Registry No.—1,1-Diphenylpropanol, 5180-33-6; phthalic anhydride, 85-44-9; 1,1-diphenylpropyl hydrogen phthalate ester, 37817-54-2; *p*-nitrobenzoyl chloride, 122-04-3; 1,1-diphenylpropyl-*p*-nitrobenzoate ester, 37816-59-4; 1,1-diphenylpropyl hydrogen phthalate methyl ester, 37816-61-8.

Thermolysis of Phenyl Glycosides

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Thermal analysis of several series of phenyl glycosides has shown that the pyrolytic cleavage of the glycosic group is facilitated by the participation of free hydroxyl groups in a transglycosidation reaction which releases the aglycone as a free phenol. The thermal stability of these compounds is considerably increased by complete acetylation of the molecule and is affected by the inductive effect of the substituents on both the phenolic aglycone and the sugar moiety.

Thermal cleavage of glycosidic bonds is of special interest in understanding the pyrolytic reactions of the carbohydrates and combustion of cellulosic materials.[1-7] In our previous studies of this subject, thermal analysis of analogous series of phenyl and substituted phenyl β-D-xylopyranosides,[4,5] β-D-glucopyranosides, and 2-deoxy-α-D-*arabino*-hexopyranosides,[6] selected as model compounds, has shown that the pyrolytic reactions proceed through the cleavage of the glycosidic group. In this process the aglycone group abstracts a proton to form free phenol, which evaporates, and the glycosyl group is condensed mainly as randomly linked oligosaccharides or an anhydro sugar which is decomposed on further heating. As in acid hydrolysis,[8] thermal cleavage of the aryl glycosides is influenced by the electron-withdrawing effect of the substituent on the phenolic group.[4,6] Furthermore, phenyl glucopyranoside is more stable than the corresponding 2-deoxyhexopyranoside or xylopyranoside.

These studies have been followed by thermal analysis of several phenyl and substituted phenyl 2-amino-2-deoxy-β-D-glucopyranosides, 2-acetamido-2-deoxy-β-D-glucopyranosides, and a variety of acetylated phenyl glycosides to determine the influence of the substituents in the sugar molecule and the availability of free hydroxyl and amino groups.

Results

The thermal analysis of phenyl 2-amino-2-deoxy-β-D-glucopyranoside (**3a**) is shown in Figure 1. The differential thermal analysis (dta), thermogravimetric analysis (tga), and derivative thermogravimetry (dtg) reflect the sequence of physical transformations and chemical reactions as the sugar is heated at a constant rate. As in the case of phenyl-β-D-glucopyranoside,[6] the first event at 80° is due to dehydration and the amount of water lost depends on previous treatment of the sample. Fresh crystals obtained from ethanol–water solution correspond to the dihydrate and contain 12% water that is lost at this temperature (see the tga curve in Figure 1). Storage in a dry atmosphere or under desiccation results in complete removal of the water. The endotherm at 178° is due to melting. At higher temperatures, these two physical transformations are followed by weight loss due to the cleavage of the glycosidic bond, evaporation of phenol, and decomposition of the sugar moiety. The tga and dtg curves show that the weight loss starts at about 225° and reaches a maximum rate at 284°. The dta curve shows only a slight thermal effect in this region due to the overlapping of endothermic and exothermic reactions. Following the rapid weight loss, there is a slow volatilization which leaves a fairly stable carbonaceous residue of 41% at 400°. This compares with 11% residue obtained from phenyl β-D-glucopyranoside.[6] The high yield of charred residue is characteristic for amino sugars, *O*-glycosides, with an amino group either in the aglycone or the glycosyl moiety, and *N*-glycosides. This aspect of the amino compound will be discussed in a following communication.

The thermal analysis features of phenyl and *p*-bromophenyl 2-amino-2-deoxy-β-D-glucopyranosides (**3a** and **3d**) are summarized in Table I. A comparison of these data with those obtained for the corresponding normal glycosides shows that the decomposition peaks for the amino compounds are about 15° lower and, as noted already, the residues are substantially higher.

The thermogram of phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**2a**) is shown in Figure 2. A comparison of this thermogram with Figure 1 shows that, after acetylation of the amino group, the melting point is shifted from 178° to 249° and is closely followed by a rapid decomposition indicated by the dtg peak at 261°.

