30% hydrogen peroxide is added. Within a few minutes an evolution of gas begins and the temperature rises spontaneously to about 55°. The reaction is complete in about half an hour as indicated by the sudden appearance of a dark purple color. After cooling to 40° a second 120 cc. volume of peroxide is added, whereupon a new reaction takes place very similarly.[11] The dark turbid solution is then filtered through carbon[12] on a Buchner funnel and concentrated in a vacuum to 250 cc. To this, 1500 cc. of methanol[13] are added with shaking and the granular precipitate which forms is filtered on a Buchner funnel precoated with carbon. Three hundred cubic centimeters of methanol are used for rinsing. To the clear filtrate is added 900 cc. of ether with shaking.[14] After five minutes of settling, the new granular precipitate is filtered on a carbon-coated Buchner funnel. The filtrate is concentrated in a vacuum to a sirup. When it has become so stiff as barely to flow[15] it is taken up in about 100 cc. of warm methanol and poured out into an Erlenmeyer flask, 25 cc. more being used for rinsing. Crystallization takes place readily without seeding. After a few hours in the refrigerator, the sugar is filtered, washed with methyl alcohol and dried. The yield is 55 to 65 g. or about 50% of the theoretical amount. It is recrystallized by dissolving in two-thirds its weight of water,[16] filtering with carbon rapidly while hot, and adding five volumes of methanol. Sharp prisms of *d*-arabinose separate in a yield of 80% of the crude substance used. After washing and drying *in vacuo* at 60° for two hours, the $[\alpha]^{20}_{D}$ at equilibrium was $-103.3°$,[17] m. p. 155.5–156.5° (corr.). After a second recrystallization, the $[\alpha]^{20}_{D}$ at equilibrium was $-104.8°$, ash 0.0% (visible). The time required to the first crystallization is about one working day.

Summary

Improved directions are given for the preparation of *d*-arabinose by oxidation of calcium gluconate with hydrogen peroxide in the presence of ferric acetate (Ruff's method). The ease with which practical quantities of this sugar can be obtained in a state of high purity recommends the *d*-isomer for use in such investigations as do not specifically require the *l*-modification, which is very difficult to prepare in good purity.

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[11] Analyses for reducing sugar at various stages showed that a second oxidation with the same amount of hydrogen peroxide greatly increases the yield of pentose. Further quantities of oxidant cause a drop in yield.

[12] The activated carbons employed often contained copper, and were therefore soaked in 3.5% hydrochloric acid and then washed acid-free with distilled water and dried before use.

[13] A commercial synthetic methanol labeled "from 99 to 100% pure" was found satisfactory, and is much cheaper than "reagent quality."

[14] Acetone may be used with equally good results.

[15] Crystallization sometimes takes place in the distillation flask. In this case the crystals may be dissolved in a little water and the concentration then continued to the proper stage.

[16] There should be very little calcium present at this point but if the amounts of lime salts are appreciable, they may be prevented from separating by adding 2 cc. of concentrated nitric acid to the solution.

[17] Hudson and Yanovsky, *loc. cit.*, found $[\alpha]^{20}_{D}$ at equilibrium $-105°$ for pure *d*-arabinose. The over-all yield of virtually pure *d*-arabinose may therefore be fairly stated as 40% of the theoretical without working up mother liquors.

WASHINGTON, D. C. RECEIVED MAY 14, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Cleavage of Glycosides by Catalytic Hydrogenation[1]

BY NELSON K. RICHTMYER

Recent investigations have shown that various benzyl and benzal compounds, including esters of benzyl and diphenylmethyl alcohols,[2] benzaldehyde acetals,[3] and benzyl ethers of phenols and alcohols[4] can be cleaved by hydrogen in the presence of palladium catalysts. For example, $C_6H_5OCH_2C_6H_5 + H_2 \longrightarrow C_6H_5OH + C_6H_5CH_3$. In 1928 this reaction was adapted to the synthesis of sugar derivatives by K. Freudenberg,[5] who found that the benzyl group could be eliminated from benzyl ethers of sugars, and from benzyl glycosides, by hydrogen and platinum in glacial acetic acid, but not in alcohol.

