bromobenzyl ether and 2-methylphenyl-4-bromobenzyl ether to give 4-hydroxy-3-methyl-3′-bromodiphenylmethane (m. p. 46.4–46.8°) and 4-hydroxy-3-methyl-4′-bromodiphenylmethane (m. p. 75.4–76.0°), respectively. These, too, were shown to be identical to the products of the respective aluminum chloride catalyzed condensations.

Summary

Nine diphenylmethane derivatives were prepared from ortho and para cresols and the three monobromobenzyl chlorides.

The structures of these compounds have been proved by reductive dehalogenation.

The six methylphenylbromobenzyl ethers obtainable from ortho and para cresols were isolated.

The monobromobenzyl-2-methylphenyl ethers obtained from *o*-cresol were rearranged in the presence of zinc chloride and hydrogen chloride to give diphenylmethane derivatives in which the hydroxyl group is in the 4-position.

EAST LANSING, MICHIGAN RECEIVED JANUARY 28, 1950

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The Reaction of Tribenzoyl-β-D-arabinopyranosyl Bromide and Tribenzoyl-α-D-xylopyranosyl Bromide with Methanol

BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

It has recently been shown that tribenzoyl-β-D-ribopyranosyl bromide[1] reacts with anhydrous methanol to give methyl β-D-ribopyranoside tribenzoate in 88% yield. Similarly tetrabenzoyl-α-D-glucopyranosyl bromide was found to give methyl β-D-glucopyranoside tetrabenzoate (90% yield)[2] while tetrabenzoyl-α-D-mannopyranosyl bromide gave methyl α-D-mannopyranoside tetrabenzoate (69% yield).[2] Attention was drawn to the fact that these reactions involved a net reversal of the configuration of carbon 1 in the D-glucose series and retention of configuration at carbon 1 in the D-ribose and D-mannose series. An extension of this investigation to the D-arabinose and D-xylose series will now be described.

Tribenzoyl-β-D-arabinopyranosyl bromide (I) which may readily be prepared from either of the anomeric D-arabinopyranose tetrabenzoates[3] reacts rapidly with anhydrous methanol even at room temperature, methyl α-D-arabinopyranoside tribenzoate (II) being isolated in 72% yield and identified through comparison with the tribenzoate of authentic methyl α-D-arabinopyranoside.[4] In order to ascertain the nature of this reaction and whether its course is as simple as would appear from these facts, a brief polarimetric study was carried out. Since the solubility of both the bromide and the glycoside in methanol at 20° is slight, the rate of the reaction was measured after diluting with methanol a solution of the bromide in pure dioxane. The changing rotation of the resulting reaction mixture is given in Table I together with the rate values derived therefrom; these latter indicate the approximately pseudo-unimolecular nature of the reaction. The initial rotation corresponds closely to that which may be calculated from the rotation of the bromide in chloroform, while the final rotation attained in one hundred and twenty minutes agrees with that derived from the specific rotation of methyl α-D-arabinopyranoside tribenzoate (II) in the same mixture of dioxane and methanol.

Tribenzoyl-α-D-xylopyranosyl bromide (III) was likewise found to react readily with methanol, the product in this case being methyl β-D-xylopyranoside tribenzoate (IV), isolated in 83%

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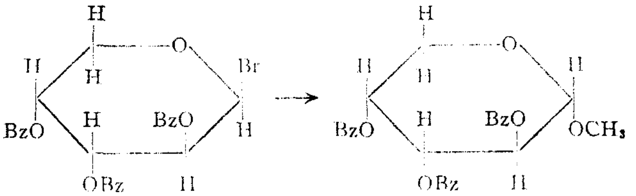
[1] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **70**, 4055 (1948).

[2] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 2200 (1950).