Table I gives a summary of the dynamic thermal analysis data for a number of 2-acetamido glycosides (**2a–g**). For these compounds the melting process is accompanied or closely followed by decomposition. Consequently, the dta peak for decomposition is superimposed as a shoulder on the melting point endotherm or appears as an adjoining peak. The maximum rates of decomposition are still shown by distinct dtg peaks, but these show no discernible trend because the decomposition is controlled by physical transition of the crystalline materials to liquid rather than the

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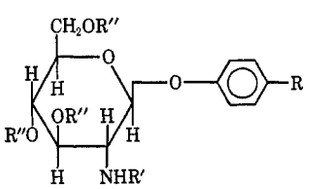
TABLE I

THERMAL ANALYSIS FEATURES OF GLYCOSIDES

Aglycone	Dta peaks: Change, °C	Dta peaks: Mp, °C	Dta peaks: Dec, °C	Dtg peaks: Change, °C	Dtg peaks: Dec, °C	Tga Residue,[a] %
2-Amino-2-deoxy-β-D-glucopyranosides						
Phenyl	80	178	264	80	284	41
p-Bromophenyl	124	165	285[b]	125	271	33
2-Acetamido-2-deoxy-β-D-glucopyranosides						
Methyl		202	307, 345[b]		318	30
p-Methoxyphenyl	74	252	263	75	264	26
p-Methylphenyl	105	241	255	106	266	27
Phenyl		249	Dec		261	32
p-Acetamidophenyl		244	266,[b] 317		266, 321	35
p-Bromophenyl	115, 130	254	Dec	116	262	25
p-Iodophenyl		248	Dec		250	28
p-Nitrophenyl	77	215	257[b]	75	220, 250	42
2-Acetamidotri-*O*-acetyl-2-deoxy-β-D-glucopyranosides						
Methyl		159	337		343	2
p-Methoxyphenyl	158, 176, 182	191	355		357	4
p-Methylphenyl		201	345		349	6
Phenyl	182, 185	201	333		337	6
p-Acetamidophenyl		252	325		323	17
p-Bromophenyl	59	227	306		305	14
p-Iodophenyl	72	250	285		291	14
p-Nitrophenyl		245	268[b]		260	28
Tetra-*O*-acetyl-β-D-glucopyranosides						
p-Methoxyphenyl	98	103	364		364	0
p-Methylphenyl		119	347		350	0
Phenyl		126	345		347	0
p-Bromophenyl		132	362		365	0
Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosides						
p-Methoxyphenyl	34	100	351		352	0.5
p-Methylphenyl		94	333		336	0.4
Phenyl		86	325		327	0.0
p-Bromophenyl		136	349		351	0.1
p-Nitrophenyl		142	313[b]		312	27.0

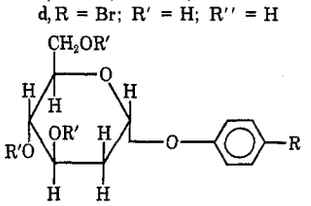
[a] Per cent residue at 400° based on anhydrous weight of the original material. [b] Exothermic.



1a, R = H; R′ = Ac; R″ = Ac
b, R = OCH_3; R′ = Ac; R″ = Ac
c, R = CH_3; R′ = Ac; R″ = Ac
d, R = Br; R′ = Ac; R″ = Ac
e, R = I; R′ = Ac; R″ = Ac
f, R = NO_2; R′ = Ac; R″ = Ac
g, R = NHAc; R′ = Ac; R″ = Ac

2a, R = H; R′ = Ac; R″ = H
b, R = OCH_3; R′ = Ac; R″ = H
c, R = CH_3; R′ = Ac; R″ = H
d, R = Br; R′ = Ac; R″ = H
e, R = I; R′ = Ac; R″ = H
f, R = NO_2; R′ = Ac; R″ = H
g, R = NHAc; R′ = Ac; R″ = H

3a, R = H; R′ = H; R″ = H
d, R = Br; R′ = H; R″ = H



4a, R = H; R′ = Ac
b, R = OCH_3; R′ = Ac
c, R = CH_3; R′ = Ac
d, R = Br; R′ = Ac
f, R = NO_2; R′ = Ac

chemical structure of the molecule. The tga curves show considerable residue at 400°, but not as much as was observed for the amino glycosides.

