

3'-Phenyl-2,4,6'-trinitrodiphenyl ether, $C_6H_5C_6H_3(NO_2)_3OC_6H_5(NO_2)_2$, from potassium hydroxide, pyridine, $C_6H_5Cl(NO_2)_2$; m. p. 131°; yield 95.7%; calcd. N, 11.03; found: N, 10.99.

3'-Phenyl-2,4,6-trinitrodiphenyl ether, $C_6H_5C_6H_3OC_6H_2(NO_2)_3$, from potassium hydroxide and picryl chloride; m. p. 143°; yield 92.4%; calcd. N, 11.03; found: N, 11.80.

?-Bromo-4-nitro-3-hydroxydiphenyl, $C_6H_5C_6H_2Br(NO_2)OH$; m. p. 109°; yield 40.0%; calcd. Br, 27.18; found: Br, 26.62.

Summary

1. When 3-hydroxydiphenyl is nitrated the first compounds formed are probably isomeric mononitro derivatives. One of these isomers has been isolated in pure form.

2. The structure of the mononitro derivative

isolated has been proved by preparation from 4-nitrodiphenyl by the use of powdered potassium hydroxide.

3. While with bromine 3-hydroxydiphenyl yields a tribromo derivative, with nitric acid only a mono and a dinitro compound have been prepared. Due to the reduced activity of the hydroxy group the dinitrophenol is believed to be 2,4-dinitro-3-hydroxydiphenyl.

4. Work is continuing in an effort to obtain higher nitro derivatives, bromo derivatives containing less than three bromine atoms, and in the expectation of obtaining definite compounds from the oily by-product obtained in the mononitration of 3-hydroxydiphenyl.

NORMAN, OKLAHOMA

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Crystalline Acetal Derivatives of *d*-Arabinose¹

BY EDNA M. MONTGOMERY, RAYMOND M. HANN AND C. S. HUDSON

Solutions of methyl glycoside acetates of the pyranose type, such as β -methyl glucoside tetraacetate, in a mixture of acetic acid and acetic anhydride, upon catalysis by sulfuric acid, have been shown to be transformed to α -acetates of the pyranose type,² while those possessing a furanoside linkage are changed under the same conditions to form either aldehyde acetates³ or ring acetates probably of furanoid structure. It seemed of interest to investigate the course of this reaction in the case of an acetylated methyl glycoside of arabinose, in which the ring, while pyranoid in structure, involves the hydroxyl group of the terminal carbon atom. The results obtained were so novel that it seemed desirable to extend the investigation to include observations upon the catalytic effect of zinc chloride; here again, a novel change was disclosed.

A solution of triacetyl- β -methyl-*d*-arabinoside (I) in a mixture of three volumes of acetic acid and seven volumes of acetic anhydride (hereafter called the acetylating mixture), containing 4% by weight of sulfuric acid, reached an equilibrium rotation (-17°)⁴ in three minutes at 20°, in con-

trast to the behavior of tetraacetyl- β -methyl glucoside, which required forty-eight hours under the same conditions. The crystalline reaction products that were isolated from the pentose derivative included 56% of an open chain compound, aldehyde-*d*-arabinose hexaacetate (II), but there was present only 11% of the expected ring compound, β -*d*-arabinose tetraacetate (III); under similar conditions β -methyl glucoside tetraacetate yielded 92% of the ring compound, α -glucose pentaacetate.

