heated to 95°. A solution of 5.5 ml. of bromine in 25.0 ml. of acetic acid was added. The reaction was rapid and the mixture boiled spontaneously for a short time. The solution was cooled to room temperature and diluted with 600 ml. of ice water. The colorless product was filtered off at 5°, washed with ice water and dried at 55°; yield, 25.5 g. (97.66%). The product was purified for analysis by recrystallization from an isopropanol–ethyl acetate mixture, m. p. 142–143°. *Anal.* Calcd. for $C_9H_9BrO_4$: C, 41.40; H, 3.47; Br, 30.61. Found: C, 41.50; H, 3.72; Br, 30.95.

3-Hydroxymethyl-5,6-dihydro-6,6-dimethyl-γ-pyronecarboxylic Acid Amide-2, XVI.—V (80.0 g.), was added in five minutes to 400.0 ml. of 28% ammonium hydroxide (temp., 15°). The mixture was stirred for fifteen minutes, at the end of which time the temperature was 3°. The colorless crystalline product was filtered off, washed with ice water, and dried in the air; yield, 74.0 g. (84.01%), m. p. 153–154° dec. The compound was recrystallized from isopropanol and dried at 55°, m. p. 157–158° dec. *Anal.* Calcd. for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.18; H, 6.73; N, 6.73. This product evolved ammonia when heated with water. When heated for a short time with dilute hydrochloric acid it reverted to V.

Summary

1. The synthesis of a clavacin isomer, 3-hydroxymethyl-5,6-dihydro-γ-pyrone-carboxylic acid-2 lactone is described. It has been shown that this compound does not exist in equilibrium with clavacin, in confirmation of the earlier tentative exclusion of it by less direct evidence.

2. A number of homologs and derivatives possessing the same isomeric structure have also been made. The chemical properties of these compounds as well as those of several intermediate α-keto-β-acyl-butyrolactones are recorded.

NEW YORK, N. Y. RECEIVED FEBRUARY 16, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF HOFFMANN-LA ROCHE, INC.]

The Preparation of L-Sorbose from Sorbitol by Chemical Methods

BY WILLIAM R. SULLIVAN

L-Sorbose is usually prepared by the bacterial oxidation of sorbitol.[1] Two chemical syntheses have been reported. Votoček and Lukeš[2] and Talen[3] oxidized sorbitol with bromine water, and from the resulting sirup were able to obtain L-gulosazone, which was considered to indicate that L-sorbose had been formed in the oxidation. Gätzi and Reichstein[4] treated L-xylonyl chloride with diazomethane and obtained L-sorbose by acid hydrolysis of the intermediate diazo ketone.

A synthesis based on the oxidation of carbon atom 5 of D-sorbitol derivatives, in which the other positions are protected by suitable substituents, is reported in this paper. A search of the literature indicates that this represents a novel approach to the synthesis of ketose sugars.

1,3:2,4-Diethylidene-D-sorbitol (II)[5] is prepared by the partial hydrolysis of triethylidene sorbitol (I). Under suitable conditions 6-tosyl-[6] or 6-benzoyl-1,3:2,4-diethylidene-D-sorbitol (III) may be prepared in substantial yield, the diesters being formed simultaneously to some extent. The remaining free hydroxyl group on carbon atom 2 is then oxidized to the carbonyl stage by chromium trioxide in acetic acid solution. From the open-chain sorbose derivative (IV) so obtained, the ethylidene groups are removed by hydrolysis with dilute mineral acid to give 1-tosyl- or 1-benzoyl-L-sorbose (V). The structue of these products is proved by their synthesis from the known 2,3:4,6-diisopropylidene-L-sorbose (VI) and by the hydrolysis of 1-benzoyl-L-sorbose to the free sugar, L-sorbofuranose.

In the preparation of diethylidene sorbitol, the intermediate triethylidene compound (I) is handled satisfactorily in the form of a crude sirup. The crystalline compound has been isolated and found to melt at 96–97°. The melting point of 174–176° reported by Appel[5] for triethylidene-D-sorbitol suggests that two forms may exist, possibly as *cis–trans* or other isomers.