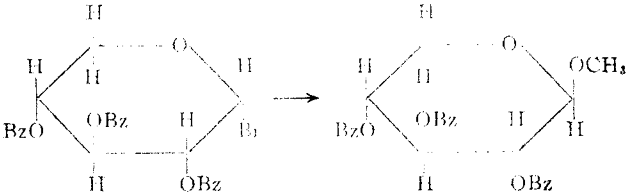
[3] Tribenzoyl-β-D-arabinopyranosyl bromide has been reported by M. L. Wolfrom and C. C. Christman [THIS JOURNAL, **58**, 39 (1936)] and by the present authors [*ibid.*, **69**, 1145 (1947)] as a substance crystallizing from methanol in the form of needles melting at 146° and showing, for the D-isomer, $[\alpha]^{20}\text{D}$ −202° (*c*, 1.27) in chloroform. While simple aliphatic alcohols have frequently been employed for the crystallization of acylohalogen sugars [E. Fischer, M. Bergmann and A. Rabe, *Ber.*, **53**, 2362 (1920); E. Fischer, *ibid.*, **49**, 584 (1916); K. Freudenberg, A. Noë and E. Knopf, *ibid.*, **60**, 238 (1927); L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," Macmillan Co., New York, N. Y., 1937, p. 391] it appeared wise, in view of recent work in this laboratory, to avoid hydroxylic solvents entirely in the repreparation of tribenzoyl-β-D-arabinopyranosyl bromide. The product obtained from a mixture of ether and pentane consisted of prismatic crystals which melted at 147–148°, showed in chloroform $[\alpha]^{20}\text{D}$ −353.3° (*c*, 1.4), and gave analytical data for carbon, hydrogen and bromine conforming with that expected for tribenzoyl-β-D-arabinopyranosyl bromide. On recrystallization from warm methanol the product was converted to needle-shaped crystals, free of halogen and showing $[\alpha]^{20}\text{D}$ −202° in chloroform; that these are in reality methyl α-D-arabinopyranoside tribenzoate is evident from the present research and we wish to join with Drs. Wolfrom and Christman in pointing out that the physical constants of tribenzoyl-β-D-arabinopyranosyl bromide recorded previously by us are in fact those of methyl α-D-arabinopyranoside tribenzoate. While tribenzoyl-β-D-arabinopyranosyl bromide is here described for the first time it should be noted that the isolation in the earlier researches of methyl α-D-arabinopyranoside tribenzoate where tribenzoyl-β-D-arabinopyranosyl bromide was expected does not in any way invalidate the conclusions resulting from those studies.

[4] The preparation of methyl α-D-arabinopyranoside through the reaction of D-arabinose with acidic methanol has been well investigated [C. S. Hudson, THIS JOURNAL, **47**, 267 (1925); F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 520]. However, the separation of this compound from its less soluble anomer which is formed at the same time and in higher yield is laborious. We therefore report here a more satisfactory method of preparation which, starting with the readily preparable triacetyl-β-D-arabinopyranosyl bromide, gives methyl α-D-arabinopyranoside in 77% yield.



I
Tribenzoyl-β-D-arabinopyranosyl bromide

II
Methyl α-D-arabinopyranoside tribenzoate



III
Tribenzoyl-α-D-xylopyranosyl bromide

IV
Methyl β-D-xylopyranoside tribenzoate

TABLE I

REACTION OF TRIBENZOYL-β-D-ARABINOPYRANOSYL BROMIDE WITH 1:9 DIOXANE–METHANOL

0.2386 g. substance in 25.0 ml. of solution at 20°

Time, min.	Rotation (1.0 dm., circular degrees)	k (min., decimal logs)
0	−3.40 (extrapolated)	....
1.5	−3.37	0.0057
3	−3.33	.0064
5	−3.21	.011
10	−3.06	.010
28	−2.47	.013
47	−2.10	.015
60	−1.98	.015
120	−1.77	....
180	−1.77	...

yield and identified by comparison both with material prepared from authentic methyl β-D-xylopyranoside and with a sample obtained in 69% yield from tribenzoyl-α-D-xylopyranosyl bromide by treatment with methanol and silver oxide in the usual manner. The rate of reaction of tribenzoyl-α-D-xylosyl bromide with methanol at 20° was measured polarimetrically in a mixture of dioxane and methanol as with the D-arabinose analog. The rate constants listed in Table II show the reaction to be essentially pseudounimolecular. The rotation at zero time, obtained by extrapolation, corresponds very closely with that of the pure bromide in chloroform; the final rotation is essentially that which may be calculated from the specific rotation of methyl β-D-xylopyranoside tribenzoate (IV) in a similar mixture of dioxane and methanol.