In the same year Kariyone and Kondo,[6] working on the glucoside aucubin, reported that catalytic hydrogenation with neutralized platinum chloride in aqueous solution resulted in cleavage to glucose and a reduced aglucone of unknown structure; with platinum oxide in alcohol, however, no cleavage took place. The Japanese investigators then studied two phenyl glucosides, arbutin and salicin. Arbutin with aqueous neutralized platinum chloride absorbed four moles of hydrogen to yield about one mole of glucose and, presumably, hexahydrophenol. Sali-

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[1] Presented in part before the Division of Organic Chemistry, at the St. Petersburg meeting of the American Chemical Society, March 27, 1934.

[2] Rosenmund and Heise, *Ber.*, **54**, 2038 (1921).

[3] Kariyone and Kimura, *J. Pharm. Soc. Japan*, No. **500**, 746 (1923).

[4] Merck, German Patents 407,487 (1924); 417,926 (1925).

[5] Freudenberg, Dürr and von Hochstetter, *Ber.*, **61**, 1739 (1928); Freudenberg, Toepffer and Andersen, *ibid.*, **61**, 1754 (1928).

[6] Kariyone and Kondo, *J. Pharm. Soc. Japan*, **48**, 684 (1928).

cin, on the other hand, was treated with neutralized palladium chloride;[7] one mole of hydrogen was absorbed readily and the product was *o*-cresyl glucoside, formed by the reduction of the $—CH_2OH$ to $—CH_3$.

The object of the present investigation was to study the conditions under which phenyl and benzyl glycosides are cleaved by catalytic hydrogenation, and to see if the cleavage of other related groups might also be effected. For this purpose the Königs–Knorr synthesis was used to prepare from acetobromoglucose and the desired alcohol a series of tetraacetyl-β-glucosides; deacetylation of these products furnished a second series, consisting of the β-glucosides. Each series included the phenyl, benzyl, phenylethyl, phenylpropyl, cyclohexyl and cyclohexylmethyl compounds. Several of these substances are either new, or obtained in the pure state for the first time.

The behavior of these twelve compounds and of several other phenyl and benzyl glycosides was first studied in the apparatus for micro-catalytic hydrogenation devised by Hyde and Scherp.[8]

TABLE I

MOLES OF HYDROGEN ABSORBED PER MOLE OF COMPOUND

2–5 mg. of compound in 5 cc. of glacial acetic acid

Glucoside	30 mg. palladium Tetra-acetate	30 mg. palladium Glucoside	10 mg. platinum Tetra-acetate	10 mg. platinum Glucoside
Phenyl	3.02	2.99	3.41	3.50
Benzyl	3.99	4.03	3.40	3.49
Phenylethyl	3.04	3.05	3.04	3.06
Phenylpropyl	3.09	2.97	3.08	3.13
Cyclohexyl	0	0	0	0
Cyclohexylmethyl	0	0	0	0
p-Xenyl			6.55	6.50
Trimethylphenyl glucoside	2.98		3.52	
Trimethylbenzyl glucoside	4.05		3.44	
Heptaacetylbenzyl lactoside	3.98		3.36	
Heptamethylbenzyl cellobioside	3.96		3.55	

TABLE II

TYPICAL RATES OF ABSORPTION

Benzylglucoside with Pd Black

Time, minutes	5	60	150	300
Hydrogen, moles	1	2	3	4

Tetraacetylbenzylglucoside with Pt Black

Time, minutes	3	10	15	60
Hydrogen, moles	2.22	3.33	3.40	3.40

The results with palladium black, and platinum black, in glacial acetic acid are recorded in Table I, while typical rates of absorption are given in Table II.

