solution and left for 6 hours. The ether then was evaporated and the residue recrystallized from methyl alcohol to give pale yellow needles, m.p. 167°, yield 0.1 g. It gave no color with concentrated sulfuric acid. This product was proved to be 2-methylchrysenoxazole by m.p. and mixed m.p. determinations.[13]

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.8; H, 4.6; N, 4.9. Found: C, 84.8; H, 4.5; N, 4.7.

(13) In ref. 9 the m.p. of 2-methylchrysenoxazole is stated as 223°.

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Tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone

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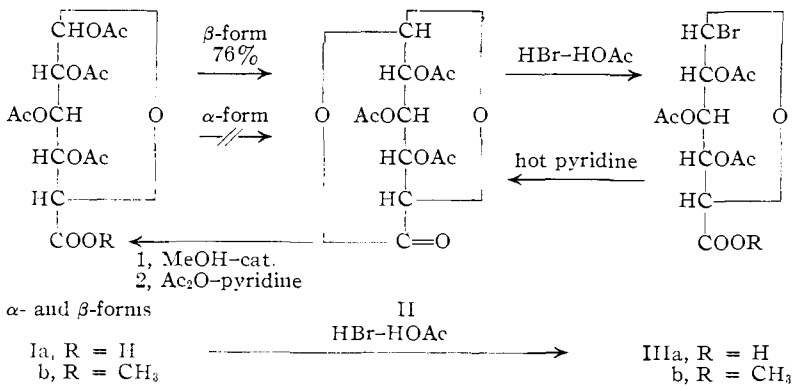
The synthesis of tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone (II) was undertaken in order to see whether or not this compound is a suitable intermediate for the preparation of alkyl β-D-glucopyranosiduronic acids. The approach was made attractive by the work of Lemieux who showed that the carbon-1 β-acetoxy group of an acetylated glucose is subject to displacement by an alkoxyl group in the presence of stannic chloride. Thus, 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose was converted into tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose in 36% yield,[1b] and penta-*O*-acetyl-β-D-glucopyranose into methyl tetra-*O*-acetyl-β-D-glucopyranoside in 50–60% yield.[1c] The configuration of the α-anomers makes them unsuitable for this type of displacement and an adequate discussion and review is to be found in Lemieux' paper.[1a]



The acetylation of sodium glucuronate in the presence of *p*-toluenesulfonic acid gave two anomeric tetraacetylglucuronic acids Ia, which were identified by conversion into the known methyl esters Ib.[2a] As expected, the α-form in benzene solution in the presence of stannic chloride was recovered for the most part unchanged, whereas the β-acid yielded a crystalline compound insoluble in sodium carbonate. The elemental analysis is that required by tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone (II) and the yield on this basis was 76%. Its structure follows from ring-opening with hydrobromic acid to give (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronic acid (IIIa) identical with the compound obtained from both α- and β-forms of tetra-*O*-acetyl-D-glucopyranuronic acid (Ia). Esterification with diazomethane gave methyl (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronate (IIIb), isolated in two crystalline modifications, one of which has been described.[2b] When the bromide IIIa was heated in pyridine it was reconverted in small yield to the lactone. The β-configuration at carbon-1 is the only one structurally possible in a lactone derived from a D-glucopyranuronic acid and its formation is consistent with previous experience in related reactions.[1a]

The lactone reacts normally with excess methanol in the presence of catalysts such as pyridine, pyridine-*p*-toluenesulfonic acid salt, and silver carbonate to give oily methyl 2,3,4-tri-*O*-acetylglucopyranuronate, identified by conversion to methyl tetra-*O*-acetyl-β-D-glucopyranuronate (Ib).

It was expected that both the lactone II and the β-form of the methyl ester Ib, would react with methanol in benzene in the presence of stannic chloride to give methyl tri-*O*-acetyl-β-D-glucopyranosiduronic acidand its methyl ester, respectively, but in no case could any of the desired material be isolated from the oily product. That the carbonyl group is favorably situated for interaction with carbon-1 is demonstrated by the ease with which it displaces an acetoxy group in this position, and it is possible that the failure of these compounds to react in the expected way with methanol is in some way related to the influence of the carbonyl group.