When the hydrolysis of the tosyl or benzoyl esters of diacetone-L-sorbose (VII) is carried out with 50% acetic acid, the intermediate monoacetone compounds (VIII) are the major products, while the use of dilute mineral acid leads to removal of both isopropylidene residues. The isopropylidene residue of the intermediates (VIII) is considered to be at positions 2 and 3, because the failure to reduce Fehling solution before hydrolysis with mineral acid proves that the carbonyl group is not free.

The author gratefully acknowledges the many helpful suggestions of Dr. M. W. Goldberg. Studies in this Laboratory on the oxidation of sorbitol derivatives were undertaken at the suggestion of Dr. H. M. Wuest.

Experimental[7]

1,3:2,4-Diethylidene-D-sorbitol (II).—The method of Appel[5] gave yields of about 26%. In an experiment on a

---

[1] Bertrand, *Bull. soc. chim.*, [3] **15**, 627 (1896); Wells, Stubbs, Lockwood and Roe, *Ind. Eng. Chem.*, **31**, 1518 (1939).

[2] Votoček and Lukeš, *Rec. trav. chim.*, **44**, 345 (1925).

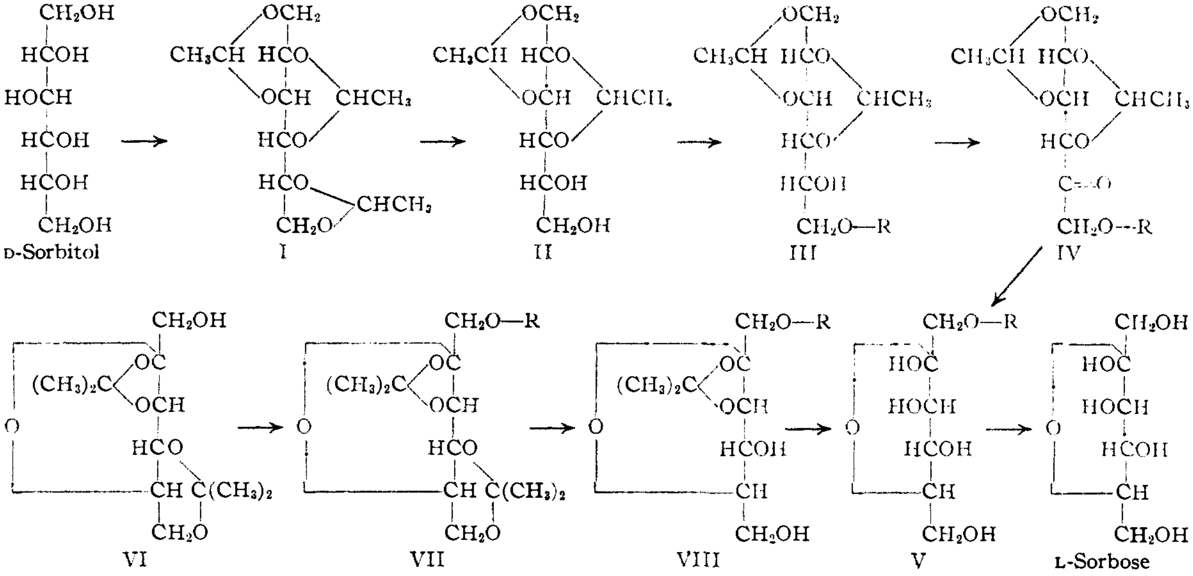
[3] Talen, *ibid.*, **44**, 891 (1925).

[4] Gätzi and Reichstein, *Helv. Chim. Acta*, **21**, 186 (1938).

[5] Appel, *J. Chem. Soc.*, 425 (1935). See also Gätzi and Reichstein[4] for final proof of structure.

[6] Since the completion of the experiments here reported, the preparation of 6-tosyl-1,3:2,4-diethylidene-D-sorbitol has been described by Vargha and Puskás, *Ber.*, **76**, 859 (1943). These authors apparently did not isolate the di-ester from the reaction mixture and therefore the details, while similar, are included here.

[7] Melting points were determined with an uncalibrated set of Anschütz thermometers. The analyses were done in the Roche Microanalytical Laboratory under the direction of Dr. Al Steyermark.



