taken into consideration. With hydrogen chloride, we can neglect the association of the acid,[1] particularly in the presence of excess menthone. Then, $a = [MA] + [A]$; $[MA] = K[M][A]$, and, because $m \gg a$, $[MA] = Km[A]$. Hence, $A = a/(1 + Km)$; $[MA] = Kma/(1 + Km)$, and $r = Kma^2/(1 + Km)$.

From the last equation follows the dependence of the reaction rate on the square of the acid concentration which is shown in Table II. The dependence on the menthone concentration is more complex. At high concentrations of the menthone, the rate should become independent of the substrate concentration. When the menthone concentration is lowered beneath a certain value, the rate should fall with increasing rapidity as the menthone concentration becomes smaller. The value of the menthone concentration above which the rate is practically independent of the menthone concentration and below which the rate sinks markedly with this concentration depends on K. If K is about equal to or greater than 10, a sinking of the rate with the menthone concentration will be unmistakable only at menthone concentrations which are lower than those reported in Table III. In view of the strong complex formation of trichloroacetic acid with menthone[4] and the still greater protolytic activity of hydrogen chloride, such a high value of K is to be expected. The results of Table III are therefore in agreement with the suggested mechanism.

It may be noted in Table III that the rate in the experiment with 0.5 mole/liter of menthone is somewhat lower than with the higher menthone concentrations, but this difference is not well enough established to be significant. In other experiments, the menthone concentration was lowered to 0.25 and to 0.1 mole/liter,[2] and a more pronounced sinking of the rate was noted—by about 20 and 40%, respectively. This dependence would roughly agree with a value for K of about 15. However, the isolated experiments in which relatively small changes of rotation were observed, would need checking before they could be considered as reliable.

Acknowledgment.—We should like to thank Professor Gerald Branch of the University of California for helpful criticism in the preparation of this paper.

Summary

1. The rate of inversion of *l*-menthone by hydrogen chloride in benzene was studied in its dependence on the concentration of both compounds.

2. The results confirm that the inversion occurs by interaction of a binary acid menthone complex with a further molecule of the acid.

ROCHESTER, NEW YORK RECEIVED OCTOBER 15, 1942

(4) Weissberger, THIS JOURNAL, **65**, 102 (1943).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 276]

Lead Tetraacetate Oxidations in the Sugar Group. III.[1] Triphenylmethyl Ethers of β-Methyl-D-arabinopyranoside and of α-Methyl-L-fucopyranoside. The Determination of their Structures[2]

BY ROBERT C. HOCKETT AND DWIGHT F. MOWERY, JR.[3]

The extraordinarily numerous glucose derivatives which have been recorded in the literature were prepared, one supposes, with the purpose of revealing the laws of substitution in the sugar molecule. The ultimate object of such work is presumably to provide a roster of reference compounds for use in studies of structure and as intermediates for controlled syntheses. This task has proved more difficult in the sugar group than, for example, it was in the study of substitutions in benzene. No simple statistical method comparable to Körner's absolute method of distinguishing the ortho, meta and para disubstituted benzenes[4] can be applied to the analogous problem of differentiating the disubstitution products

(1) Number II of this series, THIS JOURNAL, **61**, 1667 (1939). *Cf.* Hockett and Maynard, *ibid.*, **61**, 2111 (1939).

(2) This paper was read before the Division of Sugar Chemistry at the St. Louis meeting of the American Chemical Society in April, 1941. It is taken from a thesis submitted by Dwight F. Mowery, Jr., to the Graduate School of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy in November, 1940.

(3) Mr. Mowery was Louis Francisco Verges Fellow in Chemistry in 1939–1940.

(4) Körner, *Gass. chim. ital.*, **4**, 305 (1874); Cohen, "Organic Chemistry for Advanced Students," London, 1923, Vol. II, p. 408.

of glucose, and such problems have often been complicated by uncertainties regarding the size and stability of the hemiacetal rings.