It is to be noted that in the arabinose series a β-D-halide gives rise to the formation of an α-D-glycoside and that in the xylose series an α-D-halide is converted to a β-D-glycoside, inversion of the configuration of carbon 1 having occurred in both cases though in the opposite direction. The configurational changes occurring at carbon 1 as the various benzoylated glycopyranosyl halides that have thus far been investigated react with methanol in the absence of an acid acceptor are summarized in Table III. In accord with present concepts of the role of neighboring groups in replacement reactions[5] it would be expected that those halides having a *trans* relationship between the groups on carbon atoms 1 and 2 would suffer no net inversion of configuration at carbon atom 1 upon reaction with methanol. On the other hand those halides having a *cis* relationship would be expected to react with inversion at carbon atom 1. The data summarized in Table III are in complete agreement with these expectations: in the ribose and mannose series *trans* halides are converted to *trans* glycosides while in the glucose, xylose and arabinose series *cis* halides give rise to *trans* glycosides. With the *cis* halides the product is the same as that obtained in the presence of an acid acceptor; with the *trans* halides the ortho ester which is frequently formed in the presence of acid acceptors[6] is, of course, not obtained under

TABLE II

REACTION OF TRIBENZOYL-α-D-XYLOPYRANOSYL BROMIDE WITH 1:9 DIOXANE–METHANOL

0.2191 g. of substance in 25.0 ml. of solution at 20°

Time, min.	Rotation (1.0 dm., circular degrees)	k (min., decimal logs)
0	+1.04 (extrapolated)	...
1.5	+0.99	0.011
3	+ .95	.011
5	+ .87	.011
8	+ .76	.013
13	+ .54	.017
28	+ .23	.016
59	− .10	.017
178	− .21	.010
298	− .23	...
418	− .22	...

TABLE III

CONFIGURATIONAL CHANGES AT CARBON 1 INCIDENT TO THE CONVERSION OF BENZOYLATED GLYCOPYRANOSYL HALIDES TO BENZOYLATED METHYL GLYCOPYRANOSIDES BY METHANOL IN THE ABSENCE OF AN ACID ACCEPTOR

Series	Benzoylated glycopyranosyl bromide	Benzoylated methyl glycopyranoside
D-Ribose	β	β
D-Glucose	α	β
D-Mannose	α	α
D-Arabinose	β	α
D-Xylose	α	β

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(5) See particularly S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942); S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley & Sons, New York, N. Y., 1949, p. 339.

(6) For example see H. L. Frush and H. S. Isbell, *J. Research Nat. Bur. Standards*, **27**, 413 (1941); H. S. Isbell and H. L. Frush, *ibid.*, **43**, 161 (1949).

acidic conditions, the *trans* glycoside being formed instead. Further examples are currently under investigation in this Laboratory.

The utility of the direct, uncatalyzed reaction of benzoylated glycosyl halides with alcohols as a means of synthesizing glycosides has been further demonstrated through the reaction of tribenzoyl-β-D-arabinopyranosyl bromide with benzyl alcohol. Benzyl α-D-arabinopyranoside tribenzoate, a readily crystallized substance, was obtained in 74% yield; debenzoylation afforded benzyl α-arabinopyranoside, melting at 140–141° and showing in water a specific rotation of +12.3°. The tetrahydropyrane ring structure of this glycoside is highly probable from its mode of preparation; confirmation was obtained through quantitative oxidation with sodium metaperiodate. On a molar basis the substance was found to consume two moles of oxidant, one mole of formic acid being liberated in the process; it is therefore a pyranoside as expected.

