Note

Synthesis of para-substituted phenyl 1-thio- β -D-galactopyranosides

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In Table I, a series of para-substituted phenyl tetra-O-acetyl-1-thio- β -D-galactopyranosides are described. They were obtained by a modified Michael^{1,2} condensation (method 1), or by the method of Černý *et al.*³ (method 2). Method 2 (reaction of tetra-O-acetyl-1-thio- β -D-galactopyranose with the appropriate diazonium salts) was originally developed for the synthesis of phenyl 1-thio- β -D-glucosides, but is also applicable to galactosides. The arenethiols were commercial products, except for the *p*-acetylbenzenethiol which was synthesized according to Riesz and Frankfurther⁴. Catalytic deacetylation⁵ (sodium methoxide) of the galactoside acetates yielded the corresponding phenyl 1-thio- β -D-galactopyranosides (Table II).

EXPERIMENTAL

Method 1. — A solution of freshly distilled arenethiol (33 mmoles) and tetra-O-acetyl- α -D-galactopyranosyl bromide⁶ (30 mmoles) in acetone (60 ml) was mixed with a solution of potassium hydroxide (30 mmoles) in water (15 ml). The reaction mixture was kept for 24 h at room temperature and then evaporated *in vacuo*. A solution of the residue in chloroform was thoroughly washed with cold 5% aqueous sodium hydroxide and water, dried (Na₂SO₄), and evaporated *in vacuo*. The resulting syrup was then crystallized from the appropriate solvent. The melting points were determined with a Mettler FP2 instrument and are uncorrected. The optical rotations were measured on 0.5% solutions in chloroform (acetates) or methanol (galactosides) with a Perkin–Elmer Model 141 photoelectric polarimeter. The purity of the products was tested by t.l.c. on Silica Gel G (Merck) in acetic acid–water–ethyl acetate (1:1:3) for the galactosides, and ethyl acetate–benzene (3:7) for the acetates. Detection was effected with 5% sulphuric acid in ethanol (10 min at 120°).

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Substituent	Method	Yield (%)	M.p. (degrees)	Solvent ^a	[\alpha]_{58.90} [domeon]	Found	(%)	Formula	Calc. ((%)
		. .			(cool gon)	υ	H		0	Н
None	-	13								
n-Bromo		÷ 8	7/-1/	¥ '	+3.0	54.5	5.5	C20H24O9S	54.4	5.5
p-Chloro		60	C21-421	B	+1.4	46.3	4.8	C20H23BrO9S	46.3	4.5
p-Mathul		:	syrup	1	I	I	I	C ₂₀ H ₂₃ ClO ₀ S	50.6	4.9
P-MUCUIYI P-fore_Riteri	4 -	3	113-115	×.	+4.4	55.3	5.7	C21H2609S	55.5	5.8
p-tert-bury p-Methown		01	C/-E/	7	+4,9	57.8	6,6	C ₂₄ H ₃₂ O ₉ S	58.0	6.6
p-muciluxy n-Nitro		8	syrup	1.	I	l	I	C21H26O10S	53.6	5.6
p-Aretul		3	cc1-4c1	¥	- 94.6	49.4	4.8	C20H23NO11S	49.4	4.8
P-1100191	-	I	syrup	I	l	I	1	C22II26O10S	54.8	5.4
^a Crystallisation	Is from A met	hanol B li	aht nateoloum	other h. O.C						

1-THIO-B-D-GALACTOPYRANOSIDES	
PHENYL	
ACETYLATED	

TABLE I

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"Crystallisations from A, methanol; B, light petroleum-ether. ^b 0.5 (methanol).

Substituent	Yield	M.p.	Solvent ^a	[\alpha]_{58.9.0}^{23}	Found	(%)	Formula	Calc. ((%)	-
	(%)	(degrees)		(degrees)	ט	H		U	Н	
None	64	94-95	¥	-53.4	52.3	6.1	C1.3H1,04S	52.9	5.9	
<i>p</i> -Bromo	36	168-169	V	-47.2	41.0	4.3	CI,H, BrO,S	41.0	4.3	
p-Chloro	33	159160	۲	-50.4	46.9	4.9	C.,H, CIO.S	46.9	4.9	
p-Methyl	61	139-140	с С	-50.0	54.5	6.4	C13H180.S	54,4	6.3	
p-tert-Butyl	60	76–78	с С	56.0 ^b	57.9	7.4	C16H24O5S	58.5	7.4	
p-Methoxy	15	139-141	B	-36.4	51.5	6.0	C ₁₃ H ₁₀ O ₅ S	51.6	6.0	
p-Nitro	83	168-170	¥	- 108.5	45.5	4.8	C,,H,,NO,S	45.4	4.8	
<i>p</i> -Acetyl	12	212-213	D	92.1 ^b	53.1	5.9	C14H1806S	53.5	5.8	
"Crystallisation	IS ITOM A,	methanol; B, a	icetone; C, bu	tanone; D, wate	er. "c 0.5 (water).				

TABLE II phenyl 1-th10-\$-d-dalactopyranosides