Until recently, moreover, very little use has been made of *differences in reactivity* among the various hydroxyl groups for the preparation of partially substituted sugars, except in the case of the reducing group itself, which has very unique properties. The notable exception to this statement has been the use of triphenylchloromethane for etherifying primary hydroxyl groups in the presence of secondary ones.[5] The possibility of doing this in a practical fashion rests upon (1) the relatively high reactivity of the primary hydroxyl group and (2) the fortunate crystallizing properties of trityl ethers.[6] More recent studies show the possibility of using benzoyl chloride and *p*-toluenesulfonyl chloride in like fashion.[7]

The possibility of utilizing differences in the reactivities of the secondary hydroxyl groups has apparently been neglected (1) because it has been assumed that such differences would be too small to be very valuable and (2) because there was no simple method available for determining the position of substituent groups.

The observation (1) that secondary alcohols react with triphenylchloromethane fast enough for practical usefulness[8] and (2) the introduction of lead tetraacetate as a tool for structure determination[1] have now made possible the opening of a new chapter in carbohydrate chemistry.

As the first project in this direction, we elected to study the action of triphenylchloromethane mole for mole upon β-methyl-D-arabinoside in pyridine solution. As is shown in an accompanying table, the possible products are seven in number; three isomeric monotrityl-β-methyl-D-arabinopyranosides, three isomeric ditrityl ethers and one tritrityl derivative should be obtained.

It appears *a priori* that oxidations by lead tetraacetate should establish a strong presumption as to which isomer is which since formula II represents the only monotrityl ether which should be inactive toward this reagent. Compounds I and III should be distinguishable through their rates of reaction on account of their possession, respectively, of a *trans* and a *cis*-glycol struc-

(5) Helferich, *Z. angew. Chem.*, **41**, 871 (1928).

(6) Hockett, Fletcher and Ames, THIS JOURNAL, **63**, 2516 (1941).

(7) Compton, *ibid.*, **60**, 395 (1938); Cramer, Hockett and Purves, *ibid.*, **61**, 3463 (1939); Brigl and Grüner, *Ber.*, **65**, 641 (1932); Hockett and Downing, THIS JOURNAL, **64**, 2463 (1942).

(8) Hockett and Hudson, THIS JOURNAL, **53**, 4456 (1931); **56**, 945 (1934); Jackson, Hockett and Hudson, *ibid.*, **56**, 947 (1934).

ture.[9] A similar technique should also permit distinction of the ditrityl ethers. While all these should be inactive toward lead tetraacetate, it should be possible to convert them all to monoacetates and then to remove the trityl groups by acid hydrolysis to yield monoacetyl β-methyl-D-arabinosides to which the same considerations apply as to the monotrityl ethers. The unique tritrityl derivative would be identified by its analysis.

In the present work, we succeeded in isolating three of the seven possible ethers and the acetates corresponding to two of these. We have also prepared again, the monotrityl-α-methyl-L-fucopyranoside previously described by Hockett and Hudson,[10] since the same oxidation method should be applicable to the solution of its structure. The diacetate corresponding to this fucose derivative is described for the first time.

TABLE I

Compound	M. p., °C.	Rotation[14] ($CHCl_3$), °
Monotrityl-β-methyl-D-arabinopyranoside, A	143–145	− 75.8
Monotrityl-β-methyl-D-arabinopyranoside, B	157–159	−103.7
Ditrityl-β-methyl-D-arabinopyranoside	192–193	− 81.7
Monotrityl-α-methyl-L-fucopyranoside	127–128	− 58.0
Diacetyl monotrityl-β-methyl-D-arabinopyranoside (from B)	202–203	−107.6
Monoacetyl ditrityl-β-methyl-D-arabinopyranoside	193–194	− 98.8
Diacetyl monotrityl-α-methyl-L-fucopyranoside	208–210	− 32.5

An unexpected complication in the projected method of identification arose when it was found that secondary trityl ethers were slowly cleaved by glacial acetic acid[11] which is ordinarily used as the solvent in rate of oxidation experiments. The rate of cleavage could be measured either polarimetrically or by pouring aliquots of the acetic acid solution of trityl ether into cold water at measured intervals, decanting the aqueous solution from insoluble materials and determining the amount of free glycoside in the water layer (polarimetrically). All three monotrityl ethers were cleaved at very nearly the same rate and the two methods gave closely agreeing results. Hence

(9) *Cf.* Hockett and McClenahan, THIS JOURNAL, **61**, 1667 (1939).