Since the dynamic thermal analysis data on relative stability of the acetamido compounds were not reliable because of the limitation imposed by melting, the decomposition of these compounds was investigated by isothermal tga at 250° to obtain the trend shown in Figure 3. This figure shows a slow rate of weight loss or high stability for the methyl glucoside as predicted by the dynamic thermal analysis data (Table I). The aryl acetamido glycosides, which are generally less stable, follow the order of Hammett's σ factor[6] and show an induction period before reaching the maximum rate of decomposition. This period is longer for *p*-methoxyphenyl and *p*-bromophenyl derivatives, which have melting points higher than 250°. Another isothermal experiment at 240° showed the same order for the maximum rates but even larger differences in the induction period.

The *p*-nitrophenyl compound again showed the peculiarities that have been observed in other series of glycosides.[4,6] The maximum rate of weight loss was reached rapidly but the pyrolysis slowed after a short

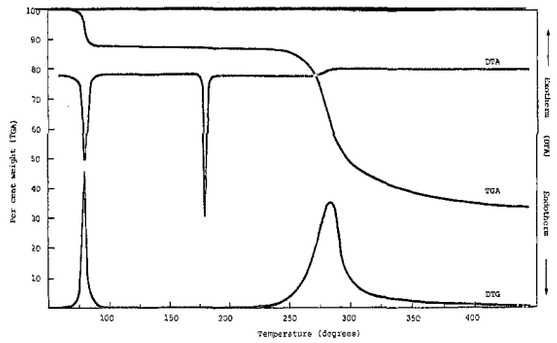


Figure 1.—Thermogram of phenyl 2-amino-2-deoxy-β-D-glucopyranoside

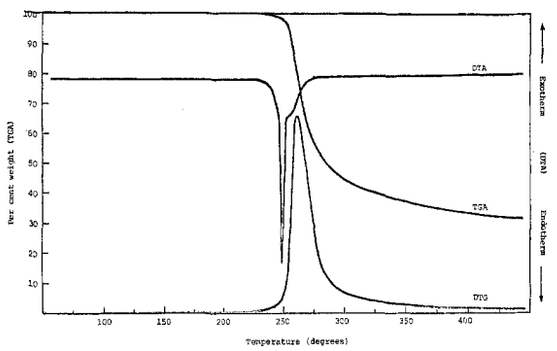


Figure 2.—Thermogram of phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside.

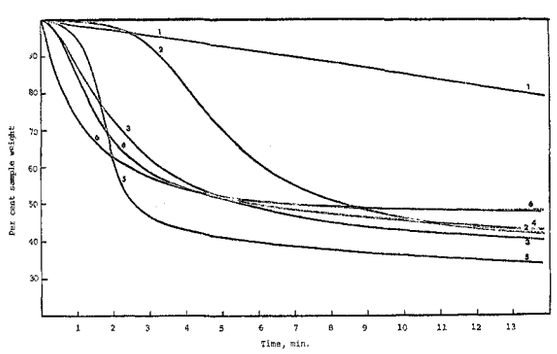


Figure 3.—Isothermal weight loss of 2-acetamido-2-deoxy-β-D-glucopyranosides at 250°: 1, methyl; 2, *p*-methoxyphenyl; 3, *p*-methylphenyl; 4, phenyl; 5, *p*-bromophenyl; 6, *p*-nitrophenyl.

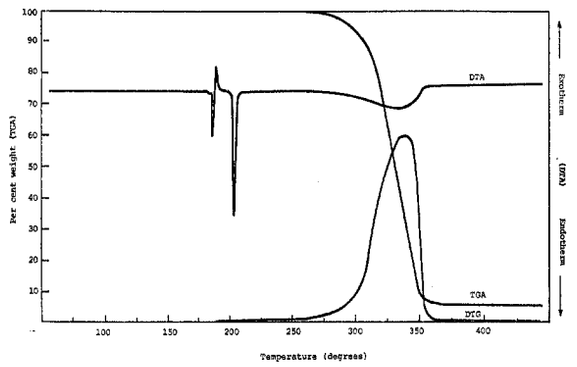


Figure 4.—Thermogram of phenyl 2-acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside.

