with methanol; crude crystals were obtained in the last evaporation, 320 mg., m.p. 155–161°. Recrystallized from water, the needles had m.p. 160–162°; $[\alpha]^{22}D$ +2.6° (*c* 0.9, methanol); soluble in methanol or ethanol, insoluble in ether, chloroform, or benzene; R_f 0.08 (system 1) and 0.17 (system 2).

Anal. Calcd. for $C_{13}H_{18}O_7$: C, 54.53; H, 6.33. Found: C, 54.32; H, 6.19.

When the 3-*O*-benzoyl-D-galactitol was ammonolyzed in the usual way, evaporation of the solution gave a crystalline product which after recrystallization from water had m.p. 187–189°, did not depress the melting point of pure galactitol, m.p. 188–190°, and gave the same R_f with both systems on paper chromatograms.

Periodate oxidation of 3-*O*-benzoyl-D-galactitol was done according to Hough, *et al.*[17] D-Mannitol was used as the standard. After 1 hr., 1 mole of D-mannitol had consumed 4.90 moles of periodate, and 1 mole of 3-*O*-benzoyl-D-galactitol, 3.06 moles of periodate; after 4 hr., the values were 4.90 and 3.37 moles. The expected values were 5.0 moles for D-mannitol and 3.0 moles for 3-*O*-benzoyl-D-galactitol.

Determination of formaldehyde by the method of Reeves[19] (precipitation with dimedone) gave 2.16 moles; by the colorimetric method of O'Dea and Gibbons,[20] 1.91 moles (calcd., 2.0 moles).

2,4,6-Tri-*O*-methyl-D-galactose (XXII) from 3-*O*-Benzoyl-D-galactose.—To a solution of 300 mg. of 3-*O*-benzoyl-D-galactose in 10 ml. of methanol, 300 mg. of Amberlite IR 120 H^+ was added, and the suspension refluxed for 24 hr. It was then filtered, and the filtrate was evaporated to dryness.

Paper chromatography (system 1) of the resulting sirup revealed the presence of D-galactose (R_f 0.07), methyl D-galactoside (R_f 0.18), and of a nonreducing compound with R_f 0.89. This compound was isolated by paper chromatography on Whatman 3 MM, and elution of the band containing it. Evaporation of the eluate gave 95 mg. of the sirupy residue, which was dissolved in a mixture of 5 ml. of *N*,*N*-dimethylformamide and 1 ml. of methyl iodide, and stirred at room temperature for 12 hr. while 1 g. of silver iodide was slowly added. The insoluble part was then separated, washed with *N*,*N*-dimethylformamide and chloroform, and the washings were added to the original solution. The mixture was shaken with 5 ml. of 20% potassium cyanide solution, and the organic phase was separated, dried, and evaporated. The residue was dissolved in 10 ml. of methanolic ammonia and kept at room temperature for 24 hr., the solution was re-evaporated, and the new residue was treated with 5 ml. of 1 *N* hydrochloric acid and heated at 100° for 4 hr.

The acid was then neutralized with Amberlite IR 400 bicarbonate, the suspension was filtered, and the filtrate was evaporated to dryness, giving 35 mg. of a sirup. On paper chromatograms (system 2) it gave two main spots having R_{TG} 0.79 and 0.92. The substances responsible for these spots were separated by paper chromatography, eluted from the paper, and identified as 2,4,6-tri-*O*-methyl-D-galactose and 2,3,4,6-tetra-*O*-methyl-D-galactose, by running them with authentic samples.