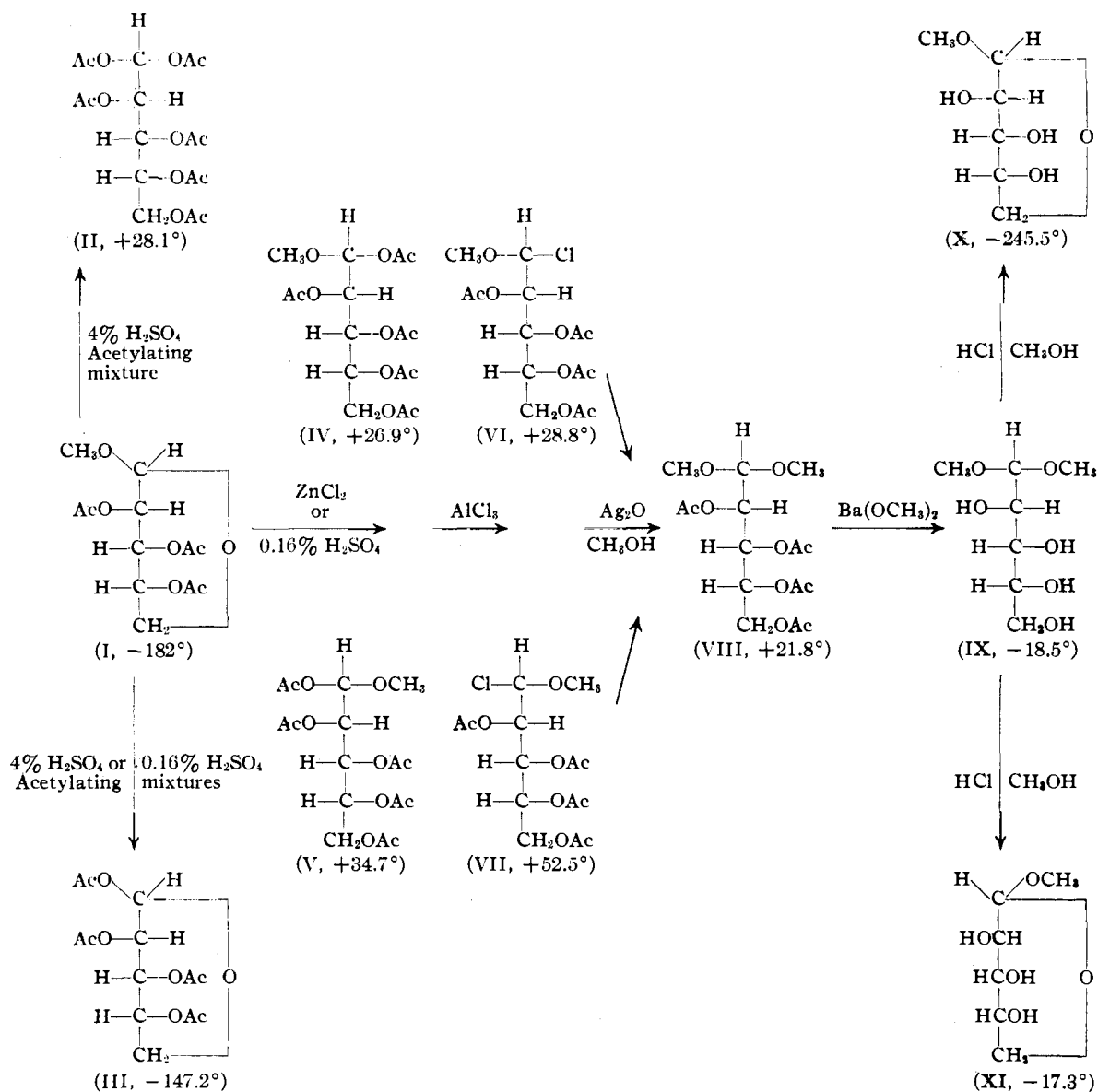
The fact that this concentration of sulfuric acid thus led largely to rupture of the pentopyranoside ring, removal of the methyl group, and peracetylation, suggested the substitution of zinc chloride or a weaker sulfuric acid concentration as milder catalytic agents. The zinc chloride (8%) caused a decided shift in the equilibrium value ($+30^\circ$) of the acetylating solution and resulted in complete rupture of the lactonyl ring, but without removal of the methyl group, the elements of acetic anhydride being added to yield a mixture of two pentaacetyl-*d*-arabinose methyl hemi-acetals (IV and V), which were isolated in high (86%) yield. No ring compound could be isolated and the rotations of the pure hemi-acetal pentaacetates, $+25^\circ$ and $+32^\circ$ (in the acetylation mixture), compared to the equilibrium rotation of $+30^\circ$, indicated the

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Hann and Hudson, *THIS JOURNAL*, **56**, 2465 (1934).

(3) Montgomery and Hudson, *ibid.*, **56**, 2463 (1934).