These data show that palladium causes cleavage only with the benzyl glycosides; one mole of hydrogen is absorbed rapidly, producing glucose and toluene, which is then reduced much more slowly to methylcyclohexane. The phenyl, phenylethyl, phenylpropyl, and xenyl glucosides are not cleaved, but do absorb hydrogen slowly until the benzene rings become saturated; the cyclohexyl derivatives absorb no hydrogen.

Platinum black reduces the phenylethyl and phenylpropyl glucosides to the corresponding cyclohexyl derivatives, which in turn absorb no hydrogen. The phenyl and benzyl glycosides, however, rapidly add about three and one-half moles of hydrogen. The explanation for this lies in the fact that two reactions are taking place: if the benzene ring is hydrogenated first, no cleavage occurs and only three moles of hydrogen are absorbed; if cleavage takes place first, then the liberated benzene or toluene is reduced and four moles of hydrogen are consumed. With both reactions progressing at equal rates, three and one-half moles of hydrogen would be the total amount added.

Since palladium catalysts produce quantitative cleavage of benzyl glycosides, and since platinum black in glacial acetic acid results in only partial cleavage of phenyl glycosides, subsequent experiments were directed toward finding conditions under which a more satisfactory cleavage of phenyl glycosides by catalytic hydrogenation could be brought about. To this end both solvent and catalyst were varied, although all reductions were carried out at room temperature and atmospheric pressure. Several naturally occurring glucosides and also benzyl glucoside have been included in the study. The extent of cleavage was determined by titration of the amount of glucose present after hydrogenation, and is summarized in Table III.

From the data in Table III it may be seen that cleavage of all of the phenyl glucosides studied occurs upon hydrogenation with any type of platinum catalyst, in water, alcohol or glacial acetic acid. This cleavage does not take place in slightly alkaline solutions, goes rather slowly in neutral solutions, but proceeds readily in solutions containing a trace of hydrochloric acid. In such

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[7] The use of palladium is specified only in the original Japanese version, Ref. 5. The German version in the same issue of that Journal implies that colloidal platinum was used, as do also the abstracts in *Chemical Abstracts*, **23**, 393 (1929), and *Chemisches Zentralblatt*, II, 1338 (1928).

[8] Hyde and Scherp, THIS JOURNAL, **52**, 3359 (1930).

TABLE III

PHENYLGLUCOSIDE (0.25 g.)

Solvent (25 cc.)	Catalyst, g.	Time in hours	Cleavage, %
H_2O	0.5 Pd black	71	[a]
H_2O	.05 Pt black	2	44.5
H_2O	.05 Pt black + 1 cc. dil. NaOH	1	No H_2 absorbed
H_2O	.05 Pt black + 1 cc. dil. HCl	2	69.8
H_2O	.05 Pt, 0.05 Pd, 1 cc. dil. HCl	4	10.8[b]
CH_3OH	.05 PtO_2	Very slow	[b]
CH_3OH	.05 PtO_2 + 1 cc. dil. HCl	1	71.1
Gl. HAc	.05 Pt black	1.5	27.2
Gl. HAc	.05 Pt black + 1 cc. dil. HCl	1.5	42.7
	Salicin (0.25 g.)		
H_2O	.1 Pt black	2	36.2
H_2O	.05 Pt black + 1 cc. dil. HCl	3	61.2
H_2O	.05 Pt black + 3 cc. dil. HCl	3	60.7
H_2O	.2 Pt black + 1 cc. dil. HCl	1.5	59.5
H_2O	.05 PtO_2	8	30.9
H_2O	.05 PtO_2 + 1 cc. dil. HCl	2.5	58.1
CH_3OH	.05 PtO_2 + 1 cc. dil. HCl	1.5	56.0
C_2H_5OH	.05 PtO_2 + 1 cc. dil. HCl	1.5	49.7
H_2O	.05 Pt on charcoal	6	36.3
H_2O	.05 Pt on charcoal + 1 cc. dil. HCl	4	45.7
H_2O	.05 Pt, from Na_2PtCl_6 + 1 cc. dil. HCl	6	64.1
H_2O	.05 Pt, from Na_2PtCl_6 + gum arabic	6	66.0
H_2O	.05 Pd black	1	[c]
H_2O	.05 Pt, 0.05 Pd, + 1 cc. dil. HCl	0.5	[c]
H_2O or C_2H_5OH	Raney nickel	No hydrogen absorbed	

Miscellaneous (0.25 g.)