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Experimental

α- and β-Anomers of Tetra-*O*-acetyl-D-glucopyranuronic Acids (Ia).—Fifty grams of glucuronolactone was dissolved in 175 ml. of water and 25 g. of sodium bicarbonate added at room temperature. Carbon dioxide was evolved and in 5 hours the solid dissolved completely. After standing overnight water was removed under reduced pressure at 40°. The residual oil was triturated with ethanol in which it is not soluble. After removing the alcohol under reduced pressure the yellow sodium salt was obtained crystalline. It weighed 66.8 g.[3] Sixty-five grams of *p*-toluenesulfonic acid hydrate was dissolved in 230 ml. of acetic anhydride and the solution chilled in acetone–Dry Ice to 0° and held at this temperature. The powdered sodium salt was added fairly rapidly with mechanical stirring. It dissolved for the most part in 30 minutes at which time sodium *p*-toluenesulfonate began to separate. After a time (not recorded but approximately one hour) the cold mixture was diluted with two volumes of ether and shaken with an aqueous solution of 7 g. of sodium acetate to remove excess *p*-toluenesulfonic acid (separation into two phases occurs only with relatively large amount of water). The aqueous phase was extracted with chloroform and the organic solutions joined and the solvents

(1) (a) R. U. Lemieux, *Can. J. Chem.*, **29**, 1079 (1951); R. U. Lemieux, *Advances in Carbohydrate Chem.*, **9**, 1 (1954); (b) R. U. Lemieux and C. Brice, *Can. J. Chem.*, **30**, 295 (1952); (c) R. U. Lemieux and W. P. Shyluk, *ibid.*, **31**, 528 (1953).

(2) (a) W. F. Goebel and F. H. Babers, *J. Biol. Chem.*, **106**, 63 (1934); (b) **111**, 347 (1935).

(3) An improved method for making this salt has been published by W. Hach and D. G. Benjamin, THIS JOURNAL, **76**, 917 (1954).

removed under reduced pressure. The residual acetic acid concentrate was allowed to evaporate on watch glasses overnight. Adding water to the oil induced crystallization. The water-washed crystals weighed 53.3 g. The oily material in the filtrate was hydrolyzed with dilute aqueous hydrochloric acid to yield 9 g. of crude glucuronolactone. The crystalline mixture was separated into its components by taking advantage of the differences in ether solubility of the pyridine salts of the anomers. It was dissolved in 55 ml. of hot pyridine, the brown solution cooled and diluted with *ca.* 150 ml. of ether. The crystalline salt of the β-anomer separated, wt. 31.8 g. The filtrate was taken to an oil under reduced pressure, the red oil dissolved in water and the solution acidified with hydrochloric acid. The precipitated oil crystallized to give 20.2 g. of the α-anomer. The β-anomer–pyridine salt was dissolved in 50 ml. of warm water, the solution cooled and the salt decomposed with a small excess of hydrochloric acid; the β-anomer separated crystalline in a hydrated form which was freed of water by refluxing in toluene with a water collector. It separated crystalline from the cooled toluene solution but was contaminated by an oil which was removed with ether, leaving 20.0 g. of the β-anomer melting at 146–152°. The oil, 4.6 g., proved to be an α–β mixture and was separated into its components by repassage through the pyridine salt. The β-anomer was further purified by means of toluene and had m.p. 152–154°, $[\alpha]^{20}D$ +16.3° (*c* 0.5 in chloroform).

Anal. Calcd. for $C_{14}H_{18}O_{11}$: C, 46.41; H, 5.01. Found: C, 46.62; H, 5.20.

By the action of diazomethane in ether this acid gave an ester which melted at 172–174° and did not depress the melting point of a sample of methyl tetra-*O*-acetyl-β-D-glucopyranuronate, m.p. 173–176°, prepared by acetylation of methyl glucuronate. For this compound Goebel and Babers[2a] reported m.p. 178°, $[\alpha]^{20}D$ +8.7° (*c* 1.0 in chloroform).

The α-anomer was recrystallized from ethanol, and appeared to contain solvent. Dried in an Abderhalden tube at 80° under reduced pressure, one sample melted at 118–119°. Under the same conditions another portion of the same sample melted at 116–119°. Another dry sample melted at 105–117°, but after moistening with alcohol and redrying, it melted at 114–118°. More than one crystalline form is thereby indicated. The material had $[\alpha]^{19}D$ +111° (*c* 0.7 in chloroform).

Anal. Calcd. for $C_{14}H_{18}O_{11}$: C, 46.41; H, 5.01. Found: C, 46.28; H, 4.90.

The methyl ester was prepared as above. The ester likewise had a broad melting range, from 113–118°. The melting point was not depressed by admixture with a sample, m.p. 117–119°, prepared by acetylation of methyl glucuronate. This compound is reported[2a] to melt at 111–112° with $[\alpha]^{24}D$ +98° (*c* 1.3 in chloroform).