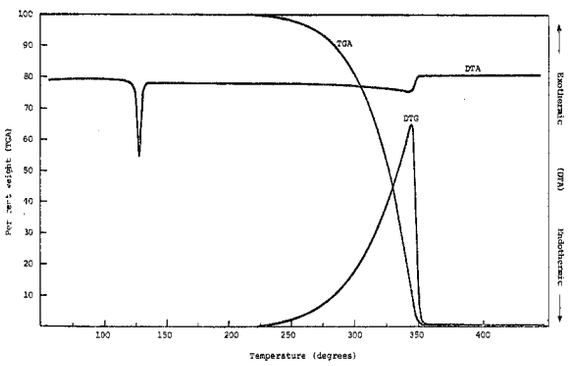


Figure 5.—Thermogram of phenyl tetra-*O*-acetyl-β-D-glucopyranoside.

while to leave more residue. Furthermore, as shown by dta (Table I), the overall decomposition process was exothermic instead of being endothermic, indicating that it proceeds differently.

Complete acetylation of the 2-aminoglucosides greatly increased the thermal stability of the products, as can be seen in the thermogram of phenyl 2-acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**1a**) (Figure 4). In this thermogram, the dta line shows a crystal transformation at 185° and melting at 201°. The dtg and tga curves show that the weight loss starts at about 250°, reaches a maximum at 337°, and leaves a residue of only 6% at 400°.

The thermal analysis data for a series of fully acetylated 2-amino glycosides are given in Table I. These data show that complete acetylation has greatly increased the stability of the glycosides and there is no longer the overlapping of the melting and decomposition processes.

The same phenomenon is observed on acetylation of the normal and 2-deoxy glycosides. Figures 5 and 6 show the thermograms of phenyl tetra-*O*-acetyl-β-D-glucopyranoside and phenyl tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside, respectively. In these cases, however, increased stability and volatility of the compound results in overlapping of the decomposition with evaporation of the intact molecule. Consequently, melting is followed by a broad endothermic weight loss which reaches a maximum rate at 347 and 327°, respectively, and leaves a negligible amount of residue at 400°.

Evaporation of the acetylated glycosides has been confirmed by analysis of the volatile products. The resulting data (see Table II) show that the free glycosides give a very high yield of free phenol and none or very little intact material, whereas the reverse is true for the acetylated compounds.

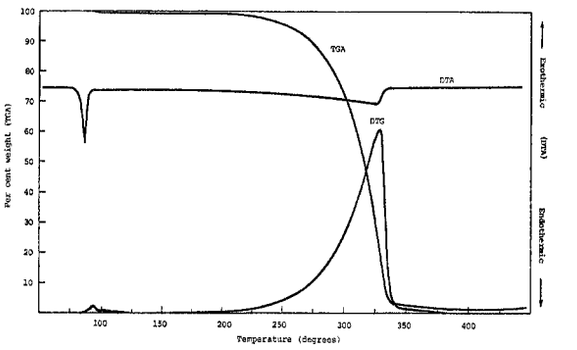


Figure 6.—Thermogram of phenyl tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside.

TABLE II
ANALYSIS OF VOLATILE PRODUCTS FROM DIFFERENT GLYCOSIDES

Glycoside	Free phenol, %	Starting material, %
Phenyl β-D-glucopyranoside	100[a]	0[a]
Phenyl 2-amino-2-deoxy-β-D-glucopyranoside	82	2
Phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside	99	0
Phenyl 2-deoxy-α-D-*arabino*-hexopyranoside	82	4
Phenyl 2-acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside	29	42
Phenyl tetra-*O*-acetyl-β-D-glucopyranoside	0	62
Phenyl tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside	0	63

[a] Theoretical value.

The dynamic thermal analysis features of other fully acetylated normal and 2-deoxy glycosides are given in Table I. Because of the evaporation of these compounds their temperature of maximum rate of weight loss (dtg peak) does not necessarily correspond with the stability order. However, as discussed below, these data show that the acetylated compounds in general are considerably more resistant to thermal degradation than the corresponding unacetylated compound and remain intact at higher temperatures.

Discussion

The thermal stability of phenyl glycosides and the corresponding fully acetylated compounds of different series are compared in Table III and Figures 7 and 8. Table III gives the dynamic thermal analysis data for all these compounds, and isothermal weight loss is shown in Figure 7 for the glycosides at 260° and in Figure 8 for the acetylated compounds at 300°.