R = Benzoyl or tosyl (benzoyl only, in the step V → L-sorbose). In the step IV → V, the formula becomes inverted in the plane of the paper.

larger scale (200 g.) it was found that the yield could be increased somewhat (33%) by concentrating the mother liquors to a sirup and heating with chloroform. Material melting at 200–205° is sufficiently pure for further synthetic work.

Triethylidene-D-sorbitol (I).—D-Sorbitol (100 g.) was shaken with 100 cc. of paraldehyde and 35 cc. of concentrated hydrochloric acid for five hours. The mixture was extracted with 200 cc. of chloroform. The chloroform extract was washed, dried, and concentrated *in vacuo*. The resulting sirup was taken up in ethanol, and on cooling the solution deposited 26 g. (18%) of needles. Recrystallization from methanol and from ligroin raised the melting point to 96–97°, and the rotation remained constant at $[\alpha]^{22}_{D}$ −21.6° in water (*c*, 5).

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 55.38; H, 7.70. Found: C, 55.56; H, 7.79.

Tosylation of 1,3:2,4-Diethylidene-D-sorbitol.—With stirring and cooling in ice, 46.8 g. (0.2 mole) of pulverized 1,3:2,4-diethylidene-D-sorbitol was added in small portions to a cold solution of 38.1 g. (0.2 mole) of *p*-toluenesulfonyl chloride in 150 cc. of dry alcohol-free chloroform containing 40 cc. of dry pyridine. The diethylidene sorbitol dissolved during two hours of mechanical shaking. After standing for twenty-four hours at room temperature, the solution was cooled and an equal volume of ice water added. The chloroform layer was washed, dried and concentrated under reduced pressure to a thin sirup. Petroleum ether was then added until two layers began to form. Scratching and cooling induced crystallization of the lower layer. The crystals were filtered off, dried, and ground in a mortar. The powdered material was dispersed in 45 cc. of methanol and filtered. The residue consisted of 9.51 g. (8.5%) of **5,6-ditosyl-1,3:2,4-diethylidene-D-sorbitol.** Recrystallized from methanol, the prisms melted at 172° and rotated $[\alpha]^{23}_{D}$ −12.8° in chloroform (*c*, 5). They are soluble in chloroform, benzene, ethyl acetate and warm ethanol and methanol, and insoluble in water and petroleum ether.

Anal. Calcd. for $C_{24}H_{30}O_{10}S_2$: C, 53.10; H, 5.57; S, 11.84. Found: C, 53.42; H, 5.79; S, 11.81.

Addition of 70 cc. of water to the heated methanolic filtrate caused separation of **6-tosyl-1,3:2,4-diethylidene-D-sorbitol (III)** which crystallized on cooling. The yield was 46.5 g. of crude product (60% of the theoretically possible amount). The monotosylate was purified by fractional precipitation by petroleum ether from its solution in ethyl acetate. It melted at 96–98° and had $[\alpha]^{22}_{D}$ +9.9° in ethyl acetate (*c*, 5). It is readily soluble in methanol, ethanol, chloroform and ethyl acetate and insoluble in water and petroleum ether. Vargha and Puskás[6] reported a 55% yield, m. p. 92°, $[\alpha]^{20}_{D}$ +11.5° in chloroform (*c*, 2.608).

Anal. Calcd. for $C_{17}H_{24}O_8S$: C, 52.54; H, 6.23; S, 8.26. Found: C, 52.62; H, 6.32; S, 8.11.

Treatment of the monotosylate in chloroform solution with one equivalent of sodium methoxide gave **5,6-anhydro-1,3:2,4-diethylidene-D-sorbitol** in 78% yield. The product melted at 135–136° and had $[\alpha]^{27}_{D}$ −6.1° in chloroform (*c*, 4) while Vargha and Puskás[6] found m. p. 132–133° and $[\alpha]^{20}_{D}$ −5.2° in chloroform (*c*, 2.692).

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.75; H, 7.43.