Glucoside	Solvent	Catalyst	Time in hours	Per cent. cleavage
Benzyl	H_2O	0.05 Pt black + 1 cc. dil. HCl	1.5	75.4
Benzyl	H_2O	.05 Pd black	3	99.2
p-Xenyl	H_2O	.2 Pt black + 1 cc. dil. HCl	7	62.6
Trimethyl phenyl	Gl. HAc	.05 Pt black + 1 cc. dil. HCl	1	54[d]
Arbutin	H_2O	.05 Pt black + 1 cc. dil. HCl	2	72.0[e]
Arbutin	H_2O	.05 Pt from Na_2PtCl_6	2.5	71.9
Arbutin	C_2H_5OH	.1 PtO_2 + 1 cc. dil. HCl	2	68.8
Aesculin	H_2O	.15 Pt black + 1 cc. dil. HCl	5	85.0[f]
Aesculin	H_2O	.15 Pt black + 2 cc. dil. HCl	5	83.7[f]
Phloridzin	CH_3OH	.1 PtO_2 + 1 cc. dil. HCl	12	47.1[f]

[a] The product obtained by the reduction of phenylglucoside in the presence of palladium black was identified as β-cyclohexylglucoside.

[b] Reduction in these two cases proceeded so slowly that they were not allowed to run to completion.

[c] The product obtained by the addition of one mole of hydrogen to salicin in the presence of palladium catalysts was identified as the *o*-cresyl glucoside, m. p. 164°, of Kariyone and Kondo, Ref. 6.

[d] The product obtained by cleavage of trimethylphenylglucoside was isolated as crystalline trimethylglucose in the yield given.

[e] The second constituent formed by cleavage of arbutin was isolated and identified as cyclohexanol.

[f] Inasmuch as the samples of aesculin and phloridzin reduced Fehling's solution to a considerable extent before as well as after reduction, the figures representing percentage cleavage may not be reliable. That cleavage did occur was evident from the fragrant oil produced upon hydrogenation.

solutions, also, the amount of cleavage appears to reach a maximum at 60–70% but may be even higher in certain phenyl glucosides such as aesculin.

Experimental

All new compounds were recrystallized until the melting point and the rotation became constant. Rotations were observed at room temperature, either in water or U. S. P. chloroform, in a concentration of about 2%.

Tetraacetyl-β-phenyl-*d*-glucoside was prepared by the method of Helferich and Schmitz-Hillebrecht.[9] Thrice

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(9) Helferich and Schmitz-Hillebrecht, *Ber.*, **66**, 380 (1933).

recrystallized from ether–petroleum ether, it melted at 125–126° and showed $[\alpha]_D$ −21.9° in chloroform.

β-Phenyl-*d*-glucoside was prepared by deacetylation of the tetraacetate with alcoholic ammonia, according to Robertson and Waters.[10]

The dihydrate was obtained by crystallization from water. The anhydrous glucoside melted at 172–173° and showed $[\alpha]_D$ −72.4° in water.

Tetraacetyl-β-benzyl-*d*-glucoside was prepared by a slight modification of the directions of Slotta and Heller.[11] Recrystallized from ether, it melted at 100–101° and showed $[\alpha]_D$ −52.3° in chloroform.

