Note

Synthesis of substituted phenyl β-D-galactopyranosides

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(Received September 21st, 1970; accepted for publication, October 20th, 1970)

In Table I, a series of tetra-*O*-acetyl-β-D-galactopyranosides of substituted phenols are described. They were obtained by the reaction of tetra-*O*-acetyl-α-D-galactopyranosyl bromide[1] or penta-*O*-acetyl-β-D-galactose[2] with the appropriate phenol. Deacetylation with sodium methoxide[3] yielded the corresponding β-D-galactopyranosides (Table II).

EXPERIMENTAL

Method 1, Koenigs–Knorr[4,5] synthesis in the presence of yellow mercuric oxide and mercuric bromide. Method 2, modified Michael[6,8] synthesis. Method 3, Helferich[7,8] melt with toluene-*p*-sulphonic acid. In each case, the acetate was crystallized from methanol or methanol–water. 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) 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°).

ACKNOWLEDGMENT

We thank Prof. Dr. L. Massart for his interest in the work, and Miss J. De Lat for performing the microanalyses.

REFERENCES

1 A. THOMPSON AND M. L. WOLFROM, *Methods Carbohyd. Chem.*, 2 (1963) 221.
2 A. I. VOGEL, *A Textbook of Practical Organic Chemistry*, Longmans, Green and Co., London, 3rd edn., 1957, p. 452.
3 A. THOMPSON AND M. L. WOLFROM, *Methods Carbohyd. Chem.*, 2 (1963) 215.
4 W. KOENIGS AND E. KNORR, *Ber.*, 34 (1901) 957.
5 L. R. SCHROEDER AND J. W. GREEN, *J. Chem. Soc., C*, (1966) 530
6 F. G. LOONTIENS AND C. K. DE BRUYNE, *Naturwissenschaften*, 51 (1964) 359.
7 B. HELFERICH AND E. SCHMITZ-HILLEBRECHT, *Ber.*, 66 (1933) 378.
8 C. K. DE BRUYNE AND F. VAN WIJNENDAELE, *Carbohyd. Res.*, 4 (1967) 102.

TABLE I

ACETYLATED PHENYL β-D-GALACTOPYRANOSIDES

Substituent	*Method*	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_{5890}^{22}$ (*degrees*)	$[\alpha]_{4360}^{22}$ (*degrees*)	*Found* (%)		*Formula*	*Calc.* (%)	
						C	*H*		*C*	*H*
m-Chloro	3	42	70–71	0	−8.3	52.3	5.0	$C_{20}H_{23}ClO_{10}$	52.3	5.0
o-Chloro	2	20	137–138	−28.3	−60.5	52.0	5.1			
p-Bromo	3	46	102–103	+0.6	+5.6	47.6	4.6			
m-Bromo	2	30	90–91	+1.2	−1.4	47.5	4.5	$C_{20}H_{23}BrO_{10}$	47.7	4.6
o-Bromo	2	30	141–142	−32.6	−70.2	47.7	4.6			
o-Methyl	2	45	109–110	−4.7	−13.9	57.4	5.9	$C_{21}H_{26}O_{10}$	57.5	5.9
p-Methoxy	1	40	102–103	+2.9	+4.4	55.4	5.6			
m-Methoxy	2	13	87–88	+0.3	−3.9	55.4	5.7	$C_{21}H_{26}O_{11}$	55.5	5.7
o-Methoxy	1	54	102–103	−16.6	−38.7	55.3	5.8			
p-Ethoxy	2	60	82–83	+3.6	+5.5	56.4	6.0			
m-Ethoxy	2	50	111–112	+1.8	0	56.4	6.0	$C_{22}H_{28}O_{11}$	56.4	6.0
p-Acetyl	2	41	146–147	−0.8	−7.8	56.5	5.8			
m-Acetyl	2	50	118–119	−8.3	−27.3	56.4	5.8	$C_{22}H_{27}O_{11}$	56.5	5.8
o-Acetyl	2	10	150–151	−27.6	−74.9	56.3	5.7			
p-Ethyl	3	44	98–99	+4.7	+7.4	58.3	6.0	$C_{22}H_{28}O_{10}$	58.4	6.2
p-*tert*-Butyl	3	40	100–102	+7.0	+12.2	59.9	6.6	$C_{24}H_{32}O_{10}$	60.0	6.7
3,4-Dimethyl	3	67	134–135	+2.1	+4.7	58.3	6.2	$C_{22}H_{28}O_{10}$	58.4	6.2
2,4-Dichloro	2	40	130–131	−25.4	−53.5	48.4	4.7			
3,4-Dichloro	2	40	81–82	+0.7	−2.7	48.3	4.7	$C_{20}H_{22}Cl_2O_{10}$	48.7	4.5
2,6-Dichloro	2	—	syrup	—	—	—	—			
2,5-Dichloro	2	61	154–155	−8.7	−20.9	48.7	4.6			
2,4-Dibromo	2	52	118–119	−23.1	−51.0	41.2	3.9	$C_{20}H_{22}Br_2O_{10}$	41.2	3.8
2-Nitro-4-methyl	2	50	192–193	+51.7	+245.0	52.1	5.3	$C_{21}H_{25}NO_{12}$	52.2	5.2
2-Nitro-4-chloro	2	31	199–200	+55.9	+252.0	47.5	4.7	$C_{20}H_{22}ClNO_{12}$	47.7	4.4
2,3,5-Trimethyl	3	33	137–138	−0.9	−8.7	59.0	6.4	$C_{23}H_{30}O_{10}$	59.2	6.4
2,4,6-Trimethyl	3	25	144–145	−11.6	−24.6	59.2	6.4			
2,4,6-Trichloro	2	48	123–124	−13.0	−27.2	45.4	4.0	$C_{20}H_{21}Cl_3O_{10}$	45.5	4.0
2,4,6-Tribromo	2	60	136–137	−12.4	−26.0	36.1	3.3	$C_{20}H_{21}Br_3O_{10}$	36.3	3.2