5,6-Dibenzoyl-1,3:2,4-diethylidene-D-sorbitol.[8]—1,3:2,4-Diethylidene-D-sorbitol (4.86 g.) was added to a cooled solution of 5.1 cc. of benzoyl chloride in 10 cc. of dry pyridine. After forty-eight hours the flask was cooled in ice and the contents poured into 300 cc. of ice water. From the sirup which separated was obtained 6.85 g. (78%) of crystals. After two recrystallizations from ethanol the prisms melted at 124° and rotated $[\alpha]^{22}_{D}$ −34.0° in chloroform (*c*, 5).

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.13; H, 5.93. Found: C, 65.38; H, 5.93.

6-Benzoyl-1,3:2,4-diethylidene-D-sorbitol (III).—To a cooled solution of 14.06 g. of benzoyl chloride and 10 cc. of dry pyridine in 100 cc. of dry alcohol-free chloroform was added 23.4 g. of finely powdered 1,3:2,4-diethylidene-D-sorbitol. The mixture was allowed to stand for 24 hours at room temperature and then poured into a separatory funnel with 100 cc. of ice water. The chloroform layer was washed, dried and concentrated to a sirup under reduced pressure. The sirup was dissolved in 75 cc. of hot ethanol and on cooling there separated 20.33 g. of crystals melting at 164–165° and having $[\alpha]^{21}_{D}$ +3.6° in chloroform (*c*, 5). Addition of water to the mother liquor gave 6.01 g. of crystals, m. p. 116–118° which were mainly dibenzoate. From the rotation of the first crop the calculated yield of monobenzoate was 18.9 g. (56%). Repeated recrystallization from ethyl acetate raised the melting point to 167° and the rotation remained constant at $[\alpha]^{23.6}_{D}$ +5.9° in chloroform (*c*, 5).

---

[8] Previously prepared by Dr. W. E. Scott of this Laboratory.

Anal. Calcd. for $C_{17}H_{22}O_7$: C, 60.32; H, 6.56. Found: C, 60.25; H, 6.59.

1-Tosyl-3,5:4,6-diethylidene-*keto*-L-sorbose (IV).—6-Tosyl-1,3:2,4-diethylidene-D-sorbitol (19.3 g.) was dissolved in 75 cc. of glacial acetic acid which had been distilled from an excess of chromic acid. A solution of 6.67 g. (two equivalents) of chromium trioxide in 5 cc. of water and 25 cc. of acetic acid was added dropwise with stirring. The temperature of the reaction mixture was kept below 20° by cooling the flask in ice.

After forty-eight hours at room temperature, 5 cc. of methanol was added and the solution concentrated under reduced pressure at 50° in an atmosphere of nitrogen. To the green sirupy residue, 1 *N* potassium hydroxide solution was added until the reaction was neutral. The mixture, from which some solid had separated, was shaken with 300 cc. of ethyl acetate in three portions and the extract washed with water until the washings no longer were green. After drying with sodium sulfate, the green solution was heated to boiling with 5 g. of charcoal and filtered. The filtrate was concentrated under reduced pressure in an atmosphere of nitrogen to a sirup (14.5 g.) in which crystals sometimes formed. This sirup was taken up in 30 cc. of boiling ethanol and on cooling 5.51 g. of needles were obtained which melted at 117–129°. Recrystallization from ethyl acetate gave 3.4 g. (17.8% of the theoretically possible yield) of essentially pure material melting at 139–141°. Recrystallized again from chloroform–petroleum ether, with charcoal treatment to remove the last traces of green color, the long silky needles melted at 141–142° and had $[\alpha]^{22}D$ −76.3° in chloroform (*c*, 5). The substance reduced hot Fehling solution. Addition of a drop of alkali to an acetone solution gave a yellow color which was discharged by acidification, a test regarded as characteristic of open-chain ketoses.[9]

Anal. Calcd. for $C_{17}H_{22}O_8S$: C, 52.82; H, 5.74; S, 8.30. Found: C, 52.95; H, 5.98; S, 8.29.