(4) All rotations are specific rotations at 20° in sodium light.



absence of a levorotating reaction product. The diastereomers, moreover, are interconvertible in the zinc chloride solution, reaching an equilibrium value of $+28^\circ$ and being present in approximately equal amounts. They are quantitatively converted to aldehydo-*d*-arabinose hexaacetate by the 1% sulfuric acid solution, indicating their formation as an intermediate step in the production of the latter substance from β methyl-*d*-arabinoside triacetate when dissolved in this solution.

The weaker sulfuric acid (0.16%) brought about the same equilibrium value (-17°) obtained with the stronger acid, and examination of the reaction products indicated a comparable degree of ring

rupture since it was possible to isolate β -*d*-arabinose tetraacetate in a yield of only 8% of the theoretical; however, with this weaker acid concentration removal of the methyl groups *did not* occur from the simultaneously formed isomeric pentaacetyl-*d*-arabinose methyl hemiacetals and they were isolated as the main reaction products. The agreement of the equilibrium rotations for the weaker and the stronger acid catalysts is thus fortuitous and is due to the fact that the rotations of the aldehydo hexaacetate and the two pentaacetyl methyl hemiacetals are nearly alike.

The results obtained with the various catalysts are summarized in Table I, which also includes ob-

TABLE I
 RESULTS OF CATALYTIC TRANSFORMATION OF ACETYLATED *D*-ARABINOSE DERIVATIVES

Substance	Rotation in non-catalyzed acetylating mixture	Rotation in acetylating mixture + 8% ZnCl ₂	Products	Rotation in mixture + 0.16% H ₂ SO ₄	Products	Rotation in mixture + 4% H ₂ SO ₄	Products
β -Methyl- <i>D</i> -arabinoside triacetate	-184°	+30° (48 hrs.)	42% IV 44% V	-17° (4 hrs.)	21% IV 20% V 8% III	-17° (3 min.)	56% II 11% III
α -Methyl- <i>D</i> -arabinoside triacetate	-19°	+30° (12 hrs.)	37% IV 37% V	-25° (5 hrs.)	18% IV 18% V 8% III	-25° (20 min.)	50% II 14% III
Pentaacetyl- <i>D</i> -arabinose methyl hemi-acetal IV	+25°	+28°	46% IV 44% V	+27°	44% IV 42% V	+25°	91% II
Pentaacetyl- <i>D</i> -arabinose methyl hemi-acetal V	+32°	+28°	48% IV 46% V	+27°	40% IV 42% V	+25°	92% II

servations upon α -methyl-*D*-arabinoside triacetate and the changes of the hemi-acetal pentaacetates in catalyzed acetylating mixtures. These data indicate that zinc chloride catalysis slowly but completely ruptures the ring and introduces an acetyl radical at each of carbon atoms 1 and 5 without breaking the methoxyl union; 0.16% sulfuric acid produces much more rapidly an equilibrium between a small amount of a ring acetate and the interconvertible open chain methyl hemi-acetal pentaacetates; and 4% sulfuric acid is believed to bring about very rapidly the same equilibrium as the dilute acid and then to remove, also rapidly, the methyl group of the hemi-acetals which is followed by acetylation to yield the aldehyd hexaacetate.

Whether these reactions which rupture the oxygen ring are a specific property of the arabinose configuration or are a general reaction of pyranoside linkages involving a terminal carbon atom is at present left undecided; further studies on this subject will be made.

It would be anticipated that the acetyl group in combination with the aldehydic carbon in a pentaacetyl-*D*-arabinose methyl hemi-acetal could be differentially substituted by halogen. Treatment of the two pure isomeric acetylated hemi-acetals with anhydrous aluminum chloride formed two different crystalline isomeric tetraacetyl-*D*-arabinose-1-chloro-1-methyl acetals (VI and VII). Upon solution in methyl alcohol and treatment with silver oxide these two compounds yielded the same crystalline tetraacetyl-*D*-arabinose dimethyl acetal (VIII) which could be deacetylated readily to form *D*-arabinose dimethyl acetal in quantitative yield. Hydrolysis of the dimethyl acetal in 0.05 *N* aqueous acid led to the isolation of crystalline *D*-arabinose, while the action of acid methyl alcohol

gave a mixture of methyl-*D*-arabinosides (X and XI), the latter reaction being consonant with Fischer's view that dimethyl acetals may be one of the intermediate products in the synthesis of glycosides.