(10) Hockett and Hudson, *ibid.*, **56**, 945 (1934).

(11) More recently we have adopted the practice of controlling the moisture content of acetic acid by direct titration as described by Almy, Griffin and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940). Acetic acid of the quality used in this research has usually been found to contain about one-half of one per cent. water but the sample used in these experiments was not analyzed.

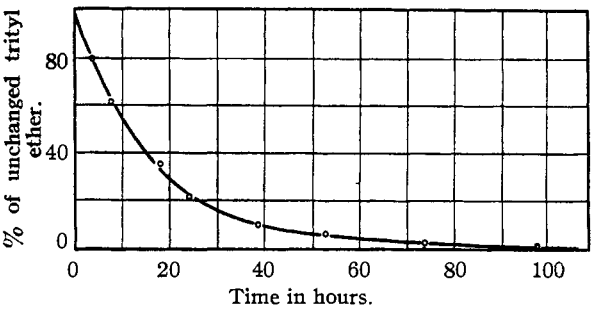


Fig. 1.—Fission of secondary trityl ethers by glacial acetic acid at 20°.

the single curve of Fig. 1 may be used to represent all six measurements. Rate constants calculated by the unimolecular law were

Substance	$k = \frac{1}{t} \log \frac{1}{1-\alpha}$ (t = hr.)
2-Trityl-β-methyl-D-arabinopyranoside (A)	0.0494
3-Trityl-β-methyl-D-arabinopyranoside (B)	.0472
2-Trityl-α-methyl-L-fucopyranoside	.0551

Since the trityl ethers were perfectly stable in pyridine, we first measured their rates of oxidation in this solvent in the hope that it might serve in place of acetic acid. Because all the reactions are more rapid in the base, it was necessary to follow them at a lower temperature (0°) and to plot the curves in terms of minutes rather than hours. The oxidations in pyridine solved definitely the structure of monotrityl-β-methyl-D-arabinoside B (m. p. 157–159°) since this one was not attacked by the lead salt.

To it, therefore, structure II was assigned. In pyridine solution, however, the structure of monotrityl-β-methyl-D-arabinoside A could not be determined satisfactorily since the difference between *cis*- and *trans*-glycols was indistinct as

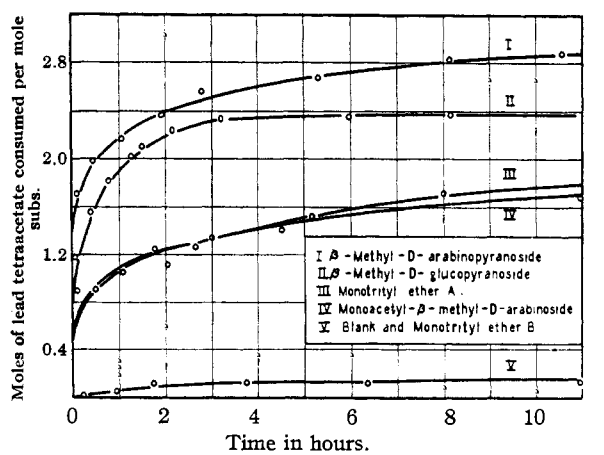


Fig. 2.—Lead tetraacetate oxidations in pyridine at 0°.

demonstrated to our satisfaction by study of a number of controls, including β-methyl-D-glucopyranoside (*trans–trans*) and β-methyl-D-arabinopyranoside (*cis–trans*), (Fig. 2).

Hence we returned to the use of acetic acid solutions and made allowance for the acetolysis of the trityl groups from the known rate of that reaction. The identified 2-trityl methyl-arabinoside provided a case for testing the validity of this procedure. By a graphical method, the rate of acetolysis curve for monotrityl-β-methyl-D-arabinoside B was combined with a curve representing the rate of oxidation of free β-methyl-D-arabinoside, to give a theoretical curve for the consumption of lead tetraacetate by the trityl ether (Fig. 3). Figure 4 shows the excellent agreement attained between theory and observation. This graph also shows the behavior to be expected of a 4-trityl-β-methyl-D-arabinopyranoside. The behavior of monotrityl isomer A is distinctly different from either of these (Fig. 4). In five hours it had consumed three-quarters of a mole of oxidant although, at such a time interval, only one-quarter of the trityl groups would have been removed. A conclusion that isomer A is 2-trityl-β-methyl-D-arabinopyranoside seems quite justifiable.