1-Benzoyl-3,5:4,6-diethylidene-*keto*-L-sorbose (IV).—The oxidation of 11.3 g. of 6-benzoyl-1,3:2,4-diethylidene-D-sorbitol was carried out as described above for the tosyl compound up to the point where the neutralized mixture is shaken with an organic solvent. Chloroform (200 cc.) was used in place of ethyl acetate. The addition of 3 cc. of methanol to the sirup remaining after removal of the chloroform under reduced pressure induced crystallization. This first crop of crystals (2.24 g., m. p. 160°) consisted mainly of unreacted starting material. The addition of water to the mother liquors gave 3.59 g. (32%) of needles melting at 90–92°. Recrystallization from methanol–water mixtures raised the melting point to 105° and the rotation remained constant at $[\alpha]^{25}D$ −110.5° in chloroform (*c*, 2). The product reduced hot Fehling solution and gave the color test described above.

Anal. Calcd. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.91; H, 6.04.

1-Tosyl-2,3:4,6-diisopropylidene-L-sorbose (VII).—The action of *p*-toluenesulfonyl chloride on 2,3:4,6-diisopropylidene-L-sorbose (VI) in dry pyridine gave a quantitative yield of the 1-tosyl compound. It was recrystallized from petroleum ether (Skellysolve B). The pure substance melted at 102–103° and had $[\alpha]^{23}D$ +4.2° in chloroform (*c*, 5).

Anal. Calcd. for $C_{19}H_{26}O_8S$: C, 55.03; H, 6.33; S, 7.74. Found: C, 55.38; H, 6.32; S, 7.91.

1-Tosyl-L-sorbose (V) **from 1-Tosyl-2,3:4,6-diisopropylidene-L-sorbose.**—1-Tosyl-2,3:4,6-diisopropylidene-L-sorbose (4.14 g.) was dissolved in 5 cc. of dioxane and 20 cc. of 0.1 *N* hydrochloric acid was added, causing separation of two layers. Heating for two hours on the steam-bath gave a homogeneous solution which was concentrated under reduced pressure in an atmosphere of nitrogen. The resulting sirup was taken up in ethanol and re-concentrated to remove hydrochloric acid. The sirup was seeded with crystals obtained in a trial experiment and crystallization ensued rapidly. Since traces of hydrochloric acid were still present, the product was not dried but was recrystallized at once from ethanol. The yield was 2.03 g. (60%). The prisms melted at 116°, the melt becoming bright red, and rotated $[\alpha]^{20}D$ −13.2° in pyridine (*c*, 5).

Anal. Calcd. for $C_{13}H_{18}O_8S$: C, 46.67; H, 5.43; S, 9.59. Found: C, 46.52; H, 5.53; S, 9.49.

1-Tosyl-L-sorbose from 1-Tosyl-3,5:4,6-diethylidene-*keto*-L-sorbose.—The hydrolysis of 4.3 g. of 1-tosyl-3,5:4,6-diethylidene-*keto*-L-sorbose with 20 cc. of 0.1 *N* hydrochloric acid followed by removal of the hydrochloric acid with silver carbonate gave 2.49 g. of 1-tosyl-L-sorbose which was identified by its rotation, melting point and mixed melting point.

1-Benzoyl-L-sorbose (V) **from 2,3:4,6-diisopropylidene-L-sorbose.**—Twenty-six grams of diacetone sorbose was benzoylated with 14 cc. of benzoyl chloride in 50 cc. of dry pyridine. The sirup which separated on the addition of water was taken up in chloroform and the solution washed with dilute hydrochloric acid and with water and dried with calcium chloride. Removal of the chloroform under reduced pressure left the ester in the form of a sirup which could not be brought to crystallization. The last traces of pyridine were removed by warming with dilute aqueous acid, added in small portions until the aqueous layer remained acidic. The liquid product was again taken up in chloroform, washed with water, dried and concentrated. The residue was twice taken up in ethanol and re-concentrated, finally at 0.05 mm. pressure. The sirup was then dissolved in 10 cc. of dioxane and 100 cc. of 0.1 *N* sulfuric acid added, which caused separation of two layers. The mixture was heated on the steam-bath for three hours, then 30 cc. more dioxane and 50 cc. more acid were added and the heating continued for four hours longer. The small lower layer which still remained was separated and re-hydrolyzed with 50 cc. of 0.1 *N* sulfuric acid and 20 cc. of dioxane for nine hours.