[The material obtained by the acetolysis of β-pachyman in the presence of perchloric acid[4] melting at 103–107°, $[\alpha]^{20}D$ +66.2° (chloroform), could be a mixture of the anomeric acids. Tetra-*O*-acetyl-β-D-glucose on potassium permanganate oxidation is reported to yield an oil consisting mainly of tetra-*O*-acetyl-D-glucuronic acid, $[\alpha]_D$ +6° (*c* 1.1 in chloroform).[5]]

Tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone. A.—A solution of 13.2 g. of tetra-*O*-acetyl-β-D-glucopyranuronic acid in 550 ml. of benzene in a flask equipped with a water trap was refluxed until all visible water was removed. The solution was rapidly cooled to 38° and 5.7 ml. of stannic chloride added. A small amount of flocculent precipitate formed. The temperature dropped to 29° in 40 minutes, when it was reduced to 20° and 13 g. of sodium carbonate in 50 ml. of aqueous solution was added with stirring. The benzene layer was separated, the solvent removed under reduced pressure and the crystalline product filtered from an alcohol suspension. A total of 8.4 g. (76%), m.p. 122–124°, was recovered. Recrystallized from alcohol, it melted at 122.5–124° and had $[\alpha]^{19}D$ −78.6° (*c* 0.9 in chloroform).

Anal. Calcd. for $C_{12}H_{14}O_9$: C, 47.68; H, 4.67. Found: C, 47.86; H, 4.56.

Under similar conditions 80% of the α-anomer was recovered from the aqueous solution after acidification and 10% by weight of an unidentified oil was present in the benzene.

B. (Tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronic acid (see below) was heated in pyridine solution for five minutes. Dilution of the cooled red solution with water gave the lactone in 8% yield. The recovery was increased to 10% by heating the solution for 30 minutes. Identity with the lactone described above was established by melting point and mixture melting point determinations.

(Tri-*O*-acetyl-α-glucopyranosyl bromide)-uronic Acid (IIIa).—A suspension of 1.0 g. of tetra-*O*-acetyl-β-D-glucopyranuronic acid in 2.0 ml. of hydrobromic acid–acetic acid solution containing 0.11 mole of hydrogen bromide was shaken for ten minutes to give a yellow solution. Crystals began to separate in an hour and after two hours water was added to the chilled suspension. The product was removed by filtration and water-washed, wt. 0.85 g. (80%). Recrystallization was effected by adding petroleum ether (30–60°) to a solution in ethyl acetate. It melted with decomposition *ca.* 165°, the temperature of decomposition varying with the rate of heating; $[\alpha]^{20}D$ +209° (*c* 0.4 in chloroform).

Anal. Calcd. for $C_{12}H_{15}BrO_9$: C, 37.61; H, 3.95; Br, 20.86. Found: C, 37.39; H, 3.87; Br, 21.06.

Under similar conditions this compound was also obtained from the α-anomer and the 6,1-lactone in *ca.* 60% yields. The optical rotations and decomposition points were in agreement with the above data but in order to get proof of identity the samples were kept separate and individually converted into the uronic acid described in the next paragraph.

Methyl Tri-*O*-acetyl-β-D-glucopyranosiduronic Acid.—Two grams of (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronic acid in a cooled methanolic solution with silver carbonate reacted in the usual manner to give a crystalline product. Contaminating oil was removed by cold ether. It weighed 0.83 g. (47%), and was recrystallized by adding petroleum ether (30–60°) to a concentrated ethereal solution. After several recrystallizations it melted at 124–127° with a slight previous sinter; $[\alpha]^{19}D$ −20.3° (*c* 1.0 in chloroform).

Anal. Calcd. for $C_{13}H_{18}O_{10}$: C, 46.71; H, 5.43. Found: C, 46.85; H, 5.46.

Samples of this material derived from the anomeric tetraacetylglucopyranuronic acids and from the 6,1-lactone were identical as determined by melting points and mixture melting points.

By the action of diazomethane in ether this acid was converted into methyl (methyl tri-*O*-acetyl-β-D-glucopyranosid)-uronate identical by melting and mixture melting point determinations with a sample prepared from methyl tetra-*O*-acetyl-β-D-glucopyranuronate.[2b]

Methyl (Tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronate (IIIb) resulted from the action of diazomethane in ether on (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronic acid. It recrystallized from alcohol solution in prisms melting at 80–82°. Recrystallization from ether gave prisms which sintered at 80°, resolidified and melted at 103–104°. Goebel and Babers[2b] reported a partial collapse at 85° with melting at 104–105°.

Methanolysis of the Lactone II.—The action of hot methanol on the lactone in the presence of either pyridine, pyridine-*p*-toluenesulfonic acid salt or silver carbonate, in no case yielded the product of abnormal ring-opening, namely, methyl tri-*O*-acetyl-β-D-glucopyranosiduronic acid. Instead the ring opened normally to give an oil which after acetylation yielded methyl tetra-*O*-acetyl-β-D-glucopyranuronate (Ib).

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(5) M. Bridgey, *J. Chem. Soc.*, 1529 (1930).

Some Tetrasubstituted Naphthyl- and Tolylsilanes

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Some of the steric factors concerned with naphthylsilanes have been discussed previously.[1] We

(1) (a) H. Gilman and C. G. Brannen, THIS JOURNAL, **72**, 1850 (1950); (b) **73**, 3600 (1951).