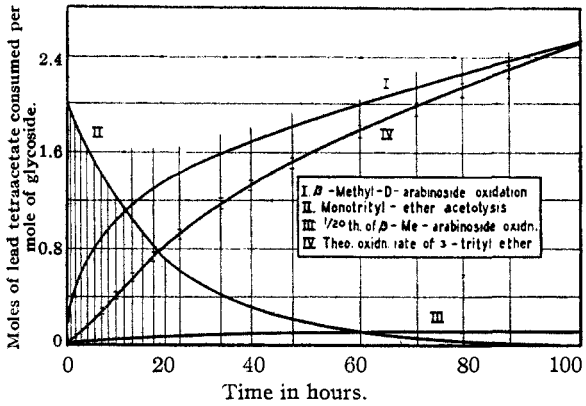


Fig. 3.—Graphical determination of theoretical rate of consumption of lead tetraacetate by 3-trityl-β-methyl-D-arabinopyranoside.

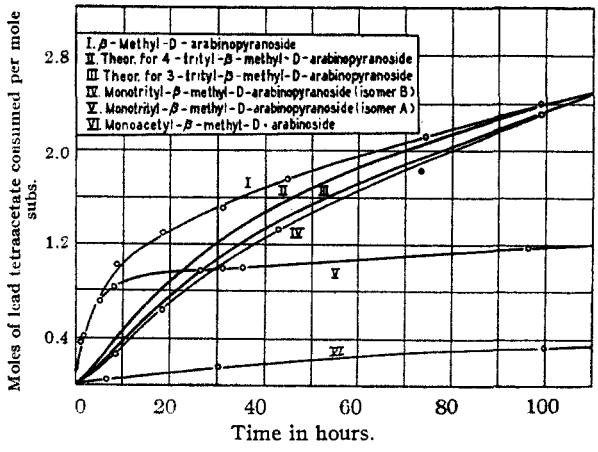
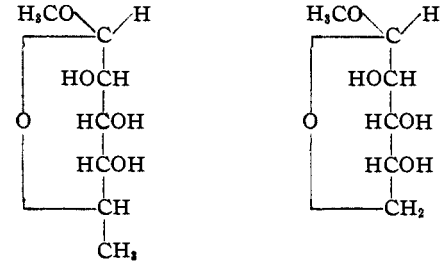


Fig. 4.—Oxidations in acetic acid at 0°.

The case of α-methyl-L-fucopyranoside is strictly analogous since this substance differs from β-methyl-D-arabinopyranoside only in that a methyl group is substituted for one hydrogen on carbon number five, a relationship somewhat obscured by the conventionalities of nomenclature



Exactly analogous procedures and reasoning led to designation of the ether (m. p. 127–128°) as 2-trityl-α-methyl-L-fucopyranoside. The conclusion that these particular trityl ethers of the two glycosides are closely related in structure is supported by the observation that their molecular rotations are very similar

Substance	$[M]D_{20}$ $CHCl_3$
2-Trityl-α-methyl-L-fucopyranoside	−24,360
2-Trityl-β-methyl-D-arabinopyranoside	−25,358

The plan for assigning structure to the ditrityl-β-methyl-D-arabinoside was carried out successfully. A weighed sample of the crystalline monoacetyl ditrityl-β-methyl-D-arabinoside was dissolved in glacial acetic acid and allowed to stand until acetolysis of trityl groups was complete. An aliquot was then oxidized with lead tetraacetate in the usual manner without removal of trityl acetate. Control experiments showed that this ester is unattacked by the oxidant. The rate of oxidation in acetic acid (Fig. 4) was characteristic of a *trans*-configuration; hence the acetyl group is assigned to carbon four and the two trityl groups to positions two and three (formula V).

This structure for the ditrityl ether suggests that either one of our monotrityl methyl arabinosides might be expected to form some of this

ditrityl ether on further treatment with triphenylchloromethane. This expectation was realized on tritylation of isomer B, but isomer A would not undergo any further reaction with this agent.

