Note

Synthesis of 1-thio-β-D-glycopyranosides

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Homologous series of *n*-alkyl β-D-xylopyranosides and the corresponding 1-thio derivatives were used in a systematic study of β-D-xylosidase specificity[1]. A specific method for the preparation of 1-thio-β-D-glycosides was introduced by Černý and his co-workers[2] who described the synthesis of methyl and ethyl 1-thio-β-D-xylopyranoside[3]. By the same method, we have prepared the four next homologues of the series, together with 2,4-dinitrophenyl 1-thio-β-D-xylopyranoside and the *p*-nitrobenzyl 1-thioglycosides of D-xylose, D-glucose, and D-galactose (Tables I and II).

In contrast to other 1-thioxylosides, 2,4-dinitrophenyl 1-thio-β-D-xylopyranoside is hydrolysed by a fungal β-D-xylosidase[1].

Catalytic hydrogenation[4] of the nitrobenzyl 1-thioglycosides yielded the corresponding amino derivatives. These thioglycosides, carrying a reactive amino-group in the aglycon, are suitable compounds for covalent attachment to insoluble carriers such as agarose beads. These derivatives are currently used for affinity chromatography of enzymes and other biologically active proteins[5,6].

EXPERIMENTAL

The acetylated *n*-alkyl 1-thio-β-D-xylopyranosides were obtained by reaction[2] of the *n*-alkyl iodides with 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranose. The 2,4-dinitrophenyl derivative was prepared from the same thiol and 1-chloro-2,4-dinitrobenzene. The *p*-nitrobenzyl derivatives were obtained by reaction of *p*-nitrobenzyl bromide with the corresponding thiols. Reduction of the deacetylated nitro derivatives to the amino compounds was performed with hydrogen under atmospheric pressure[4] with platinum as catalyst. The acetates were crystallized from methanol. The deacetylated[7] *n*-alkyl 1-thioxylosides were crystallized from acetone, the dinitrophenyl derivative from water–acetone, and the other glycosides from methanol.

The melting points were determined with a Mettler FP 2 instrument and are uncorrected. The optical rotations were measured on 0.5% solutions in chloroform or methanol with a Perkin–Elmer model 141 photoelectric polarimeter. The purity of the products was tested by t.l.c. on Silica Gel G (Merck) with acetic acid–water–ethyl acetate (1:1:3) for the glycosides, and ethyl acetate–benzene (3:7) for the acetates. Detection was effected with 5% sulphuric acid in ethanol (10 min at 120°).

TABLE I

ACETYLATED 1-THIO-β-D-GLYCOPYRANOSIDES

Glycoside	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_{5890}^{22}$ (*degrees*)	*Found* (%)		*Formula*	*Calc.* (%)	
				C	*H*		*C*	*H*
Xylosides								
n-Propyl	70	96–97	−71.2	50.2	6.6	$C_{14}H_{22}O_7S$	50.3	6.6
n-Butyl	75	68–70	−86.3	51.7	7.0	$C_{15}H_{24}O_7S$	51.7	7.0
n-Pentyl	81	39–40	−80.0	53.0	7.1	$C_{16}H_{26}O_7S$	53.0	7.2
n-Hexyl	72	syrup				$C_{17}H_{28}O_7S$	54.2	7.4
p-Nitrobenzyl	78	88–90	−88.9	50.5	4.9	$C_{18}H_{21}NO_9S$	50.6	4.9
2,4-Dinitrophenyl	83	157–158	−196.5	45.5	4.3	$C_{17}H_{18}N_2O_{11}S$	45.8	3.9
Glucoside								
p-Nitrobenzyl	50	99–100	−101.5	50.5	5.1	$C_{21}H_{25}NO_{11}S$	50.5	5.0
Galactoside								
p-Nitrobenzyl	62	94–95	−87.6	50.5	5.1	$C_{21}H_{25}NO_{11}S$	50.5	5.0

TABLE II

1-THIO-β-D-GLYCOPYRANOSIDES

Glycoside	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_{5890}^{22}$ (*degrees*)	*Found* (%)		*Formula*	*Calc.* (%)	
				C	*H*		*C*	*H*
Xylosides								
n-Propyl	70	106–107	−73.0	46.0	7.7	$C_8H_{16}O_4S$	46.1	7.7
n-Butyl	56	109–110	−84.5	48.6	8.1	$C_9H_{18}O_4S$	48.6	8.1
n-Pentyl	41	114–115	−78.5	50.9	8.6	$C_{10}H_{20}O_4S$	50.9	8.5
n-Hexyl	50	158–160	−76.6	52.7	8.7	$C_{11}H_{22}O_4S$	52.8	8.8
p-Nitrobenzyl	80	193–194	−143.3	47.7	5.0	$C_{12}H_{15}NO_6S$	47.8	5.0
p-Aminobenzyl	74	169–171	−187.7	53.1	6.3	$C_{12}H_{17}NO_4S$	53.0	6.3
2,4-Dinitrophenyl	77	213–215	−211.5	39.9	3.7	$C_{11}H_{12}N_2O_8S$	39.8	3.6
Glucosides								
p-Nitrobenzyl	72	162–163	−178.0	47.1	5.5	$C_{13}H_{17}NO_7S$	47.1	5.2
p-Aminobenzyl	71	149–151	−169.5	52.1	6.2	$C_{13}H_{19}NO_5S$	51.7	6.3
Galactosides								
p-Nitrobenzyl	75	183–185	−154.5	47.1	5.2	$C_{13}H_{17}NO_7S$	47.1	5.2
p-Aminobenzyl	60	211–215	−146.0	49.8	6.2	$C_{13}H_{19}NO_5S$	51.7	6.3

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REFERENCES

1 H. KERSTERS-HILDERSON, M. CLAEYSSENS, F. G. LOONTIENS, A. KRYNSKI, AND C. K. DE BRUYNE, *Eur. J. Biochem.*, 127 (1970) 403.
2 M. ČERNÝ AND J. PACÁK, *Collection Czech. Chem. Commun.*, 24 (1959) 2566.
3 J. STANĚK, M. SINDLEROVA, AND M. ČERNÝ, *Collection Czech. Chem. Commun.*, 30 (1965) 297.
4 A. I. VOGEL, *A Textbook of Practical Organic Chemistry*, Longmans Green, London, 3rd edn., 1957, p. 471.
5 P. CUATRECASAS, M. WILCHEK AND C. B. ANFINSEN, *Proc. Nat. Acad. Sci. U.S.*, 61 (1968) 636.
6 M. CLAEYSSENS, H. KERSTERS-HILDERSON, J. P. VAN WAUWE, AND C. K. DE BRUYNE, *FEBS Lett.*, 11 (1970) 336.
7 A. THOMPSON AND M. L. WOLFROM, *Methods Carbohyd. Chem.*, 2 (1963) 215.