35 p.p.m. relative to H-1 in the D-galactose derivative 9b. This paramagnetic effect is of the same order of magnitude as that produced on an axial H-1 of glycopyranoses by changing the hydroxyl group on C-2 from an equatorial to an axial disposition^{9a, 11}. Consequently, H-1 in compounds 12a and 15a should be axial, and have the β -D- and β -L-anomeric configurations, respectively. Assignments on the same basis have been previously made^{1b} in ethyl 3-(glycosylamino)crotonates.

Data of the p.m.r. spectra of the condensates of 1-phenyl-1,3-butanedione and those of their corresponding O-acetyl derivatives are presented in Tables VI and VII. The chelated structures (17) of these substances were deduced from the presence of the N-H signals at very low fields and from the similarity of these spectra with those of the intramolecularly bonded forms of enamines obtained in the reactions of 1-phenyl-1,3-butanedione with simple amines¹² and with 2-amino-2-deoxy-Dglucose^{3c}. The value for $J_{1,2}$ proved the β -D-anomeric configuration in the derivatives of D-glucose (compounds 8a and 8b) and D-galactose (compounds 10a and 10b). The H-1 protons in the condensates of D-mannosylamine and L-rhamnosylamine (13a and 16a, respectively) showed paramagnetic shifts of approximately 0.30 p.p.m. relative to H-1 in compound 8a having the D-gluco configuration; similarly, the H-1 signals in the corresponding O-acetyl derivatives (13b and 16b) were shifted approximately 0.15 p.p.m. to lower field compared to compound 8b having the D-gluco configuration. These paramagnetic shifts are those expected^{1b,9,11} for an A. GÓMEZ SÁNCHEZ, M. TENA ALDAVE, J. VELASCO DEL PINO, U. SCHEIDEGGER

axial disposition of H-1 in all of these compounds. Therefore, the derivatives of D-mannose (13a and 13b) were tentatively assigned the β -D-anomeric configuration and those of L-rhamnose (16a and 16b) the β -L-anomeric configuration.

TABLE VI				M	や ア
CHEMICAL SHIF 100 MHz in m	TS (δ, p.y.m.) AN ETHYL SULPHOXID	D COUPLING CO E-d ₆	onstants (Hz) of	COMPOUNDS G-	T Ph AT
Substance	. N-H	H-2′	Me-3'	Aromatic protons	H-1
8a	11.27da J _{NH,1} 8.2	5.84	2.18	~7.44m ^b ~7.84m ^c	4.62t J _{1.2} 8.0
10a	11.28d J _{NH.1} 8.5	5.84	2.13	~7.43m ^b ~7.85m ^c	4.56t J _{1.2} 7.4
13a	11.34d J _{NH.1} 9.0	5.82	2.16	~7.41m ^b ~7.82m ^c	4.90q $J_{1,2} \sim 1.0$
16a	11.27d J _{NH,1} 9.0	5.81	2.13	\sim 7.42m ^b \sim 7.82m ^c	4.87q $J_{1,2} \sim 1.0$

^aSignal multiplicities are indicated as following: d, doublet; t, triplet; q, quartet; and m, multiplet. The absence of any indication implies that a singlet was observed. ^bComplex signal of intensity three. ^cComplex signal of intensity two.

The reaction between a primary amine and an unsymmetrical β -dicarbonyl compound can, in principle, give rise to two isomeric enamines. Thus, the condensates of glycosylamines with benzoylacetaldehyde might have structure 20 instead of the structure of type 22 considered above. The former possibility, however, can be

Ph	0	R	0
1	11]	[]
G-NH-C=C	CH-C-R	G-NH-C=CH	-C-Ph
20 R = H	21 R = Me	22 $R = 2$	H

ruled out purely on the basis of the p.m.r. spectra already discussed (Tables IV and V). They clearly indicate the formation of di-substituted olefins rather than of α,β -unsaturated aldehydes. This is further confirmed by the similarity of these spectra with those corresponding to the condensates of benzoylacetaldehyde with primary amines⁸ and with 2-amino-2-deoxy-D-glucose^{3c}. It has been well established that these substances react with the carbonyl group of benzoylacetaldehyde and of 1-phenyl-1,3-butanedione which is further away from the phenyl group. Similar arguments precluded structure **21** for the condensation products of glycosylamines and 1-phenyl-1,3-butanedione.