β-Benzyl-*d*-glucoside was prepared from the tetraacetate by deacetylation with alcoholic ammonia, or with sodium methylate according to the method of Zemplén.[12] The product, crystallized from ethyl acetate and dried two hours at 110° in a Fischer pistol, melted at 122–124° and showed $[\alpha]_D$ −53.5° in water.

Tetraacetyl-β-(β-phenylethyl)-*d*-glucoside.[13]—An anhydrous ethereal solution (700 cc.) containing 85 g. of acetobromoglucose and 250 g. of phenylethyl alcohol was shaken with 50 g. of dry silver oxide for four hours, until the solution no longer gave a test for halogen. The mixture was filtered, the ether evaporated, and the excess phenylethyl alcohol removed by distillation with steam. The product was crystallized with the aid of ether–petroleum ether in 58% yield. It separates from that medium in large prisms with square ends; it melts at 72–73° and shows $[\alpha]_D$ −19.2° in chloroform.

Anal. Calcd. for $C_{22}H_{28}O_{10}$: C, 58.4; H, 6.2. Found: C, 58.5; H, 6.2.

β-(β-Phenylethyl)-*d*-glucoside.[14]—Deacetylation of the tetraacetate by sodium methylate or by alcoholic ammonia led to isolation of the glucoside in excellent yield. The product, recrystallized six times from ethyl acetate, separated in very fine needles which united to form small hard lumps. It melted at 119–120° and showed $[\alpha]_D$ −30.5° in water.

Anal. Calcd. for $C_{14}H_{20}O_6$: C, 59.1; H, 7.1. Found: C, 59.3; H, 7.2.

Tetraacetyl-β-(γ-phenylpropyl)-*d*-glucoside.[13]—Acetobromoglucose, phenylpropyl alcohol, and silver oxide were shaken in dry benzene for five hours, and the resulting mixture treated as in the preparation of tetraacetylphenylethylglucoside. The yield was 56%. The product crystallizes from ether–petroleum ether in silky needles, melts at 79–80°, and shows $[\alpha]_D$ −13.1° in chloroform.

Anal. Calcd. for $C_{23}H_{30}O_{10}$: C, 59.2; H, 6.5. Found: C, 59.2; H, 6.6.

β-(γ-Phenylpropyl)-*d*-glucoside.—Deacetylation of the tetraacetate was carried out with alcoholic ammonia, with sodium methylate, and finally with barium hydroxide according to the method used by Fischer and Helferich;[15] this last method yielded crystals in three days, whereas the other two methods produced sirups which could not be induced to crystallize for a month until seed crystals had been obtained. The product separates from ethyl acetate in clusters of rectangular prisms, melts at 100–101°, and shows $[\alpha]_D$ −27.3° in water.

Anal. Calcd. for $C_{15}H_{22}O_6$: C, 60.4; H, 7.4. Found: C, 60.4; H, 7.7.

Tetraacetyl-β-cyclohexyl-*d*-glucoside was prepared according to Pacsu.[16] It melted at 120–121°.

β-Cyclohexyl-*d*-glucoside[17] was prepared by deacetylation of the tetraacetate with alcoholic ammonia. Recrystallized from ethyl acetate, it melted at 133–135° and showed $[\alpha]_D$ −41.5° in water.

Tetraacetyl-β-cyclohexylmethyl-*d*-glucoside.[18]—Acetobromoglucose, cyclohexylmethyl alcohol and silver oxide were shaken together in anhydrous ether and the tetraacetate isolated in a 90% yield by the procedure already mentioned above. The product crystallizes from ether–petroleum ether in very fine needles, melts at 94–95°, and shows $[\alpha]_D$ −22.2° in chloroform.

Anal. Calcd. for $C_{21}H_{32}O_{10}$: C, 56.7; H, 7.3. Found: C, 56.6; H, 7.3.

β-Cyclohexylmethyl-*d*-glucoside.—Deacetylation of the tetraacetate with sodium methylate gave the free glucoside. It crystallizes from ethyl acetate in small prisms which form button-like groups, and becomes granular when filtered. It melts at 122–124°, and shows $[\alpha]_D$ −37.0° in water.