We are indebted to Dr. O. E. May of the Industrial Farm Products Laboratory, U. S. Department of Agriculture, for a supply of calcium gluconate, to Mr. George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture, for optical-crystallographic examination of crystals, and to Dr. W. T. Haskins, of the National Institute of Health, for microchemical analyses of some of the described compounds.

Experimental

General.—The 4% acid acetylation solution was prepared by adding 4% by weight of concentrated sulfuric acid dropwise to an ice cold mixture of 70 cc. of acetic anhydride (99.5%) and 20 cc. of acetic acid (99.5%). The weak acid solution (0.16%) was prepared by diluting the 4% acid solution with the anhydride-acid mixture. The zinc chloride solution contained 8 g. of the fused salt in 100 cc. of the anhydride acid mixture. All polarimetric observations of the acetylating reaction were made at $20 \pm 0.5^\circ$ in a 1-dm. glass polariscope tube with sealed glass end-plates. Specific rotations of pure compounds were measured in 2-dm. tubes in the specified solvent.

Transformation of Triacetyl- β -methyl-*D*-arabinoside in the 4% Acid Acetylating Mixture. Isolation of Aldehydo-*D*-arabinose Hexaacetate.—A solution of 10 g. of triacetyl- β -methyl-*D*-arabinoside in 250 cc. of the strong acid reagent changed in rotation from -184° to a constant equilibrium value of -17° in three minutes at 20° . After standing twenty-four hours, the solution was poured into crushed ice, yielding 7.0 g. of a crystalline precipitate (rotation, $+26^\circ$ in chloroform). Extraction of the aqueous solution yielded 5.8 g. of sirup (rotation, -60° in chloroform) which slowly deposited about 3 g. of crystalline material. The combined crystals were fractionally recrystallized from a mixture of 20 cc. of alcohol and 10 cc. of water, yielding 8.2 g. (56%) of aldehydo-*D*-arabinose hexaacetate and 1.2 g. (11%) of β -*D*-arabinose tetraacetate.

Aldehyde-*D*-arabinose hexaacetate crystallizes from 3 parts of 70% alcohol in needles melting at 89.5° (corr.). Its specific rotation in chloroform is +28.1° (*c*, 1.33), comparable in value with but opposite in sign to Wolf-⁵ observation of -27° for the 1-isomer which also melts at 89.5°.

Optical-crystallographic examination by Mr. G. L. Keenan showed the crystals to be rodlike, many with six sides. The refractive indices were $n_\alpha = 1.455$, $n_\beta = 1.472$ and $n_\gamma = 1.495$, all ± 0.003 . In parallel light with crossed nicols the extinction was straight, the double refraction strong, the sign of elongation \pm , and in convergent parallel light interference figures were rare.

Anal. Calcd. for $C_8H_{10}O_6(COCH_3)_6$: C, 48.6; H, 5.8; acetyl, 14.28 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 48.8; H, 6.0; acetyl, 14.25 cc.

Transformation of Triacetyl- β -methyl-*D*-arabinoside in the 8% Zinc Chloride Acetylating Mixture. Isolation of Two Isomeric Crystalline Pentaacetyl-*D*-arabinose Methyl Hemi-acetals.—A solution of 10 g. of the acetylated methyl glycoside in 125 cc. of the zinc chloride reagent slowly changed in specific rotation from -184° to an equilibrium value of +30° in forty-eight hours at 20°. The slightly yellow solution was poured into one liter of ice water and after decomposition of the excess acetic anhydride the solution was extracted with chloroform. The solvent-free sirup that was obtained (13 g.) by removal of the chloroform was dissolved in 30 cc. of absolute ether and after one week crystallization of clusters of rodlike prisms, rotating +26.9° in chloroform when pure, occurred in a yield of 5.7 g. (42%). From the mother liquors a crop of a second type of prisms, short, many faced with one pyramidal end, rotating +34.7° in chloroform when pure, was recovered in an amount of 5.9 g. (44%). Upon analysis these substances proved to be isomeric, and contained one methoxyl and five acetyl groups. These facts and other evidence to be presented indicated their structure as pentaacetyl-*D*-arabinose methyl hemi-acetals. Their isomerism is due to the stereo-arrangement of the groups attached to carbon atom I. In further discussion the compound rotating +26.9° will be designated the first isomer, and the one of rotation +34.7° the second isomer. It is emphasized however that the assignment of the relative stereo positions of the methoxyl and acetyl groups on the aldehyde carbon atom in the hemi-acetal formulas is arbitrary.