The p.m.r. spectra of the enamine portion of the 2,4-pentanedione derivatives 11a, 11b, and 14b (Table VIII) were very similar to those of the chelated form of

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Substanı	ce N-H	H-2'	:C-Me	Aromatic protons	I-H	Н-2	Н-3	H-4	H-5	9-H	,9-H	оус
88	11.19da JNR,18.3	5.82	2.12	~7.40m ^b ~7.85m ^c	4.87t J _{1,2} 8.5	\$	i.05-5.30m		3.75m J _{5,6} 4.8	4.22q J _{6,6} ' -	4.10 -12.4	2.02 2.064
10b	11.24d	5.81	2.12	~7.40m ^b	4.82t	5.39t	5.10g	5.41q	J _{5,6} ′ 3.0 3.3	85-4.15m		1.98, 2.01
(3h	JNB,19,0 11,47d JNB,19,4	5.77	2.11	~/.80m ^c ~7.40m ^b ~7.80m ^c	J1,2 8.8 5.04q J1,2 1.5	J2,3 9.5 5.51q J2,3 3.0	J _{3,4} 3.0 5.11a J _{3,4} 10.0	J4,5~1 5.23t J4,5 9.5	3.72m J _{5,6} 5.5	4.24q J _{6,6} '	4.11 q 12.4	2.00, 2.04 2.06, 2.41 2.06, 2.41
(6b	11.47d J _{NH,1} 9.5	5.75	2.11	∼7.40m ^b ~7.85m ^c	5.00q J _{1,2} 1.5	5.48m			J _{5,6} , 3.0 3.58m J _{5,6} 6.2		1.25d ^J	1.99, 2.04 2.40

Ь 5 b C-5 methyl group.

TABLE VI CHEMICAL SI	ll IIFTS (Ô, p.p.m.) AND COU	JPLING CONST	ANTS (Hz) of compounds and the second	-Me AT 10() MHz				
Substance	Solvent	H-N	Н-2'	Me-1', Me-3', and OAc	I-H	Н-2	H-5	9-H	н-б'	
11 a	Methyl sulphoxide-da	11,69da JNH,1 9.1	5.01	1.88, 1.97	4.75q J₁₂~1.0					
11b	Chloroform-d	10.91d <i>J</i> ин,1 9.5	5.12	2.0 ⁶ , 2.02, 2.05, 2.08, 2.35	4.95q J _{1,2} 1.5	5.46q J _{2,3} 3.2	3.70m J _{5,6} 5.5	4.11q J _{6,6} ′ -	4.24q - 12.0	
14b	Chloroform- <i>d</i>	10.86d J _{NH,1} 9.5	5.10	2.04°, 1.99, 2.04°, 2.32	4.92q J _{1,2} 1.5	5.43m	J _{5,0} 6.0	1.25d ^d		
^a Signal mul	tiplicities are indicated	as following	: d, doub	let; q, quartet; and m, mul	ltiplet. The	absence of	any indica	tion implie	s that a singlet	was

ور با	iplet. The absence of any indication implies that a singlet v 4, twelve. ${}^{d}C$ -5 methyl signal.	
	"Signal multiplicities are indicated as following: d, observed. ^b Signal of intensity six. σ Total intensity of	

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4-(alkylamino)-3-penten-2-one^{8,12} and to that^{3c} of the tetra-O-acetyl derivative of compound 4. On the other hand, H-1 in compound 11a had almost the same δ -value as ethyl 3-(β -D-mannopyranosylamino)crotonate^{1b}; similarly, H-1 of the O-acetyl derivatives 11b and 14b had the same δ -values as the O-acetyl derivatives of ethyl 3-(β -D-mannopyranosylamino)crotonate and ethyl 3-(β -L-rhamnopyranosylamino)crotonate^{1b}. Compounds 11a, 11b, and 14b were therefore formulated with the chelate structure 17 (R = R' = Me) and, tentatively, with the β -D- or β -L-anomeric configurations.

The above results and those previously reported^{1,3} lead to the conclusion that the reaction of β -dicarbonyl compounds and primary amines is extensible to amino sugars (glycosylamines and 2-amino-2-deoxy-D-glucose). The N-glycosyl derivatives of β -amino α,β -unsaturated ketones and esters produced in these reactions tend to adopt the chelate structure 17 which requires that the amino and keto (or ester) groups are in *cis* disposition. Furthermore, the compounds of this kind having the D-gluco, D-galacto, and D-manno configurations are obtained as β -D anomers, and those having the L-*rhamno* configurations as β -L anomers.

EXPERIMENTAL

Melting points are uncorrected. Solutions were evaporated below 40°. Identification of compounds was based on mixed melting points and comparison of i.r. spectra. Paper chromatography was performed on Whatman No. 1 paper, with butyl alcohol-ethanol-water-ammonia (40:10:49:1, organic phase) as the developer and indication with alkaline silver nitrate. Optical rotations at 5461Å were determined with a Bendix-Ericsson Type 143C polarimeter. The u.v. spectra were obtained on a Beckman DU spectrophotometer, and i.r. spectra on a Perkin-Elmer 621 instrument. The p.m.r. spectra were measured on a Varian HA-100 spectrometer, with tetramethylsilane ($\delta = 0$) as the internal standard. The glycosylamines were prepared as described previously^{1a}. Fnysical constants, crystallization solvents, yields, and analytical data of new compounds are indicated in Table I.