Anal. Calcd. for $C_{13}H_{24}O_6$: C, 56.5; H, 8.8. Found: C, 56.4; H, 9.1.

Tetraacetyl-β-(*p*-xenyl)-*d*-glucoside.[19]—This compound was prepared by the method of Helferich and Schmitz-Hillebrecht,[9] using *p*-hydroxydiphenyl (*p*-xenol) instead of phenol. The product, obtained in a 50% yield, crystallizes from ethyl alcohol in lustrous needles; it melts at 151–152°, and shows $[\alpha]_D$ −13.2° in chloroform.

Anal. Calcd. for $C_{28}H_{28}O_{10}$: C, 62.4; H, 5.6. Found: C, 62.1; H, 5.9.

β-(*p*-Xenyl)-*d*-glucoside.[19]—Deacetylation of the tetraacetate with alcoholic ammonia yielded the desired glucoside. In contrast to the other glucosides listed in this paper, xenylglucoside is not bitter, but tasteless. It is sparingly soluble in hot acetone, benzene, chloroform and acetylene tetrachloride, moderately soluble in hot ethyl acetate, ethyl alcohol, and water. For purification it was recrystallized from hot methyl alcohol, from which it separates in transparent prisms with high luster; upon standing in air the crystals lose their transparency, probably by loss of alcohol of crystallization. The product, after being dried in the air overnight, lost an additional 2% before reaching constant weight on further drying in a Fischer pistol at 100°. The dried glucoside appears to melt at 200°, resolidifies, and then melts finally and sharply at 214–215°. It is readily soluble in pyridine, and in it shows $[\alpha]_D$ −43.3°.

Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.1; H, 6.0. Found: C, 64.9; H, 6.1.

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(10) Robertson and Waters, *J. Chem. Soc.*, 2731 (1930).

(11) Slotta and Heller, *Ber.*, **63**, 1026 (1930).

(12) Zemplén, *Ber.*, **59**, 1254 (1926), and especially Pacsu, THIS JOURNAL, **52**, 2574 (1930).

(13) Prepared and analyzed by Miss Elizabeth M. Hewston.

(14) *Cf.* Bourquelot and Bridel, *Compt. rend.*, **156**, 827 (1913).

(15) Fischer and Helferich, *Ann.*, **383**, 72 (1911).

(16) Pacsu, THIS JOURNAL, **52**, 2569 (1930).

(17) Fischer and Helferich, *Ann.*, **383**, 75 (1911).

(18) Prepared and analyzed by Miss Marion H. Armbruster.

(19) Prepared and analyzed by Miss Eleanor H. Yeakel.

The trimethylphenyl and trimethylbenzyl glucosides are new compounds, in which the methyl groups are presumably located in the 2,4,6-positions of the glucose chain. They are to be described in a later paper, as well as the **heptaacetyl-β-benzyllactoside.** The **heptamethyl-β-benzylcellobioside** has already been reported.[20]

Salicin and aesculin were obtained from the Pfanstiehl Chemical Company, **arbutin** and **phloridzin** from Eimer and Amend.

Catalysts.—**Platinum black** was prepared according to Feulgen;[21] **palladium black** according to Tausz and von Putnoky;[22] **platinum oxide** according to Adams, Voorhees and Shriner;[23] **platinized charcoal** by a method similar to that of Hartung for palladinized charcoal;[24] **Raney nickel** according to Covert and Adkins.[25]

Notes on the Procedures.—The micro-catalytic hydrogenations involving the use of only 2–5 mg. of compound were carried out according to Hyde and Scherp.[8] By connecting the apparatus in suitable fashion with a gas buret it served also for hydrogenation of the 0.25-g. samples. In the latter case, the mixture, after reduction, was filtered from the catalyst, and, if water had been the medium, diluted to 100 cc., and an aliquot part taken for the determination of glucose with Fehling's solution.[26] If glacial acetic acid or alcohol had been used, the solvent was evaporated *in vacuo*, the residue taken up in 100 cc. of water, and the amount of glucose determined as before.