On seeding, the 2,4,6-tri-*O*-methyl-D-galactose (R_{TG} 0.79) crystallized from ether, giving prisms, m.p. 103–104°, that did not depress the melting point of an authentic preparation melting at 104–105°. For further identification, it was transformed into the 2,4,6-tri-*O*-methyl-*N*-phenyl-D-galactosylamine as needles, m.p. 174–175°, in agreement with the data in the literature.[21]

3-*O*-Benzoyl-carbonyl-C^{14}-4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose, m.p. 172–174°, $[\alpha]^{16}D$ +118.1°, 8.290 ± 78 c.p.m. activity, was obtained by the method described above, by benzoylation of the 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose with benzoyl-carbonyl-C^{14} chloride with 8.296 ± 80 c.p.m. activity. On hydrolysis of the protecting groups, a chromatographically pure sirup of **3-*O*-benzoyl-carbonyl-C^{14}-D-galactose** was prepared, which, on reduction, gave **3-*O*-benzoyl-C^{14}-D-galactitol**, m.p. 161–163°, with an activity of 8.250 ± 79 c.p.m., and which on benzoylation produced the needed **3-*O*-carbonyl-C^{14}-1,2,4,6-tetra-*O*-benzoyl-α-D-galactose**, m.p. 156–157°, $[\alpha]^{21}D$ +185.4°, 8.266 ± 80 c.p.m. activity.

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Two Related Syntheses of 2-Amino-2,6-dideoxy-D-galactose (D-Fucosamine)[1]

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Two syntheses of 2-amino-2,6-dideoxy-D-galactose (D-fucosamine), an amino sugar present in bacterial polysaccharides, from derivatives of 2-amino-2-deoxy-D-galactose are described. In both syntheses, the primary 6-hydroxy group of the *galacto* derivative was removed by conversion into the 6-O-*p*-tolylsulfonyloxy compound, replacement of the *p*-tolylsulfonyloxy group by iodide, and hydrogenolysis of the iodo compound.

In 1958, Crumpton and Davies[3] reported the isolation of the crystalline hydrochloride of a new amino sugar from a lipopolysaccharide of *Chromobacterium violaceum*. From elementary analysis, deamination, and periodate oxidation studies, and examination of its phenylosazone, they concluded that the sugar could be either 2-amino-2,6-dideoxy-D-galactose or 2-amino-2,6-dideoxy-D-talose. The infrared spectrum of the amino sugar resembled that of fucose and was different from that of its epimer, 6-deoxytalose, and its molecular rotation was also consistent with a D-*galacto* configuration. Accordingly, the structure assigned to the newly isolated compound was that of 2-amino-2,6-dideoxy-D-galactose (D-fucosamine).

Synthesis of the enantiomorphic sugar, L-fucosamine, subsequently carried out by Kuhn and his co-workers,[4] did not provide unambiguous evidence for the configuration at C-2 of the product; these investigators had used 5-deoxy-L-lyxose as starting material, and a new asymmetric center was formed. More recently, 2-amino-2,6-dideoxy-L-galactose (L-fucosamine) has been isolated from type V *Pneumococcus* capsular polysaccharide,[5] in which it occurs together with 2-amino-2,6-dideoxy-L-talose.[6] The assignment of the *talo* configuration to the latter sugar was also based mainly on rotation data,