The first isomer, when recrystallized to constant physical properties from ether, melted at 76° and showed a specific rotation of +26.9° in chloroform (*c*, 1.33). It was very soluble in the usual organic solvents, insoluble in petroleum ether, and soluble in water to the extent of 0.6 g. in 100 cc. at 20°. It reduced Fehling's solution slowly on boiling. Optical-crystallographic examination by Mr. Keenan showed that in ordinary light the refractive indices of the crystals were: $n_\alpha = 1.448$, $n_\beta = 1.500$, $n_\gamma = 1.510$, all ± 0.003 . In parallel light, with crossed nicols, the double refraction was very strong. In convergent polarized light, crossed nicols, biaxial interference figures showing sections normal to the acute bisectrix were common, the axial angle being large, $2E = 70^\circ (\approx 5^\circ)$. The optic sign was negative.

(5) Wolf, THIS JOURNAL, 57, 2498 (1935).

Anal. Calcd. for $C_8H_{10}O_6(OCH_3)(COCH_3)_5$: C, 49.0; H, 6.2; OCH_3 , 7.9; acetyl, 12.75 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.1; H, 6.2; OCH_3 , 7.9; acetyl, 12.70 cc.

The second isomer when pure melted at 68-70°, gave a specific rotation in chloroform of +34.7° (*c*, 1.33) and showed the same solubility behavior as the first isomer. Optical-crystallographic examination by Mr. Keenan showed that its optical properties are distinctly different, the refractive indices being $n_\alpha = 1.455$, $n_\beta = 1.464$, $n_\gamma = 1.490$, all ± 0.003 . In convergent polarized light, crossed nicols, partial biaxial interference figures are frequently obtained, usually showing sections normal to an optic axis or oriented obliquely to the bisectrices. The double refraction is strong.

Anal. Calcd. for $C_8H_{10}O_6(OCH_3)(COCH_3)_5$: C, 49.0; H, 6.2; OCH_3 , 7.9; acetyl 12.75 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.0; H, 6.0; OCH_3 , 7.9; acetyl, 12.65 cc.

Transformation of Triacetyl- β -methyl-*D*-arabinoside in 0.16% Acid Acetylating Mixture.—A solution of 10 g. of the acetylated glycoside in 250 cc. of the acetylating mixture declined in rotation from -184 to -17° in four hours at 20°. The solution was worked up in the usual manner and the resulting sirup brought to crystallization by solution in 30 cc. of ether and addition of 10 cc. of petroleum ether. The first yield was fractionally recrystallized, and 2.8 g. (21%) of the first and 2.7 g. (20%) of the second isomeric acetylated methyl hemi-acetals were obtained. The remaining sirup was taken up in 20 cc. of 50% alcohol and upon long standing at 5° separated 0.85 g. (8%) of β -*D*-arabinose tetraacetate.

Transformation of Triacetyl- α -methyl-*D*-arabinoside in Acetylating Mixtures.—Triacetyl- α -methyl-*D*-arabinoside was obtained as a colorless sirup rotating -17° in chloroform by the action of methyl alcohol and silver carbonate on crystalline acetobromo-*D*-arabinose. (1) A solution of 5 g. of the sirup in 67 cc. of the zinc chloride reagent changed slowly from an initial rotation of -19° to an equilibrium value of +30° in about twelve hours. No rise in rotation in a levo direction was observed, indicating the absence of an α to β shift prior to the breaking of the lactonyl ring (contrast the action of acid mixtures). The isolable reaction products were 2.5 g. (37%) of each of the isomeric acetylated methyl hemi-acetals. The rotational behavior and equilibrium value indicated the absence of a ring tetraacetate. (2) A solution of 10 g. of the sirup in 250 cc. of 0.16% acid reagent rose rapidly in rotation from -19 to -116° within forty minutes and then declined slowly to an equilibrium value of -25° at the end of five hours. The products isolated were 2.5 g. (18%) of each of the crystalline acetylated methyl hemi-acetals and 0.9 g. (8%) of β -*D*-arabinose tetraacetate. The ring acetate was isolated in only one case because of the extreme difficulty in getting it to crystallize, but the rotational data in all experiments of this group indicated its presence. (3) A solution of 5 g. of the sirup in 125 cc. of 4% acid reagent rose sharply in rotation from -19 to -114° in one minute and declined to an equilibrium value of -25° at the end of twenty minutes. The products isolated were 3.6 g. (50%) of aldehyde-*D*-arabinose hexaacetate and 0.8 g. (12%) of β -*D*-arabinose tetraacetate. A second experiment was interrupted at the rotation peak