Several experiments in addition to those listed in the tables are described below.

Identification of Glucose from Phenylglucoside.—A small sample of phenylglucoside was reduced with hydrogen and platinum black in glacial acetic acid containing a small amount of hydrochloric acid; the filtered product was evaporated *in vacuo*, the residue taken up and treated with phenylhydrazine.[27] Phenylglucosazone was obtained in about 30% of the calculated amount; it showed no depression in melting point when mixed with an authentic specimen. A second sample treated in the same way but without the platinum black yielded no osazone. Similarly, no glucose was found when phenylglucoside was shaken with platinum black, water and hydrochloric acid in the absence of hydrogen.

Identification of Cyclohexanol from Arbutin.—Five grams of arbutin in 150 cc. of water and 5 cc. of dilute hydrochloric acid, in the presence of 0.5 g. of platinum oxide, absorbed about 2100 cc. of hydrogen at room temperature in two hours. An ethereal extract of the resulting solution, on evaporation left cyclohexanol; this was treated with α-naphthyl isocyanate to form the urethan, which melted at 128–129° and showed no depression when mixed with an authentic specimen.[28]

***o*-Cresylglucoside from Salicin.**—A quarter-gram sample of salicin was hydrogenated in water containing a trace of hydrochloric acid in the presence of 0.05 g. each of platinum black and palladium black. Absorption of hydrogen stopped abruptly after one mole of hydrogen was absorbed (twenty minutes); titration showed a negligible amount of glucose. Evaporation of the remainder of the solution left crystalline *o*-cresylglucoside; once recrystallized from hot ethyl acetate it melted at 162–163° (Kariyone and Kondo give 163–164° for the pure substance[6]). The same product was obtained from salicin, palladium black and water by the rapid absorption of one mole of hydrogen.

Cyclohexylglucoside from Phenylglucoside.—With palladium black as catalyst, phenylglucoside absorbs only three moles of hydrogen. The product, obtained by evaporation of the solution and crystallization from ethyl acetate was identified by its melting point and mixed melting point as cyclohexylglucoside.

The microbalance and weights, and the platinum and palladium used as catalysts, were purchased with the aid of a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. The following new β-glucosides and their tetraacetates have been described: β-phenylethyl, γ-phenylpropyl, cyclohexylmethyl, *p*-xenyl.

2. Catalytic hydrogenation with palladium catalysts results in the complete cleavage of benzyl glycosides; the phenyl, phenylethyl and phenylpropyl glycosides are reduced to the corresponding cyclohexyl derivatives, which are not further affected.

3. Platinum catalysts, of various types and in various solvents, at room temperature and atmospheric pressure, are capable of cleaving both phenyl and benzyl glycosides. This cleavage is incomplete but, in the case of the phenyl compounds, reaches a maximum of about 70% in the presence of a trace of hydrochloric acid.

BRYN MAWR, PENNA. RECEIVED MAY 16, 1934

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[20] Freudenberg, Andersen, Go, Friedrich and Richtmyer, *Ber.*, **63**, 1965 (1930).

[21] Feulgen, *ibid.*, **54**, 360 (1921).

[22] Tausz and von Putnoky, *ibid.*, **52**, 1576 (1919).

[23] "Organic Syntheses," John Wiley and Sons, Inc., New York, Collective Volume I, 1932, p. 452.

[24] Hartung, THIS JOURNAL, **50**, 3372 (1928).

[25] Covert and Adkins, *ibid.*, **54**, 4116 (1932).

[26] The procedure was that described by van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, 1920, p. 121.

[27] Ref. 26, p. 213.

[28] French and Bickel, THIS JOURNAL, **48**, 749 (1926).