Some fifty-six years ago Fischer and Beensch[7] reported the preparation of a benzyl L-arabinoside, through the reaction of benzyl alcohol with L-arabinose in the presence of hydrogen chloride. As is well known, arabinose reacts with methanolic hydrogen chloride to give predominantly methyl β-arabinopyranoside[8] and by analogy it would appear that the compound obtained by Fischer and Beensch is benzyl β-L-arabinopyranoside, *i. e.*, the enantiomorph of the anomer of the lower-melting benzyl α-D-arabinopyranoside obtained in the course of the present research. To confirm this tentative conclusion, D-arabinose was treated with benzyl alcohol and hydrogen chloride and there was easily obtained a benzyl D-arabinoside melting at 172–173° and showing in water $[\alpha]^{20}\text{D}$ −209°, clearly the enantiomorph of the compound reported by Fischer and Beensch. On a molar basis the substance consumed two moles of periodate and liberated one mole of formic acid; the pyranose structure is thus apparent. That this benzyl D-arabinoside belongs to the β-D-series becomes evident from Table IV where it may be seen that the difference between the molecular rotations of the two benzyl D-arabinopyranosides is in fair agreement with that between the molecular rotations of the previously known anomeric benzyl D-glucopyranosides; the relationship of these latter to each other has been shown by Pigman and Richtmyer[9] from the fact that benzyl β-D-glucopyranoside is hydrolyzed by the β-glucosidase of sweet almonds.

TABLE IV

COMPARISON OF THE MOLECULAR ROTATIONS OF SOME BENZYL GLYCOSIDES

Pyranoside	Mol. wt.	$[\alpha]\text{D}$ (H_2O)	$[\text{M}]\text{D}$	Diff.
Benzyl α-D-arabino-	240	+ 12.3°	+ 2,950	
Benzyl β-D-arabino-	240	−209°	−50,200	53,150
Benzyl α-D-gluco-	270	+ 13.4°[a]	+36,200	
Benzyl β-D-gluco-	270	− 55.8°[b]	−15,100	51,300

[a] L. J. Heidt and C. B. Purves, THIS JOURNAL, **66**, 1385 (1944); *cf*. B. Helferich and R. Gootz, *Ber*., **62**, 2788 (1929). [b] E. Fischer and B. Helferich, *Ann*., **383**, 68 (1911).

Acknowledgments.—We are indebted to Mrs. Evelyn G. Peake for combustion analyses and to Mr. Harry W. Diehl for assistance in certain of the preparations.

Experimental[10]

Tribenzoyl-β-D-arabinopyranosyl Bromide.—Twenty-three grams of a mixture of crystalline α- and β-D-arabinose tetrabenzoates,[11] dissolved in 23 ml. of ethylene dichloride, was mixed with 46 ml. of a solution of hydrogen bromide in glacial acetic acid (32%) and left at room temperature for 2.75 hours. The reaction mixture was then diluted with 100 ml. of ethylene dichloride and poured on ice; the resulting non-aqueous layer was freed of acid by successive washings with ice-water and aqueous sodium bicarbonate. After desiccation with sodium sulfate the solution was filtered through a thin layer of decolorizing carbon and concentrated *in vacuo* (40–45° bath) to a light sirup. Upon solution in 10 ml. of anhydrous ether and addition of 30 ml. of pentane, the material began to deposit prismatic crystals. When the rate of crystallization had diminished, 20 additional ml. of pentane was added. After standing overnight at +5° the crystalline mass amounted to 19.6 g. or 92%; it melted at 147–148° and showed in chloroform a rotation of −350.7° (*c*, 1.89). Two recrystallizations from a mixture of ethylene dichloride and pentane gave material with the same melting point and a specific rotation in chloroform of −353.3° (*c*, 1.4).

Tribenzoyl-β-D-arabinopyranosyl bromide is soluble in methylene dichloride and acetone, relatively insoluble in boiling ether and quite insoluble in pentane.

Anal. Calcd. for $C_{26}H_{21}O_7Br$: C, 59.44; H, 4.03; Br, 15.21. Found: C, 59.35; H, 4.30; Br, 15.55.