of -114° and yielded 1 g. (14%) of crystalline β -methyl-*d*-arabinoside triacetate. The experiments on the α -acetylated glycoside confirm in every instance the similar experiments on the crystalline β -isomer.

Transformation of the Pentaacetyl-*d*-arabinose Methyl Hemi-acetals in Acetylating Mixtures.—(1) A solution of 5 g. of the first isomer ($+26.9^\circ$) in 67 cc. of the zinc chloride reagent reached an equilibrium rotation of $+28^\circ$ within three minutes. From the reaction mixture 2.3 g. (46%) of unchanged material and 2.2 g. (44%) of the second isomer ($+34.7^\circ$) was recovered. A similar experiment using 5 g. of the second isomer resulted in the same equilibrium rotation and yielded 2.4 g. (48%) of unchanged material and 2.3 g. (46%) of the first isomer. (2) A solution of 2.0 g. of the first isomer ($+26.9^\circ$) in 50 cc. of the 0.16% acid mixture gave an equilibrium rotation of $+26.8^\circ$ after two minutes. The reaction products were 0.88 g. (44%) of the second isomer and 0.85 g. (42%) of the first isomer. The second isomer ($+34.7^\circ$) in a similar experiment gave an equilibrium rotation of $+27^\circ$ in two minutes, the reaction products being 0.80 g. (40%) of the first isomer and 0.85 g. (42%) of the second one. No evidence was obtained of the presence of ring isomers. (3) A solution of 5.0 g. of the first isomer in 125 cc. of the 4% acid mixture showed no change in rotation from an initial value of $+25^\circ$ upon standing for eighteen hours. From the reaction mixture aldehydo-*d*-arabinose hexaacetate was recovered in a yield of 4.9 g. (91%). A similar experiment with the second isomer showed a change in rotation from $+32$ to $+25^\circ$ and yielded 5.0 g. (92%) of the aldehydo-*d*-arabinose hexaacetate.

2,3,4,5-Tetraacetyl-1-chloro-*d*-arabinose Methyl Hemi-acetal from Pentaacetyl-*d*-arabinose Methyl Hemi-acetal of Rotation $+26.9^\circ$ (the First Isomer).—A solution of 10 g. of the first isomeric acetylated hemi-acetal in 100 cc. of anhydrous alcohol-free chloroform was cooled to 5° and 10 g. of pulverized anhydrous aluminum chloride added, with gentle agitation; a light brown granular addition product separated. After one-half hour the mixture was washed with ice and water and the chloroform layer was dried with calcium chloride and concentrated *in vacuo* to a sirup, which separated crystalline material upon solution in 20 cc. of ether and addition of 10 cc. of petroleum ether. The crude product was recrystallized once in the same way, yielding 6.3 g. (67%). The compound melts at 71° (corr.) and shows a specific rotation of $+28.8^\circ$ in chloroform (*c*, 1.33). It is quite unstable, decomposing slightly upon recrystallization, and quite rapidly upon standing. A confirmatory experiment was conducted by Freudenberg's⁶ method, yielding 65% of the chloro compound, melting at 70° and having a rotation of $+29^\circ$.

Anal. Calcd. for $C_{14}H_{21}O_9Cl$: Cl, 9.6; OCH_3 , 8.4. Found: Cl, 8.8; OCH_3 , 7.8.