The sulfuric acid was removed from the hydrolyzates by adding the theoretical amount of 0.1 *N* barium hydroxide solution and filtering through asbestos. The filtrates were concentrated under reduced pressure to sirups, which were dissolved in ethanol and re-concentrated. The crystals which had formed were filtered off and the filtrates concentrated again. The addition of ether to the residues induced crystallization. The total yield of crude product was 21.05 g. (74%), melting at 122–128°. Recrystallized three times from alcohol, the prisms melted at 133.5° and rotated $[\alpha]^{26}D$ −3.4° in methanol (*c*, 5).

Anal. Calcd. for $C_{13}H_{16}O_7$: C, 54.93; H, 5.67. Found: C, 54.89; H, 5.67.

1-Benzoyl-L-sorbose from 1-Benzoyl-3,5:4,6-diethylidene-*keto*-L-sorbose.—A mixture of 1.69 g. of 1-benzoyl-3,5:4,6-diethylidene-*keto*-L-sorbose, 7.5 cc. of dioxane and 10 cc. of 0.1 *N* sulfuric acid was heated on the steam-bath for four hours. The mixture, which had become homogeneous, was cooled and 9.3 cc. of 0.125 *N* barium hydroxide solution added with stirring. The barium sulfate was removed by filtering through a pad of asbestos covered with a layer of charcoal and washed well with water. The combined filtrate and washings were concentrated to a sirup which was taken up in 10 cc. of methanol and re-concentrated. Addition of a little ethyl acetate to the residue induced crystallization. A small second crop was obtained by adding petroleum ether to the mother liquor. The yield was 1.20 g. (85%). The recrystallized product agreed in melting point and rotation with that obtained from diacetone sorbose and a mixed melting point showed no depression.

1-Tosyl-2,3-isopropylidene-L-sorbose (VIII).—1-Tosyl-2,3:4,6-diisopropylidene-L-sorbose (33 g., 0.08 mole) was heated on the steam-bath for three and one-half hours with a mixture of 100 cc. of glacial acetic acid and 100 cc. of water. Concentration under reduced pressure left a sirup from which a further amount of acetic acid was removed by adding 30 cc. of water and re-concentrating. From the residue a total of 9.67 g. (0.029 mole) of 1-tosyl-L-sorbose was obtained in four crops by seeding, filtering,

---

[9] Cramer and Pacsu, THIS JOURNAL, **59**, 1467 (1937).

concentrating the mother liquors, and adding ether. The mother liquor from the fourth crop, which now contained 500 cc. of ether, was concentrated to a sirup and taken up in 15 cc. of ethanol. Water was added until a permanent turbidity resulted and seed crystals (obtained in a test-tube by rubbing the walls with a glass rod) were added. The crystals which formed on cooling were filtered off. A further amount was obtained by adding water to the filtrate. In this way 16.55 g. (0.044 mole) of impure monoacetone compound was obtained, making a recovery of 0.073 mole (91%) of the starting material. The monoacetone compound was soluble in methanol, ethanol, ether, chloroform and ethyl acetate and insoluble in petroleum ether and water. Recrystallized from ethanol–water and ethyl acetate–petroleum ether mixtures, the pure substance consisted of long needles melting at 120° and having $[\alpha]^{28}\mathrm{D}$ +15.7° in chloroform (*c*, 4). It did not reduce Fehling solution, but after boiling it with dilute hydrochloric acid, reducing action was present in the hydrolysate.

Anal. Calcd. for $C_{16}H_{22}O_8S$: C, 51.32; H, 5.92; S, 8.56. Found: C, 51.28; H, 6.01; S, 8.55.

Hydrolysis of 1.12 g. in 10 cc. of 0.1 *N* sulfuric acid and 5 cc. of dioxane gave 0.32 g. of 1-tosyl-L-sorbose after one recrystallization. The product was identified by its melting point, rotation and mixed melting point.