The question of relative reactivity of the hydroxyl groups receives a partial answer from the present data. The yield of 2-trityl ether from α-methyl-L-fucopyranoside was 81.5% of the glycoside which entered into reaction. This indicates a much higher reactivity of the hydroxyl group in the 2-position, under the conditions employed. In the case of β-methyl-D-arabinoside, the reactivity ratio is not quite so favorable to the 2-hydroxyl group. The isolated 2-trityl ether represented 40% of the glycoside etherified while the 3-isomer represented 28% and the ditrityl ether represented 6% of the glycoside converted. The remaining 26% of sirupy product unfortunately was not studied further. It represents the maximum possible yield of the third isomer but probably is contaminated by some of the 2- and 3-trityl ethers.

These studies will be continued in order to learn how generally the 2-hydroxyl group is the most reactive of the secondary alcohol groups in glycosides and the extent to which its relative reactivity may be altered by changing the configuration of carbon one.

The potential usefulness of these compounds in synthesis is manifest. The ditrityl ether is available for introducing substituents into the four position, after which the trityl groups may be removed by acetolysis at room temperature. The 2- and 3-monotrityl ethers can perhaps be acetylated and acetolyzed to yield arabinose derivatives with free hydroxyl groups at the 2- and 3-positions, respectively. It is our intention to investigate several syntheses based upon these intermediates.

Experimental

D-Arabinose.—This sugar was prepared from calcium D-gluconate by a modification of the method of the senior author and C. S. Hudson.[12]

β-Methyl-D-arabinopyranoside.—This compound, prepared as described by Hudson[13] for the L-isomer, showed a rotation[14] of −243° (*C*, 1.1200; H_2O).

L-Fucose.—The sugar was obtained from *Ascophyllum nodosum* as described by Hockett and Hudson.[15]

α-Methyl-L-fucopyranoside.—Prepared as described by Hockett and Hudson, this glycoside rotated[14] −194.3° (*C*, 1.0768; H_2O).

2-Trityl-β-methyl-D-arabinopyranoside (A).—Twenty grams (0.133 mole) of the glycoside was dissolved in 200 cc. of pyridine which had been dried over solid potassium hydroxide and redistilled, 40.8 g. (0.16 mole) of triphenylchloromethane was added and the mixture was kept at room temperature until no further change in rotation occurred (eighteen days). Then water was added dropwise to turbidity and the solution, on standing overnight, deposited 11 g. of triphenylcarbinol. By further addition of water to the filtrate, the separation of 8 g. of another substance was induced. This optically active compound was purified to constant properties from absolute ethanol. The clustered needles became solvent-free after six days of drying in high vacuum at 80° and then melted 143–145° (uncor.) and rotated[14] −79.7° (*C*, 1.698; ethanol, 21°) or −75.8° (*C*, 3.001; $CHCl_3$, 21°). The remaining sirup was poured into three liters of ice-water. The optical rotation of the aqueous extract showed that approximately nine grams of the glycoside had failed to react. The precipitated gum was dried and then taken up in 95% alcohol, whereupon 2.4 g. of material failed to dissolve or crystallized out promptly on cooling. From the alcoholic extract, there was obtained 4.5 g. of material melting at 143–145° (uncor.) which proved to be identical with that whose isolation was described above; total yield, 12.5 g. or 40% of the arabinoside which reacted. This compound is soluble in alcohol, chloroform and ether, insoluble in water.

Anal. Calcd. for $C_{25}H_{26}O_5$: C, 73.90; H, 6.40. Found: C, 73.7, 74.1; H, 7.00, 7.11.

By the method of Valentin[16] we obtained 98.5, 101.3 and 100.7% of the tritanol calculated for a monotrityl ether of β-methyl-D-arabinopyranoside.

2,3-Ditrityl-β-methyl-D-arabinopyranoside.—The alcohol-insoluble material described above could be recrystallized from hot ethyl acetate from which it separates without solvent of crystallization. After one such treatment it attained constant properties, melting 191–192° (uncor.) and rotating[14] −81.7° (*C*, 1.695; $CHCl_3$) −58.6° (*C*, 2.103; pyridine; 26°). It is soluble in chloroform, ethyl acetate and ether, very difficultly soluble in alcohol and insoluble in water.