The Isomeric 2,3,4,5-Tetraacetyl-1-chloro-*d*-arabinose Methyl Hemi-acetal from Pentaacetyl-*d*-arabinose Methyl Hemi-acetal of Rotation $+34.7^\circ$ (the Second Isomer).—Under the same experimental conditions of chlorination by aluminum chloride the second isomeric acetylated hemi-acetal yielded 73% of a second chloro tetraacetyl methyl hemi-acetal melting at 73° (corr.) and showing

a rotation of $+52.5^\circ$ in chloroform. The Freudenberg procedure gave a yield of 60% of the same product.

Anal. Calcd. for $C_{14}H_{21}O_9Cl$: Cl, 9.6; OCH_3 , 8.4. Found: Cl, 8.8; OCH_3 , 7.4.

Tetraacetyl-*d*-arabinose Dimethyl Acetal.—(1) A solution of 10 g. of crystalline tetraacetyl-1-chloro-*d*-arabinose methyl hemi-acetal, of rotation $+28.8^\circ$, in a mixture of 25 cc. of absolute ether and 25 cc. of methyl alcohol was cooled to 0° and agitated with 10 g. of silver oxide. After five minutes, the separated silver salts were removed, the solution was concentrated to a sirup, the sirup was dissolved in 15 cc. of ether and brought to crystallization by addition of 5 cc. of petroleum ether. A yield of 4.2 g. (42%) of the acetylated dimethyl acetal was obtained readily. (2) A similar experiment employing the crystalline chloro derivative of rotation $+52.5^\circ$ yielded 4.4 g. (44%) of the same tetraacetyl-*d*-arabinose dimethyl acetal.

Tetraacetyl-*d*-arabinose dimethyl acetal crystallizes in prisms, melting at 80° (corr.) and showing a specific rotation of $+21.8^\circ$ in chloroform (*c*, 1.33). It is readily soluble in ether and chloroform, almost insoluble in water, and insoluble in petroleum ether. It does not reduce Fehling's solution.

Anal. Calcd. for $C_8H_{10}O_4(OCH_3)_2(COCH_3)_4$: C, 49.4; H, 6.6; OCH_3 , 17.0; acetyl, 10.98 cc. 0.1 N NaOH per 100 mg. Found: C, 49.5; H, 6.7; OCH_3 , 16.9; acetyl, 11.00 cc.

***d*-Arabinose Dimethyl Acetal.**—A solution of 6 g. of tetraacetyl *d*-arabinose dimethyl acetal in 120 cc. of absolute methyl alcohol was cooled to 0° , 0.4 cc. of 2 N barium methylate added, and allowed to stand at 0° for two hours. Upon volatilization of the solvent a crystalline residue of 3.3 g. (quantitative) rotating -16.8° in water was obtained, and recrystallization from 5 parts of methyl alcohol to constant rotation, yielded 2.8 g. (88%) of pure *d*-arabinose dimethyl acetal. This compound crystallizes in clear hexagonal prisms melting at 122° and showing a specific rotation of -18.5° in water. It does not reduce Fehling's solution, but upon hydrolysis at 98° in 0.05 N hydrochloric acid it yielded *d*-arabinose, and upon treatment with acid methyl alcohol it gave a mixture of methyl-*d*-arabinosides. We expect to study its change to glycosides in more detail later.

Anal. Calcd. for $C_8H_{10}O_4(OCH_3)_2$: C, 42.8; H, 8.2; OCH_3 , 31.6. Found: C, 42.8; H, 8.2; OCH_3 , 31.6.

Summary

Studies have been made of the action of catalyzed acetylating mixtures upon α and β methyl-*d*-arabinopyranoside triacetates. The results indicate: (1) that zinc chloride catalysis completely ruptures the lactonyl linkage without hydrolysis of the methyl group, to yield two isomeric pentaacetyl-*d*-arabinose methyl hemi-acetals; (2) that 0.16% sulfuric acid causes an equilibrium between a small amount of ring acetate and these hemi-acetals; and (3) that 4% sulfuric acid brings

(6) Freudenberg, Hochstetter and Engels, *Ber.*, **58**, 668 (1925).

about a similar equilibrium followed by hydrolysis of the methyl group and peracetylation to yield aldehydo-*d*-arabinose hexaacetate.