Methyl α-D-Arabinopyranoside.—A mixture of 10 g. of triacetyl-β-D-arabinopyranosyl bromide (m. p. 140–141°; $[\alpha]^{20}\text{D}$ −288° in $CHCl_3$), 10 g. of Drierite, 10 g. of powdered silver carbonate and 100 ml. of absolute methanol was shaken at 20° for six hours. After filtration through a layer of decolorizing carbon the resulting solution was cooled to 0°, treated with 5 ml. of approximately 2 *N* barium methoxide and left overnight at 0°. The barium was then removed with an equivalent quantity of sulfuric acid and the solution concentrated *in vacuo* to dryness. After solution in 50 ml. of hot ethyl acetate the product (3.4 g., m. p. 132–133°, $[\alpha]^{20}\text{D}$ −18.1° in water, *c*, 0.83) crystallized readily. A second crop of similar material increased the yield to 3.74 g. or 77%. Recrystallization of the first crop from seven parts of absolute ethanol failed to change its melting point and rotation significantly. The enantiomorph of this substance, methyl α-L-arabinopyranoside, has been reported[8] to melt at 131° and show a rotation of +17.3° in water.

Methyl α-D-Arabinopyranoside Tribenzoate. (a) From Methyl α-D-Arabinopyranoside.—Methyl α-D-arabinopyranoside (0.5 g.) was benzoylated in the usual manner using 10 ml. of pyridine and 1.5 ml. of benzoyl chloride. Solution of the product, previously freed of pyridine and excess benzoyl chloride, in 15 ml. of warm methanol led to the rapid development of well-formed clusters of fine, colorless, needle-shaped crystals (1.08 g., 74%) which

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[7] E. Fischer and L. Beensch, *Ber.*, **27**, 2478 (1894).

[8] C. S. Hudson, THIS JOURNAL, **47**, 265 (1925).

[9] W. W. Pigman and N. K. Richtmyer, *ibid.*, **64**, 369 (1942).

[10] Melting points were measured with an Anschütz-type thermometer completely immersed in the bath liquid. Rotations are specific rotations for the D line of sodium at 20°; concentration is expressed in g. of substance per 100 ml. of solution.

[11] H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **69**, 1145 (1947).

melted at 146° and showed in chloroform a rotation of −202° (*c*, 1.27). Recrystallization from 14 parts of methanol failed to change these constants significantly.

Methyl α-D-arabinopyranoside tribenzoate is soluble in ethylene dichloride, acetone, ethyl acetate and warm methanol, insoluble in cold methanol and pentane.

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 68.24; H, 5.24.

(b) **From Tribenzoyl-β-D-arabinopyranosyl Bromide with Methanol.**—Finely powdered tribenzoyl-β-D-arabinopyranosyl bromide (2.00 g.), prepared as described above, was dissolved in 30 ml. of anhydrous methanol by boiling for about eight minutes. Upon cooling, the solution promptly deposited a mass of well-formed, needle-shaped crystals (1.3 g., 72%) which showed a rotation in chloroform of −199° (*c*, 2.07) and melted at 146° either alone or in admixture with a sample of the authentic methyl α-D-arabinopyranoside tribenzoate prepared above.

The Rate of Reaction of Tribenzoyl-β-D-arabinopyranosyl Bromide with 1:9 Dioxane–Methanol at 20°.—Pure tribenzoyl-β-D-arabinopyranosyl bromide (0.2386 g.) was dissolved in 2.50 ml. of pure anhydrous dioxane, diluted to 25.0 ml. with absolute methanol and the reaction followed polarimetrically in a 1-dm. tube at 20°. After 1.5 minutes a rotation of −3.37° was obtained; this was equivalent to a specific rotation of −353.5° and corresponds well with the specific rotation of the starting material in chloroform (−353.3°). The successive readings together with the rate constants calculated therefrom are listed in Table I; practical completion was attained after one hundred and twenty minutes, the solution then showing a rotation of −1.77°. The specific rotation of methyl α-D-arabinopyranoside tribenzoate in 1:9 dioxane–methanol (−202°) leads to a calculated value of −1.75° on the assumption that the bromide was converted quantitatively to this compound.