These data show that the acetylated compounds are considerably more stable than the parent compounds and that the free hydroxyl groups must play a significant role in the thermolysis of the glycosides. Considering that nearly 100% free phenol is generated by this process (see Table II), and after the cleavage of the glycosidic group the glycosyl moiety forms condensation products containing anhydro sugars and oligosaccharides,[6] it becomes clear that the thermoly-

TABLE III
COMPARATIVE THERMAL PROPERTIES OF PHENYL GLYCOSIDES

Glycoside	Dta peaks Mp, °C	Dta peaks Dec, °C	Dtg Dec, °C	Tga Residue, %
β-D-Glucopyranoside	175	305, 330	311, 336	11
Tetra-*O*-acetyl-β-D-glucopyranoside	126	344	348	0
2-Deoxy-α-D-*arabino*-hexopyranoside	165	296	299	7
Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside	86	324	327	1
2-Amino-2-deoxy-β-D-glucopyranoside	178	264	284	41
2-Acetamido-2-deoxy-β-D-glucopyranoside	249	255	261	32
2-Acetamido-tri-*O*-acetyl-β-D-glucopyranoside	201	333	337	6

sis process consists of inter- and intramolecular transglycosidation reactions. As shown before, the thermal reactions are less specific[7] and different hydroxyl groups could participate in the transglycosidation reaction to provide randomly linked condensation products.[5]

Substituents on the aglycone or glycosyl moiety produce an inductive effect on the cleavage of the glycosidic group, as in acid hydrolysis.[8] The para-substituted phenyl glycosides in each series follow the order of Hammett's σ factor, with the better leaving groups being less stable. This trend is clearly shown by the thermal analysis data, unless the thermolysis of the glycoside overlaps with melting or evaporation.

The substituents on the sugar moiety, however, in addition to the inductive effect on the glycosidic bond, could also change the availability or reactivity of the transglycosidation sites. Consequently, the net result is not necessarily parallel with the order of stability observed on acid hydrolysis. For the free glycosides, the combination of the two effects produces the order of stability shown in Table III and Figure 7, with normal glucoside being more stable than the 2-deoxy, 2-amino, and 2-acetamido compounds, respectively.

These data also show that, although C-2 hydroxyl groups could participate in the transglycosidation reaction, they do not play a specific role similar to that in the alkaline cleavage of the phenyl β-D-glucopyranoside,[9,10] because phenyl 2-deoxy-α-D-glucopyranoside is pyrolyzed at a comparative rate. This observation is in line with the random participation of the hydroxyl group discussed above.

The proposed mechanism for cleavage of the glycosidic group has further implications on the thermolysis of oligosaccharides and polysaccharides and the effect of water and nitrogen compounds on the course of pyrolytic reactions and flammability of cellulosic materials, that will be discussed in subsequent reports.

Experimental Section

Aryl 2-Acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside.—Phenol or a para-substituted phenol (5 g) and 2-acetamidotri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[11] (5 g) were dissolved in cold acetone (105 ml) and treated with 3.3% aqueous sodium hydroxide (45 ml).[12] The mixture was kept for 6 hr at room temperature and overnight at 5°. The acetone was removed at room temperature and the products were shaken with chloroform (100 ml). The chloroform layer was extracted with cold dilute alkali, washed with water, dried over $CaCl_2$, and evaporated *in vacuo*. The residue was recrystallized from 2-propanol, methanol, or 1:1 methanol–chloroform to give the compounds listed in Table IV.

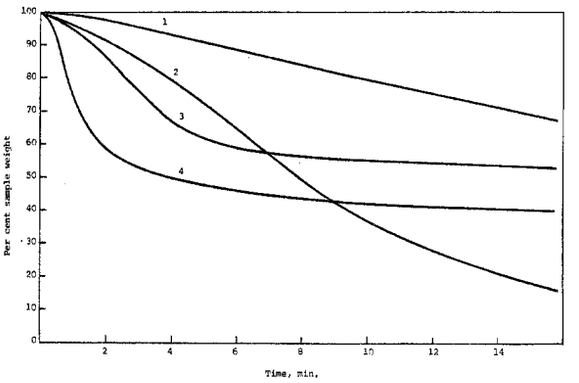


Figure 7.—Isothermal weight loss of phenyl glucosides at 260°: 1, phenyl β-D-glucopyranoside; 2, phenyl 2-deoxy-α-D-*arabino*-hexopyranoside, 3, phenyl 2-amino-2-deoxy-β-D-glucopyranoside; 4, phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside.