Anal. Calcd. for $C_{44}H_{40}O_5$: C, 81.47; H, 6.17. Found: C, 81.4, 81.5; H, 6.79, 7.03.

Trityl determinations by Valentin's method[16] gave 94.5 and 98.2% of the tritanol calculated for a ditrityl-β-methyl-D-arabinopyranoside. When the ditrityl ether is the desired product, it will obviously be better to use a

Molar ratio of chloride to sugar derivative (5 g. β-Me-arab.)	Vol. of pyridine soln., cc.	Temp., °C.	Time, days	Unreacted β-Me-arab., g.	Yield of ditrityl ether, %
1	63.0	23	16	2.4	3
2	93.0	23	31	1.2	5
4	132.0	23	38	0.7	12
2	70.5	60	12	2.5	4
*4	139.0	60	7	0.1	50
6	196.0	60	7	0.25	45

(12) R. C. Hockett and C. S. Hudson, THIS JOURNAL, **56**, 1632 (1934).

(13) Hudson, *ibid.*, **47**, 265 (1925).

(14) All rotations cited in this paper are specific rotations of the D line of sodium at 20° unless otherwise specified.

(15) Hockett and Hudson, THIS JOURNAL, **61**, 1658 (1939).

(16) Valentin, *Coll. Czechoslov. Chem. Comm.*, **3**, 499 (1931).

larger proportion of triphenylchloromethane. Several experiments were made in order to learn what conditions are more favorable for production of this substance. The table summarizes our findings.

A 50% yield of the pure compound may be obtained very easily under the conditions marked with a star, by pouring the reaction products into ice-water, decanting the water from the insoluble gum, leaching alcohol-soluble products from the gum with cold absolute ethanol and recrystallizing the residue once or twice from hot ethyl acetate. The ease of separation suggests that this procedure will give a good estimate of the ditrityl ether present in mixtures.

3-Trityl-2,4-diacetyl-β-methyl-D-arabinopyranoside.—The alcoholic mother liquors from separation of ditrityl-methyl-arabinoside and from 2-trityl-methyl-arabinoside were concentrated solvent-free under reduced pressure. The residue was treated for six days at 0° with 150 cc. of dry pyridine and 150 cc. of acetic anhydride. The product, recovered by pouring the mixture into ice-water and neutralizing the excess acetic acid with sodium bicarbonate, separated as thick hexagonal prisms from a concentrated absolute ethanol solution; yield, 10 g. The compound is soluble in chloroform and ethyl acetate, less soluble in alcohol and insoluble in water. After recrystallization to constant properties from ethyl acetate and drying at 85° in high vacuum, the substance melted 202–203° (uncor.) and rotated[14] −107.6 (*C*, 1.958; $CHCl_3$).

Anal. Calcd. for $C_{28}H_{30}O_7$: C, 71.01; H, 6.12. Found: C, 71.3, 71.0; H, 6.50, 6.70. Trityl determination according to Valentin[16] gave 97.2 and 98.3% of the calculated amount of tritanol.

3-Trityl-β-methyl-D-arabinopyranoside (B).—Two grams of the diacetate was heated under reflux for two and one-half hours with 30 cc. of methanol containing sodium methylate (0.02 g. of Na per cc.). Following removal of sodium as sodium carbonate, and cooling of the solution, 1.6 g. of crystals separated. After recrystallization from methanol to a constant rotation and drying ten hours at 50° in a high vacuum, the substance melted 157–159° (uncor.) and rotated[14] −103.7° (*C*, 1.957; $CHCl_3$); −93.3° (*C*, 1.924; CH_3OH). The compound separates from methanol with two molecules of solvent. Loss in weight on drying was 12.7%; calculated for two CH_3OH, 14.6%.

Anal. Calcd. for $C_{25}H_{26}O_5$: C, 73.90; H, 6.40. Found: C, 73.7, 73.5; H, 6.70, 7.10. Trityl determination according to Valentin[16] gave 96.4 and 97.7% of the calculated amount of tritanol.