Methyl β-D-Arabinopyranoside Tribenzoate.—Benzoylation of methyl β-D-arabinopyranoside[8] (1.0 g.) with 10 ml. of pyridine and 2.5 ml. of benzoyl chloride was carried out in the conventional manner. Solution of the resulting sirup, freed of excess reactants, in methanol gave 2.8 g. (96%) of prismatic crystals which, after recrystallization from 9 and then from 5 parts of methanol, melted at 84–85° and showed in chloroform a rotation of −294° (*c*, 0.88). Further recrystallizations failed to change these constants. The solubility of methyl β-D-arabinopyranoside tribenzoate in various solvents closely resembles that of its α-anomer reported above.

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 68.17; H, 5.18.

Benzyl α-D-Arabinopyranoside Tribenzoate.—Six grams of finely powdered tribenzoyl-β-D-arabinopyranosyl bromide was dissolved in 60 ml. of pure benzyl alcohol by shaking gently at 40–50° for about eight minutes. When solution was complete the mixture was cooled to room temperature and seeded[12]; after three days the mass of fine needle-like crystals was removed and washed with ether; yield 3.40 g. The mother liquor and washings were combined and concentrated *in vacuo*, the residual sirup being held at 90° (bath) and a pressure of 0.2–0.4 mm. until the major portion of the benzyl alcohol was removed; solution in approximately 50 ml. of ether then gave an additional 1.25 g. of crystalline material (74% total yield). Two recrystallizations of the crude product (m. p. 144–145°) from 27 parts of hot absolute alcohol afforded, with little loss, material melting at 146–147° and rotating in chloroform −146.7° (*c*, 2.11). Further recrystallizations failed to change these values.

Benzyl α-D-arabinopyranoside tribenzoate is soluble in acetone, sparingly soluble in hot alcohol and ether, insoluble in water and pentane.

Anal. Calcd. for $C_{33}H_{28}O_8$: C, 71.73; H, 5.11. Found: C, 71.74; H, 5.29.

Benzyl α-D-Arabinopyranoside.—Benzyl α-D-arabinopyranoside tribenzoate (3.05 g.) was dissolved in warm chloroform (5 ml.) and treated with absolute methanol (15 ml.) and 2 *N* barium methoxide (0.5 ml.). After twenty-four hours at room temperature the mixture was freed of barium with sulfuric acid and concentrated *in vacuo* (50° bath) to a crystalline mass. Dissolved in 17 ml. of warm absolute alcohol, this residue gave bunches of fine needle-like crystals amounting to 1.15 g. (87%) and melting at 140–141°. After two recrystallizations from warm water the product melted at 140–141° and showed in water a rotation of +12.3°. Benzyl α-D-arabinopyranoside is readily soluble in hot water and alcohol, practically insoluble in cold water.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.82; H, 6.68.

Sodium Metaperiodate Oxidation of Benzyl α-D-Arabinopyranoside.—The glycoside (0.1281 g.) was oxidized in aqueous solution with sodium metaperiodate, using the technique of Jackson and Hudson.[13] After twenty-five hours at room temperature (27°), analysis showed the consumption on a molar basis of 1.99 moles of oxidant and the formation of 0.97 mole of formic acid.

Benzyl β-D-Arabinopyranoside.—Ten grams of pure, powdered D-arabinose was suspended in 40.0 ml. of pure benzyl alcohol and 2.0 g. of dry hydrogen chloride was then passed in. The mixture was warmed to 65° and agitated vigorously with a mechanical stirrer; in about twelve minutes the D-arabinose dissolved and after a total of thirty-one minutes the dark reaction mixture was cooled to room temperature. Three and one-half hours later the reaction mixture was found to have become semi-solid through the precipitation of fine needle-like crystals. An excess (30 g.) of powdered silver carbonate suspended in acetone (to minimize foaming) was then added and, when neutral, the mixture was filtered, the residue being washed with acetone. Concentration of the filtrate *in vacuo* at 60° gave a benzyl alcohol solution which, diluted with 10 ml. of absolute alcohol and held at 5° for two days gave 2.5 g. of white crystalline material melting at 164–167°. Extraction of the residue of silver salts with two 100-ml. portions of boiling absolute alcohol afforded 2.92 g. of similar material making the total yield 5.42 g. or 21%. After three recrystallizations from approximately 17 parts of ethanol the melting point became constant at 172–173° and the substance rotated in water −209° (*c*, 0.41). Fischer and Beensch[7] reported a melting point of 172–173° and a specific rotation in water of +215.2° for the enantiomorph of this compound, benzyl β-L-arabinoside.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.01; H, 6.85.