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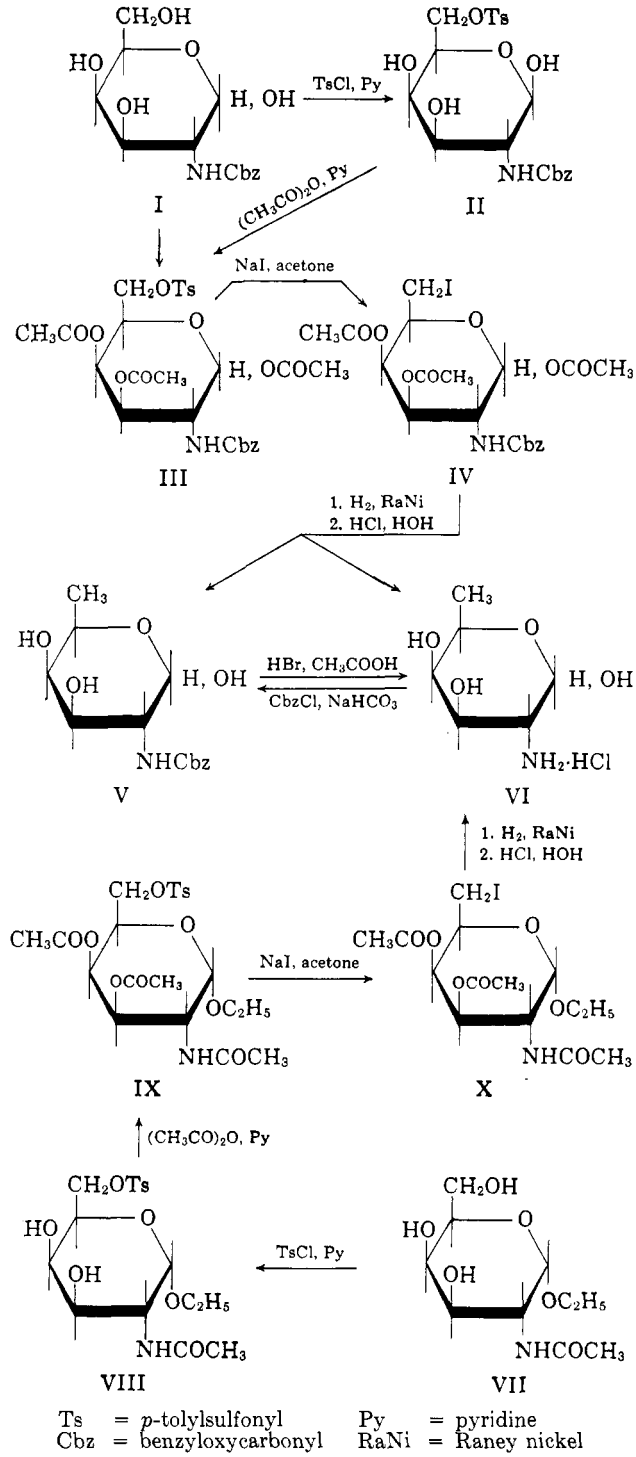
and comparison of its properties with those of the corresponding *galacto* derivative (fucosamine).

Although syntheses of 2-amino-2,6-dideoxy-D-talose[6] and of 2-amino-2,6-dideoxy-L-talose[7] have been reported, reactions involving changes of configuration at C-2 were employed in both cases. Neither of these syntheses, then, afforded conclusive evidence concerning the stereochemistry of C-2 in the two amino sugars.

In the course of our studies of the amino sugars produced by *Bacillus licheniformis*,[8] previously classified as *Bacillus subtilis*,[8] we have found in this organism an amino sugar identical with D-fucosamine from *C. violaceum*. The synthesis of this amino sugar was therefore undertaken. Using 2-amino-2-deoxy-D-galactose as a starting material, we have removed the hydroxy group on C-6 without altering the configuration of the molecule, and have obtained a product identical with the bacterial amino sugar. This synthesis proves unequivocally that, as originally suggested,[3] natural D-fucosamine belongs to the D-*galacto* series, and thus natural 2-amino-2,6-dideoxy-L-talose indeed should belong to the *talo* series.

Similar approaches have been described in the literature for the synthesis of other 6-deoxy hexoses, including 2-amino-2,6-dideoxy-D-glucose (quinovosamine)[9,10] and 2,3-di-O-methyl-6-deoxy-D-galactose.[11] Compared with the corresponding reaction with the D-*gluco* compounds, the replacement of *p*-tolylsulfonyloxy groups by iodo groups in the *galacto* series required a longer time of reaction (13 hr., as opposed to 2–3 hr.)[9,10,12,13]