4-Acetyl-2,3-ditrityl-β-methyl-D-arabinopyranoside.—A sample of 1.6 g. of the ditrityl ether was mixed with 30 cc. each of pyridine and acetic anhydride and kept at room temperature for fourteen days. The mixture was poured into water, excess acetic acid was neutralized with sodium bicarbonate and the insoluble material which crystallized in the mixture was filtered; yield, 1.7 g. Twice recrystallized from ethyl acetate, the product melted 193–194° (uncor.) and rotated[14] −98.8° (*C*, 1.340; $CHCl_3$) and −109.7° (*C*, 2.280; pyridine; 26°). Because the melting point was very close to that of the starting material, a mixed melting point was taken and a depression of fifteen degrees was observed.

Anal. Calcd. for $C_{46}H_{42}O_8$: C, 80.0; H, 6.08. Found: C, 78.7, 78.4; H, 6.06, 6.04.

2-Trityl-α-methyl-L-fucopyranoside.—Prepared as described by Hockett and Hudson,[8] this compound melted at 127–128° (cor.) and rotated −58.0° (*C*, 2.158; $CHCl_3$).

2-Trityl-3,4-diacetyl-α-methyl-L-fucopyranoside.—The pyridine mother liquor from which 2-trityl-α-methyl-L-fucopyranoside separated, was poured into water and the insoluble gum was dried and dissolved in absolute ethanol. When no crystalline material was obtained from ethanol solution, the solvent was removed and the residue was acetylated just as described above in the case of the arabinose derivative. A product was obtained which was recrystallized from ethyl acetate as large clear prisms. Dried to constant weight these melted 208–210° (uncor.) and rotated −37.5° (*C*, 2.335; $CHCl_3$). They are readily soluble in chloroform and ethyl acetate, less soluble in alcohol and insoluble in water.

Anal. Calcd. for $C_{30}H_{32}O_7$: C, 71.50; H, 6.35. Found: C, 71.3, 71.6; H, 6.85, 6.48. Trityl analysis according to Valentin[16] gave 100.0% of the tritanol calculated.

Deacetylation of 2-Trityl-3,4-diacetyl-α-methyl-L-fucopyranoside.—When this monoacetate was deacetylated as described above in the case of an arabinose derivative, there was obtained a monotrityl-α-methyl-L-fucopyranoside identical with that obtained directly by crystallization. No isomeric monotrityl ether or ditrityl ether of α-methyl-L-fucopyranoside was isolated.

Action of Four Moles of Triphenylchloromethane upon α-Methyl-L-fucopyranoside at 60°.—Since these conditions gave high yields of ditrityl-β-methyl-D-arabinopyranoside, 5 g. of the α-methyl-L-fucopyranoside and 31.3 g. of triphenylchloromethane were dissolved in 100 cc. of dry pyridine and kept at 60° for seven days. No product difficultly soluble in alcohol was obtained. All ditrityl ethers so far known are very sparingly soluble in ethanol.

Action of Triphenylchloromethane upon 2-Trityl-β-methyl-D-arabinopyranoside.—A sample of 1.1 g. of the monotrityl ether was mixed with 10 cc. of dry pyridine and 3.28 g. (4.36 moles to one) of triphenylchloromethane and kept at 60° for ten days. Darkening prevented polarimetric observation. A quantity of 1.9 g. of $(C_6H_5)_3CCl \cdot C_5H_5N$ equivalent to 1.5 g. of triphenylchloromethane separated from the solution. After pouring into water, 1.5 g. of tritanol was recovered. No ditrityl ether was found despite the favorable characteristics of the substance.

Action of Triphenylchloromethane upon 3-Trityl-β-methyl-D-arabinopyranoside.—A very similar experiment was conducted with 2.0 g. of the 3-trityl isomer and 0.8 g. of 2,3-ditrityl-β-methyl-D-arabinopyranoside was isolated melting 192–193° (uncor.); mixed melting point with previously prepared material, 190–192°; rotation[14] −81.5° ($CHCl_3$).

Rate of Oxidation Measurements in Acetic Acid (Fig. 4).—These were conducted as described by Hockett and McClenahan.[9] The mole fractions of substances used as samples varied somewhat but were in the vicinity of 0.0005 mole. Since the excess of lead tetraacetate was large (about 7 moles to one), the rates were not very sensitive to small variations in concentration of substrate. No extreme precautions were taken to dry the acetic acid. Similarly prepared acid has subsequently been found to contain about one-half of one per cent. water which is just suf-

ficient to have a measureable influence on oxidation rates.[17] The acid was rendered aldehyde-free by treatment with chromic acid.