Sodium Metaperiodate Oxidation of Benzyl β-D-Arabinopyranoside.—The glycoside (0.1285 g.) was oxidized in the same fashion as for its anomer described above. On a molar basis, 2.00 moles of oxidant were found to be consumed while 1.03 moles of formic acid were formed.

Methyl β-D-Xylopyranoside Tribenzoate. (a) **From Methyl β-D-Xylopyranoside.**—Methyl β-D-xylopyranoside (m. p. 156°; $[\alpha]^{22}D$ −65.2° in water) was benzoylated in a manner similar to that used for the corresponding compound of the D-arabinose series. From a concentrated ethanolic solution the product formed a mass of fine needle-shaped crystals in a yield of 85% of the theory. Recrystallized thrice from 4 parts of warm methanol, once from a mixture of 3.6 parts of ether and 2.9 parts of pentane and finally again from 4 parts of methanol, the product melted at 95–96° and showed a rotation of −24.1° in chloroform (*c*, 1.63).

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 68.04; H, 5.30.

(b) **From Tribenzoyl-α-D-xylopyranosyl Bromide with Methanol and Silver Oxide.**—Tribenzoyl-α-D-xylopyranosyl bromide (2.5 g.), prepared as previously de-

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[12] Seed crystals were initially obtained by cooling the reaction mixture in a Dry-Ice and acetone mixture until the major portion of the benzyl alcohol had solidified.

[13] E. L. Jackson and C. S. Hudson, THIS JOURNAL, **59**, 994 (1937).

scribed by Fletcher and Hudson,[14] was mixed with 1.65 g. of dry, finely powdered silver oxide and 17 ml. of methanol and shaken at 20° for seven hours. The solid phase was then removed by filtration and the filtrate concentrated *in vacuo* to a sirup. From a solution in 10 ml. of ethanol this product deposited 1.31 g. of fine needles; a second crop of 0.25 g. raised the yield to 69%. Recrystallized twice from methanol and once from a mixture of ether and pentane the material melted at 93–96°. A mixed melting point with the material obtained in (**a**) above was undepressed.

(**c**) **From Tribenzoyl-α-D-xylopyranosyl Bromide with Methanol.**—Two grams of pure tribenzoyl-α-D-xylopyranosyl bromide was dissolved in 20 ml. of anhydrous methanol by boiling for five minutes. Cooled to room temperature, seeded and left at +5° overnight, the reaction mixture yielded 0.95 g. of material melting at 94–96°. Concentration of the mother liquor led to the isolation of 0.55 g. more material (m. p. 91–95°), raising the yield to 83% of theory. Recrystallized from methanol and then from a mixture of ether and pentane the product melted at 93–96° either alone or in admixture with a sample of methyl β-D-xylopyranoside tribenzoate prepared as described in (**a**).

The Rate of Reaction of Tribenzoyl-α-D-xylopyranosyl Bromide with 1:9 Dioxane–Methanol at 20°.—This measurement was conducted in the same manner as that employed for the arabinose analog described above. The bromide (0.2191 g.) was dissolved in 2.50 ml. of pure anhydrous dioxane and diluted with anhydrous methanol to 25.0 ml., the changing rotation of the resulting solution being observed in a 1-dm. tube at 20° and listed in Table II. The extrapolated rotation at zero time (+1.04°) corresponds to a specific rotation of +118.0°, *i. e.* close to the specific rotation of +118.7° recorded[14] for tribenzoyl-α-D-xylopyranosyl bromide in chloroform. The reaction was essentially completed in one hundred and eight minutes, the final rotation being identical to that (−0.23°) which may be calculated from the specific rotation of methyl β-D-xylopyranoside tribenzoate in 1:9 dioxane–methanol (−28.4° (*c*, 0.77)), upon the assumption that this product was formed in quantitative yield.