1-Benzoyl-2,3-isopropylidene-L-sorbose (VII).—The sirupy 1-benzoyl-2,3:4,6-diisopropylidene-L-sorbose obtained as described above from 26 g. of diacetone sorbose was heated on the steam-bath for four hours with a mixture of 100 cc. of glacial acetic acid and 100 cc. of water. The solution was treated with charcoal and filtered and the filtrate concentrated to a sirup under reduced pressure. Water (50 cc.) was added, and the concentration repeated. Attempts to separate 1-benzoyl-L-sorbose by its insolubility in ether were fruitless. The addition of 4 cc. of ethyl acetate to the sirup caused the 2,3-isopropylidene derivative to crystallize. A second crop was obtained by adding petroleum ether to the mother liquor, raising the yield to 18.43 g. (57% of the theoretical). Recrystallized from ethyl acetate by the addition of petroleum ether, the needles melted at 92° and had $[\alpha]^{25}\mathrm{D}$ +7.2° in chloroform (*c*, 4). They are soluble in methanol, ethanol, acetone, dioxane, chloroform, warm ethyl acetate and to some extent in boiling water, but insoluble in petroleum ether. As in the case of the corresponding tosyl ester, Fehling solution was reduced only after acid hydrolysis.

Anal. Calcd. for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.17; H, 6.35.

Hydrolysis of 3.24 g. with 10 cc. of 0.1 *N* sulfuric acid and 5 cc. of dioxane gave 1.045 g. of 1-benzoyl-L-sorbose, identified by its melting point, rotation and mixed melting point.

L-Sorbose from 1-Benzoyl-L-sorbose.—The excellent method of Hudson and Brauns[10] was employed for the saponification. 1-Benzoyl-L-sorbose (7.1 g., 0.025 mole) was added to 125 cc. of 0.4487 *N* barium hydroxide solution at 5° and this mixture cooled in ice with frequent shaking. The ester dissolved during the first thirty minutes. The solution was then saturated with carbon dioxide, filtered, and the rest of the barium removed by the addition of *N* sulfuric acid and filtration through asbestos-charcoal. The filtrate was concentrated under reduced pressure to a thin sirup in which crystals formed. Addition of 25 cc. of ethanol and cooling gave 3.74 g. (83%) of crystalline L-sorbose. Recrystallized from dilute alcohol, the product had $[\alpha]^{27}\mathrm{D}$ −42.8° in water (*c*, 4) and melted at 165°. A mixed melting point with a known sample of L-sorbose was not depressed.

Summary

1. The transition from D-sorbitol to L-sorbose has been accomplished by the following reactions: (1) esterification of carbon atom 6 of 1,3:2,4-diethylidene-D-sorbitol, (2) chromic acid oxidation of carbon atom 5 to the carbonyl stage, (3) removal of the ethylidene groups by acid hydrolysis, and (4) saponification of the ester linkage by barium hydroxide. This represents the first synthesis of a ketose by the chemical oxidation of straight chain sugar alcohol derivatives.

2. In conjunction with the above transformation, the following new compounds were prepared and their constants and analyses recorded: 6-benzoyl-1,3:2,4-diethylidene-D-sorbitol, 5,6-ditosyl- and 5,6-dibenzoyl-1,3:2,4-diethylidene-D-sorbitol, 1-tosyl- and 1-benzoyl-3,5:4,6-diethylidene-*keto*-L-sorbose, and 1-tosyl- and 1-benzoyl-L-sorbose.

3. Triethylidene-D-sorbitol was isolated in crystalline condition and its melting point found to be 96–97°.

4. The structure of the intermediates, 1-tosyl- and 1-benzoyl-L-sorbose was proved by their synthesis from 2,3:4,6-diisopropylidene-L-sorbose. This involved the preparation of the new esters 1-tosyl- and 1-benzoyl-2,3:4,6-diisopropylidene-L-sorbose, and subsequent removal of the acetone residues therefrom. When this hydrolysis was conducted with aqueous acetic acid, intermediate monoacetone products could be isolated, but the use of mineral acid gave only the acetone-free esters.

NUTLEY 10, NEW JERSEY RECEIVED FEBRUARY 21, 1945

---

[10] Hudson and Brauns, THIS JOURNAL, **38**, 1216 (1916).