Reactions of aldosylamines with benzoylacetaldehyde. — A suspension of 0.01 mole of glycosylamine in methanol (40 ml) containing 0.01 mole of benzoylacetaldehyde was shaken at room temperature until complete dissolution occurred (1-14 h). Evaporation of the solvent left a crystalline residue which, after recrystallization from the appropriate solvent, gave pure 3-(glycosylamino)-1-phenyl-2-propen-1-one (9a, 12a, and 15a). The derivative 7a from β -D-glycopyranosylamine was obtained as a syrup that could not be crystallized.

Reactions of aldosylamines with 1-phenyl-1,3-butanedione. — A suspension of 0.01 mole of glycosylamine in methanol (40 ml) containing acetic acid (2 ml) and 0.01 mole of 1-phenyl-1,3-butanedione was shaken at room temperature till dissolution (1-18 h). The crystalline residue left after evaporation of the solvent was recrystallized from the appropriate solvent, yielding 3-(glycosylamino)-1-phenyl-2-buten-1-one (3a, 10a, 13a, and 16a).

Reactions of aldosylamines with 2,4-pentanedione. — A suspension of 0.01 mole of D-mannosylamine or L-rhamnosylamine in methanol (20 ml) containing 0.03 mole of 2,4-pentanedione was shaken at room temperature until dissolution. Evaporation of the solvent left a syrup which crystallized upon treatment with ether and then with warm methanol. Several recrystallizations from methanol or ethanol gave the pure product 11a or 14a. The reactions with β -D-glucopyranosylamine and β -Dgalactopyranosylamine gave syrups that could not be crystallized.

Acetylation of compounds 7a-16a. — A solution or suspension of the sample (1.0 g) in pyridine (10 m) was treated with acetic anhydride (5 m) for 24-48 h at 0° with occasional shaking. The mixture was poured onto ice, and the material that separated was washed thoroughly with water. In most cases, crystalline substances were obtained at this stage and were readily recrystallized in the solvents indicated in Table I. When the product remained syrupy, it was dissolved in chloroform. The solution was washed successively with 0.2N sulphuric acid, saturated, aqueous sodium carbonate, and water, and was then dried (MgSO₄). The residue obtained after evaporation was crystallized from the appropriate solvent.

Hydrolysis of 3-(β -D-glucopyranosylamino)-1-phenyl-2-buten-1-one (8a). — A solution of compound 8a (1.0 g) in 0.2N hydrochloric acid (50 ml) was kept for 24 h at room temperature. The crystalline solid that separated was filtered off and, after recrystallization from propan-2-ol, identified as 1-phenyl-1,3-butanedione (0.47 g, 94%). Paper chromatography of the filtrate showed the presence of substances having the same mobilities as di-D-glucosylamine, D-glucosylamine, and D-glucose (main product). Evaporation of this solution gave a syrupy residue. A portion (0.3 g) of this syrup was treated with *p*-nitroaniline (0.5 g) and conc. hydrochloric acid (0.02 ml) in boiling methanol (20 ml). Refrigeration of the reaction mixture gave N-*p*-nitrophenyl- β -D-glucopyranosylamine dihydrate (0.2 g), m.p. 187–189°, identical with an authentic specimen.

Deacetylation of 1-phenyl-3-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylamino)-2-buten-1-one (8b). — A sample (1.0 g) of compound 8b was deacetylated by treatment with methanol (10 ml) and 1 ml of a 0.2M solution of sodium methoxide in methanol for 3 h at room temperature. Evaporation of solvent gave a crystalline residue (0.7 g) which, after recrystallization from ethanol-ethyl acetate, gave pure 3-(β -D-glucopyranosylamino)-1-phenyl-2-buten-1-one (8a).

Hydrolysis of 1-phenyl-3-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylamino)-2buten-1-one (**8b**). — A solution of compound **8b** (1.0 g) in a mixture of 1% formic acid (50 ml) and ethanol (15 ml) was boiled for 7 h. The solid that separated was filtered off, recrystallized from propan-2-ol, and identified as 1-phenyl-1,3-butanedione (0.2 g, 40%). The filtrate was concentrated, and extracted with chloroform (4×5 ml). The combined extracts were washed successively with 0.2N hydrochloric acid, 5% aqueous sodium hydrogen carbonate, 2% aqueous sodium bisulphite, and water (10 ml of each), and dried (CaCl₂). The solvent was removed, and the residual syrup was crystallized from chloroform-light petroleum, yielding 2,3,4,6-tetra-O-acetyl-Dglucose (0.16 g), m.p. 121–122°, identical with an authentic specimen.

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