Summary

Tribenzoyl-β-D-arabinopyranosyl bromide reacts with anhydrous methanol to give methyl α-D-arabinopyranoside tribenzoate in good yield. Similarly tribenzoyl-α-D-xylopyranosyl bromide reacts with methanol to give methyl β-D-xylopyranoside tribenzoate.

In the absence of an acid acceptor all the benzoylated glycopyranosyl halides thus far investigated which have a benzoyloxy group at carbon 2 *trans* to the halogen, react with methanol without net Walden inversion while those halides having a *cis* relationship between the groups on carbon atoms 1 and 2 react with inversion at carbon 1. These facts are in accord with current concepts of the influence of neighboring groups in replacement reactions.

The value of the reaction as a preparative method has been demonstrated through the synthesis of benzyl α-D-arabinopyranoside.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

The Isolation of Quercitrin from Peanut Hulls

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In a search for abundant sources of vitamin P active flavonoid pigments,[2,3] quercitrin, the 3-rhamnoside of quercetin (3,5,7,3′,4′ pentahydroxyflavone) has been isolated from waste peanut hulls.

Lavollay and Neumann[4] report that this substance arrests the autoxidation of epinephrine. Richardson, El-Rafey and Long[5] found quercitrin to be an effective antioxidant for lard and for milk fat.

Quercitrin has previously been isolated from several sources, such as *Quercus tinctoria*[6] and golden rod.[7]

Experimental

Isolation.—The peanuts were grown on a farm near Norman and were harvested about September 1, 1948. They were shelled within a week after harvesting. One thousand ninety grams of peanut hulls was extracted exhaustively with boiling 95% ethanol. After the extract was filtered with suction, using Johns–Manville Celite as a filter-aid, it was concentrated to one-twelfth of its original volume in a flash-type evaporator.[8] The concentrate was next filtered, and water was added dropwise to precipitate a brown resinous material. This brown material was removed by swirling the flask vigorously. The resin adhered to the walls of the flask and the clear, straw-colored supernatant liquid was decanted. More water was added to the supernatant liquid until a yellow precipitate formed. After remaining in the cold for several days, this precipitate was filtered off and dissolved in acetone. Water was added to the acetone solution until incipient precipitation had occurred. The cloudy solution was set aside for three days and then filtered—the precipitate being discarded. To the filtrate, water was again added, this time until a yellow precipitate formed. The precipitate was filtered off and resuspended in water. The suspension was heated on the water-bath until only a small amount of undissolved matter remained. This undissolved material was removed by filtration. On cooling the filtrate, a yellow precipitate separated. This precipitate was recrystallized twice from boiling water.

The resulting yellow solid, after air drying, melted at 185° uncor. Moore reports that quercitrin melts at 185°.[9]

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[1] At present, Rhodes Scholar, Oxford University, Oxford, England.

[2] Rusznyak and Szent-Gyorgy, *Nature*, **138**, 27 (1936).

[3] Bentsath, Rusznyak and Szent-Gyorgy, *ibid.*, **138**, 789 (1936).

[4] Lavollay and Neumann, *Compt. rend.*, **212**, 251 (1941).

[5] Richardson, El-Rafey and Long, *J. Dairy Sci.*, **30**, 397 (1947).

[6] Bolley, *Ann.*, **37**, 101 (1841).

[7] Guthrie, O'Connor, Stansberg and Savich, THIS JOURNAL, **66**, 1794 (1944).

[8] Ciereszko, presented before the Fifth Southwestern Regional Meeting of the American Chemical Society at Oklahoma City, December, 1949.

[9] Moore, *Proc. Chem. Soc.*, **26**, 182 (1910).