The isomeric pentaacetyl-*d*-arabinose hemiacetals have been converted to two isomeric chloro derivatives, which by the usual methods are con-

verted into the same tetraacetyl-*d*-arabinose dimethyl acetal.

d-Arabinose dimethyl acetal has been synthesized in crystalline condition by deacetylation of its tetraacetate.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Densities and Vapor Pressures of Some Alkylbenzenes, Aliphatic Ketones and *n*-Amyl Chloride¹

BY J. C. RINTELEN, JR., J. H. SAYLOR AND P. M. GROSS

During the course of an investigation of the solubility of some organic compounds being carried out in this Laboratory, it became necessary to know the vapor pressures and densities of these compounds at 10, 30 and 50°. An examination of the literature showed that there were no available density and vapor pressure data for some of the substances and that there were rather serious discrepancies in the vapor pressure data for ethylbenzene, the xylenes and mesitylene. Therefore, their vapor pressures together with the vapor pressures and densities of *n*-amyl chloride and some ketones were determined. After the experimental part of this work was completed, Kassel² called attention to the erroneous data of Woringer³ for the vapor pressures of the xylenes and mesitylene that are given in the "International Critical Tables." Kassel redetermined the vapor pressures of these compounds.

Experimental

Materials.—The ethylbenzene and the dibutyl ketone were prepared in this Laboratory. The other substances were the best grades commercially available. All were subjected to a careful purification by successive fractionation using efficient stills and calibrated thermometers. Boiling points were corrected to 760 mm. by means of Craft's rule whenever the value of dT/dP could not be found in the literature. The boiling ranges of the samples used are given in Table I.

Method.—The vapor pressures were measured by a differential static method. As the form of apparatus used has been found to be particularly convenient, it is shown in Fig. 1.

Mercury was introduced into the manometer through the vertical tube, water placed in one bulb and the organic liquid in the other. The mercury in the manometer was

(1) Taken in part from a thesis submitted by J. C. Rintelen, Jr., in partial fulfillment of the requirement for the degree of Doctor of Philosophy at Duke University, June, 1936.

(2) Kassel, *THIS JOURNAL*, **58**, 670 (1936).

(3) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

TABLE I

Substance	B. p. range, °C.	BOILING POINT RANGES OF THE COMPOUNDS	
		Previously observed b. p., °C.	Ref.
Ethylbenzene	136.13–136.18	136.15	4a
<i>o</i> -Xylene	144.0–144.1	144.0	4b
<i>m</i> -Xylene	138.99–139.15	139.3 (139.00)	4b (6)
<i>p</i> -Xylene	138.27–138.37	138.4 (138.3)	5 (6)
Mesitylene	164.5–164.6	164.6	4b
<i>n</i> -Amyl chloride	107.74–107.78	105.7 (106.6, 740 mm.)	6, (7)
Methyl isopropyl ketone	94.0–94.52	95–96, 93–94, 95–95.3	8, 9, 10
Methyl isobutyl ketone	116.71–116.78	116.85	4c
Diethyl ketone	101.59–101.74	101.7	8
Dipropyl ketone	144.05–144.12	144.1	4b
Dibutyl ketone	187.4–188.4	187.65	4d

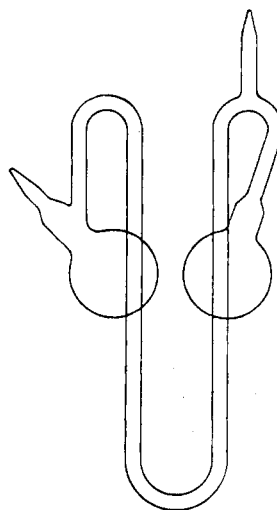


Fig. 1.—Vapor pressure apparatus.

(4) (a) Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911); (b) **30**, 62 (1921); (c) **27**, 334 (1913); (d) **36**, 506 (1927).

(5) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

(6) "International Critical Tables."

(7) Lieben and Rossi, *Ann.*, **159**, 72 (1871).

(8) Timmermans and Matthaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

(9) Henderson, Henderson and Heilbron, *Ber.*, **47**, 887 (1914).

(10) Clarke, *THIS JOURNAL*, **33**, 528 (1911).