Rate of Oxidation Measurements in Pyridine (Fig. 2).—Since lead tetraacetate attacks picolines, it was necessary to free pyridine from homologs by heating under reflux with chromic acid. Standard solutions of lead tetraacetate in such pyridine were stable enough to be used in making rate of oxidation measurements. Since the reactions are more rapid in pyridine, reaction mixtures were kept at 0° in a thermostat. Oxidation curves were measured for about eight glycosides previously measured in acetic acid as well as for the trityl ethers. Because of the slow decomposition of the standard solution, blanks were run in parallel with samples.

The Action of Glacial Acetic Acid upon 2,3-Ditrityl-β-methyl-D-arabinopyranoside.—A sample of 0.1725 g. of ditrityl methylarabinoside in 10 cc. of glacial acetic acid kept at 60° for two days, gave the calculated quantity of tritanol (weighed in a Gooch crucible) when poured into water.

The Action of Glacial Acetic Acid upon 2,3-Ditrityl-4-acetyl-β-methyl-D-arabinopyranoside.—A weighed sample of this substance was allowed to stand for three days at 60° in glacial acetic acid solution. Then the acetic acid was removed by distillation under reduced pressure, the residue was dissolved in dry, picoline-free pyridine and a measured volume of standard lead tetraacetate in pyridine was added. Titration of aliquot parts showed a rapid utilization of one mole (plus) of lead tetraacetate, showing that removal of trityl groups was complete under the conditions used (Fig. 2).

The Action of Glacial Acetic Acid upon 2,4-Diacetyl-3-trityl-β-methyl-D-arabinopyranoside.—No detritylation was observed with this ether at room temperature. Addition of 1 cc. of glacial acetic acid saturated with hydrogen bromide, however, caused a rapid change of rotation signifying removal of trityl groups.

Graphical Prediction of the Rate of Oxidation of 3-Trityl-β-methyl-D-arabinopyranoside (Fig. 3).—The oxidation curve for β-methyl-D-arabinopyranoside and the acetolysis curve for 3-trityl-β-methyl-D-arabinopyranoside were plotted on the same time axis. Vertical lines were drawn to represent the times at which successive 5% portions of the ether have become hydrolyzed. If the hydrolysis of each 5% of material were instantaneous, it would initiate an oxidation curve exactly one-twentieth of that observed for an equimolar sample of β-methyl-arabinopyranoside. With assumption of such instantaneous hydrolyses of 5% fractions of the whole, alternatively at the beginning and end of each time interval, and adding together the proper number of fractions of the methyl-arabinoside oxidation curve, there was set an upper and lower limit to the amount of oxidation which should have occurred at the end of each interval. A smooth curve was then drawn between these limits. The predicted and observed rates were very close for the 3-trityl ether. In a similar manner the oxidation curve for 4-trityl-β-methyl-D-arabinopyranoside was predicted, the known rate of oxidation of the *trans* glycol structure in 4-acetyl-β-methyl-D-arabinopyranoside being assumed as identical with the rate of oxidation of 4-trityl-β-methyl-D-arabinopyranoside.

(17) Baer, Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607, 3379 (1939); Criegee and Buchner, *Ber.*, **73**, 563 (1940).

Summary

1. The action of triphenylchloromethane upon β-methyl-D-arabinopyranoside and α-methyl-L-fucopyranoside in pyridine solution has been studied under several different conditions.

2. Two isomeric monotrityl-β-methyl-D-arabinopyranosides, a monotrityl-diacetyl-β-methyl-D-arabinopyranoside, a ditrityl-β-methyl-D-arabinopyranoside and its monoacetate and a monotrityl-diacetyl-α-methyl-L-fucopyranoside have been prepared and described.

3. Assignments of probable structure for these compounds and of a previously described mono-trityl-α-methyl-L-fucopyranoside have been made on the basis of their behavior toward lead tetraacetate in pyridine and in acetic acid solutions.

4. Certain conclusions regarding the relative reactivities of the secondary hydroxyl groups in these glycosides have been drawn.

5. Possible applications of the new compounds in synthesis have been pointed out.

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