TABLE II

PHENYL β-D-GALACTOPYRANOSIDES

Substituent	*M.p.* (*degrees*)	*Solvent*[a]	$[\alpha]^{22}_{5890}$ (*degrees*)	$[\alpha]^{22}_{4360}$ (*degrees*)	*Found* (%)		*Formula*	*Calc.* (%)	
					C	*H*		*C*	*H*
m-Chloro	168–169	A	−35.7	−76.9	49.7	5.4	$C_{12}H_{15}ClO_6$	49.6	5.2
o-Chloro	203–205	B	−45.4	−94.5	49.6	5.2			
p-Bromo	176–177	A	−44.6	−96.4	42.7	4.5	$C_{12}H_{15}BrO_6$	43.0	4.5
m-Bromo	169–170	A	−45.8	−98.4	42.9	4.6			
o-Bromo	217–218	A	−39.7	−85.1	42.9	4.5			
o-Methyl	179–180	A	−42.0	—	57.6	6.6	$C_{13}H_{18}O_6$	57.8	6.6
p-Methoxy	157–158	A	−43.1	−93.4	54.2	6.3	$C_{13}H_{18}O_7$	54.6	6.3
m-Methoxy	141–142	A	−48.8	−104.2	54.4	6.3			
o-Methoxy	207–209	A	−47.3	−103.9	54.6	6.3			
p-Ethoxy	182–183	A	−42.5	−92.7	55.9	6.7	$C_{14}H_{20}O_7$	56.0	6.7
m-Ethoxy	150–151	A	−49.5	−105.9	55.9	6.7			
p-Acetyl	220–221	B	−66.9	−158.4	56.2	6.1	$C_{14}H_{19}O_7$	56.2	6.4
m-Acetyl	170–171	A	−62.4	−142.7	56.1	6.3			
o-Acetyl	177–178	A	−39.0	−74.1	56.3	6.4			
p-Ethyl	144–145	B	−54.1	−92.4	59.0	6.9	$C_{14}H_{20}O_6$	59.2	7.0
p-tert-Butyl	155–156	B	−39.0	−82.6	61.0	7.7	$C_{16}H_{24}O_6$	61.5	7.7
3,4-Dimethyl	181–182	A	−42.6	−91.8	59.1	7.1	$C_{14}H_{20}O_6$	59.2	7.0
2,4-Dichloro	210 (decomp.)	A	−46.8	−100•	44 5	4.3	$C_{12}H_{14}Cl_2O_6$	44.3	4.3
3,4-Dichloro	169–170	B	−52.1	−108.2	44.4	4.3			
2,6-Dichloro	172–174	B	0	−3.0	44.3	4.3			
2,5-Dichloro	207–208	B	−54.9	−118.0	44.6	4.5			
2,4-Dibromo	220–222	A	−37.6	−79.1	34.7	3.5	$C_{12}H_{14}Br_2O_6$	34.8	3.4
2-Nitro-4-methyl	197–198	A	−46.3	−115.1	49.5	5.5	$C_{13}H_{17}NO_8$	49.5	5.4
2-Nitro-4-chloro	201–202	A	−64.8	−184.4	42.6	4.5	$C_{12}H_{14}ClO_8$	42.9	4.2
2,3,5-Trimethyl	207–208	C	−38.5	−84.6	60.3	7.4	$C_{15}H_{22}O_6$	60.4	7.4
2,4,6-Trimethyl	228–230	A	−0.8	−5.8	60.3	7.5			
2,4,6-Trichloro	211–215	A	−1.9	−6.4	40.0	3.5	$C_{12}H_{13}Cl_3O_6$	40.1	3.6
2,4,6-Tribromo	224–225	A	+3.0	+6.0	29.2	2.7	$C_{12}H_{13}Br_3O_6$	29.2	2.6

[a]Crystallisations were effected from the following solvents A, methanol; B, water; C, water–methanol.