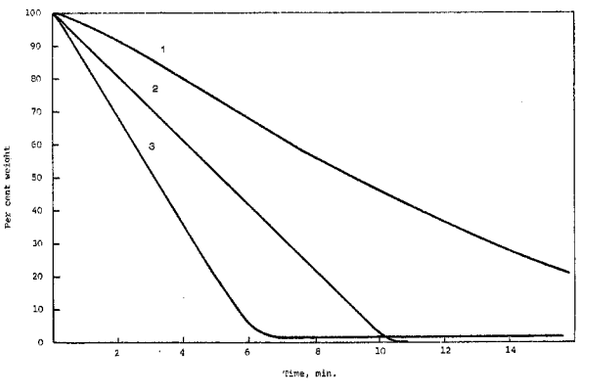


Figure 8.—Isothermal weight loss of fully acetylated phenyl glycosides at 300°: 1, phenyl 2-acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside; 2, phenyl tetra-*O*-acetyl-β-D-glucopyranoside; 3, phenyl tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside.

Aryl 2-Acetamido-2-deoxy-β-D-glucopyranosides.—Aryl 2-acetamido-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosides (1 g) were dissolved (suspended) in methanol (25 ml) and then treated with methanolic ammonia (50 ml) and left overnight at room temperature.[13] The acetamido derivatives that separated after evaporation were filtered, washed with cold water, and recrystallized from water or EtOH–H_2O to give the products listed in Table IV.

Aryl 2-Amino-2-deoxy-β-D-glucopyranosides.—Aryl 2-acetamido-2-deoxy-β-D-glucopyranoside (1 g) and hydrazine hydrate (85%) (5 ml) were kept in a sealed tube at 100–140° for 24–48 hr.[14] Excess hydrazine was then removed in an evacuated desiccator over H_2SO_4 for 2 days and the residue was triturated with EtOH. The resulting compounds are listed in Table IV.

Methyl 2-Acetamido-2-deoxy-β-D-glucopyranoside.—Methyl 2-acetamidotri-*O*-acetyl-2-deoxy-β-D-glucopyranoside was prepared by the Leaback and Walker method in 40% yield, mp 163° (lit.[12] mp 163°). Treatment of this compound with ammonia gave the title compound, mp 204° (lit.[12] mp 204°), $[\alpha]_D$ −47.0° (*c* 1.0, H_2O).

Aryl Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosides.—Tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose (1 g) and para-substituted phenol (1 g) were mixed with powdered anhydrous $ZnCl_2$ (0.2 g) and stirred vigorously at 70–80° for 40 min.[15] At

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TABLE IV

SYNTHESIS OF THE GLYCOSIDES

Compd	Yield, %	Solvent	Mp, °C	Found, % C	H	N	Empirical formula	Required, %[a] C	H	N
Aryl 2-Acetamidotri-*O*-acetyl-2-deoxy-β-D-glucopyranosides										
1a (H)	32	Propanol	204[b,c]							
1b (OMe)	28	MeOH	196	55.83	6.04	3.11	$C_{21}H_{27}NO_{10}$	55.60	6.01	3.09
1c (Me)	30	MeOH	197	57.48	6.21	3.16	$C_{21}H_{27}NO_9$	57.64	6.22	3.20
1d (Br)	35	MeOH	228–229	47.70	4.69	2.76	$C_{20}H_{24}BrNO_9$	47.80	4.82	2.79
1e (I)	31	MeOH	250	43.68	4.36	2.63	$C_{20}H_{24}INO_9$	43.71	4.40	2.55
1f (NO_2)	39	MeOH–$CHCl_3$	240[b]							
1g (NHAc)	26	MeOH	252–253	54.72	5.58	5.79	$C_{22}H_{28}N_2O_{10}$	54.97	5.88	5.83
Aryl 2-Acetamido-2-deoxy-β-D-glucopyranosides										
2a (H)	70	EtOH–H_2O	250[b]							
2b (OMe)	72	EtOH–H_2O	249	52.42	6.87	3.94	$C_{15}H_{21}NO_7 \cdot H_2O$	52.15	6.72	4.06
2c (Me)	73	EtOH–H_2O	238	54.53	7.05	4.15	$C_{15}H_{21}NO_6 \cdot H_2O$	54.68	7.04	4.25
2d (Br)	77	EtOH–H_2O	241	42.75	5.16	3.28	$C_{14}H_{18}BrNO_6 \cdot H_2O$	42.63	5.12	3.55
2e (I)	75	EtOH–H_2O	239	39.50	4.47	3.34	$C_{14}H_{18}INO_6$	39.71	4.29	3.31
2f (NO_2)	83	EtOH–H_2O	214[b]							
2g (NHAc)	65	EtOH–H_2O	236–237	53.95	5.98	7.84	$C_{16}H_{22}N_2O_7$	54.21	6.26	7.91
Aryl 2-Amino-2-deoxy-β-D-glucopyranosides										
3a (H)	72	EtOH	172[d]							
3d (Br)	75	EtOH	166.5	43.26	4.82	4.21	$C_{12}H_{16}BrNO_5$	43.11	4.83	4.19
Aryl Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosides										
4b (OCH_3)	40	EtOH	100	57.72	6.42		$C_{19}H_{24}O_9$	57.55	6.11	
4d (Br)	43	EtOH	134.5	48.71	4.74		$C_{18}H_{21}BrO_8$	48.53	4.76	

[a] Analysis is given for new compounds. [b] Reference 12. [c] B. Weissmann, *J. Org. Chem.*, **31**, 2505 (1966). [d] C. G. Greig, D. H. Leaback, and P. G. Walker, *J. Chem. Soc.*, 879 (1961).

short intervals the acetic acid generated was removed under diminished pressure. The mixture was extracted with benzene (100 ml). The extract was filtered, repeatedly washed with 5% NaOH solution and water, dried ($CaCl_2$), and evaporated to a syrup which crystallized on trituration with EtOH. The new products obtained are listed in Table IV.

Thermal Analysis.—The dta data were obtained with a Du Pont Model 990 thermal analyzer equipped with a calorimeter cell. All experiments were performed with 2-mg samples in covered 6-mm aluminum pans and an empty pan was used as the reference. A small hole was made in the cover to allow volatile products to escape. In all dta experiments, the samples were heated at the rate of 15°/min in a 75 ml/min flow of nitrogen.

For tga, a Cahn R-100 Electro-balance was used for weighing. The Du Pont thermal analyzer was used to program a furnace surrounding the sample tube. For dynamic tga the sample size, configuration, atmosphere, and heating rate were the same as in dta so that the two methods would be comparable. The derivative of the tga signal (dtg) was taken with a Cahn time derivative computer (Mark II). For isothermal tga the temperature was increased rapidly to the desired temperature and held within ±0.5°.

Decomposition Product Analysis.—The liberation of free phenol was determined under conditions identical with the dynamic dta and tga. Phenol which vaporized from the reaction pan was trapped quantitatively by bubbling the nitrogen purge gas through 1 *M* NaOH solution. The starting materials which were condensed in the cooler regions of the apparatus were washed out with ethanol. The resulting solutions were then analyzed by the uv absorption method to provide the data shown in Table II. Since some of the starting materials could have escaped condensation, the data gives only a lower limit for the evaporated starting materials.

Registry No.—**1a**, 13089-21-9; **1b**, 38229-72-0; **1c**, 38229-73-1; **1d**, 38229-74-2; **1e**, 38229-75-3; **1f**, 13089-27-5; **1g**, 14419-60-4; **2a**, 5574-80-1; **2b**, 38229-78-6; **2c**, 35694-99-6; **2d**, 38229-80-0; **2e**, 38229-81-1; **2f**, 3459-18-5; **2g**, 14419-61-5; **3a**, 38223-13-1; **3d**, 38223-14-2; **4a**, 20196-78-5; **4b**, 38223-16-4; **4c**, 38223-17-5; **4d**, 38223-18-6; **4f**, 38223-19-7; methyl 2-acetamido-2-deoxy-β-D-glucopyranoside, 3946-01-8; methyl 2-acetamido-2-deoxy-β-D-glucopyranoside triacetate, 2771-48-4; *p*-methoxyphenyl β-D-glucopyranoside tetraacetate, 14581-81-8; *p*-methylphenyl β-D-glucopyranoside tetraacetate, 14581-78-3; phenyl β-D-glucopyranoside tetraacetate, 4468-72-8; *p*-bromophenyl β-D-glucopyranoside tetraacetate, 14581-80-7.

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