In the first route of synthesis 2-[(benzyloxycarbonyl)-amino]-2-deoxy-D-galactose (I) was prepared by a modification of the method described in the literature.[14] Reaction with *p*-toluenesulfonyl chloride in pyridine yielded the 6-O-*p*-tolylsulfonyl derivative (II) which was then acetylated with acetic anhydride in pyridine to afford 1,3,4-tri-O-acetyl-2-[(benzyloxycarbonyl)-amino]-2-deoxy-6-O-*p*-tolylsulfonyl-D-galactose (III). This product is probably a mixture of both α- and β-anomers and therefore compound IV described below is also a mixture of anomers. Compound III was also obtained directly from I, without the isolation of II. The *p*-tolylsulfonyloxy group in III was substituted by an iodo group (IV) by treatment with sodium iodide in acetone at high temperature and for a prolonged time (110°, 13 hr.). Compound IV, after hydrogenolysis catalyzed by Raney nickel, gave an undefined oil which on hydrolysis with dilute hydrochloric acid afforded a mixture of 2-[(benzyloxycarbonyl)amino]-2,6-dideoxy-D-galactose (V) and 2-amino-2,6-dideoxy-D-galactose hydrochloride (VI). Compound V was found to be identical with an authentic sample prepared from D-fucosamine isolated from *C. violaceum*.[3,15] Compound VI had the same physical properties and behaviour on paper chromatograms as D-fucosamine from *C. violaceum*. Interconversion of V and VI was also carried out.



In the second route of synthesis ethyl 2-acetamido-2-deoxy-α-D-galactopyranoside[16] (VII) served as the starting material. Treatment of VII with *p*-toluenesulfonyl chloride in pyridine gave the 6-O-*p*-tolylsulfonyl derivative VIII. Acetylation with acetic anhydride in pyridine afforded compound IX which, after reaction with sodium iodide in acetone at high temperature and for prolonged time gave compound X. Hydrogenolysis of X by Raney nickel followed by acid

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hydrolysis yielded 2-amino-2,6-dideoxy-D-galactose hydrochloride (VI). This final product was shown to be identical with natural D-fucosamine from *C. violaceum* by comparison of their physical properties, their behavior on paper chromatograms, and by comparison of their N-acetyl derivatives. It should be noted that compounds IX and X were not isolated in pure crystalline form.

The ultraviolet spectra of the various *p*-tolylsulfonyloxy compounds synthesized by us were in accordance with those found for similar *p*-tolylsulfonyloxy derivatives,[17] and exhibited several maxima in the absorption range. Spectral measurements in the ultraviolet were used by us to distinguish free 6-hydroxy, 6-*p*-tolylsulfonyloxy, and 6-iodo compounds from each other as well as to follow the extent of conversion of one to the other (*e.g.*, III to IV). These measurements were also used to determine the number of *p*-tolylsulfonyloxy groups in the purified intermediates. It should be noted that compound IV absorbs in the ultraviolet owing to the presence of iodo[18] and benzyl[19] residues, and that compound X absorbs owing to the presence of the iodo residue only. In both cases, however, the absorption maximum at 273–274 mμ, characteristic of the *p*-tolylsulfonyloxy group,[17] is missing.

Experimental

All melting points are corrected. The ultraviolet spectra were read on a Beckman Model DK1 recording spectrophotometer between 240 and 280 mμ in chloroform (unless the solvent is noted).

Descending paper chromatography was carried out on Whatman No. 1 paper developed with the upper phase of *n*-butyl alcohol–acetic acid–water (25:6:25 v./v.) (BAW) and with *n*-butyl alcohol–ethanol–water (4:1:1) (BEW). R_{Gm} values refer to mobility relative to that of 2-amino-2-deoxy-D-glucose hydrochloride. Some variations in the R_{Gm} values were observed in different experiments.

The silica gel used for column chromatography was Silica Gel Davison, Will Corp., grade 950, 60–200 mesh.

Thin layer chromatography was carried out on silica gel G (E. Merck, Germany); R_{SR} refers to mobility relative to sudan red, a component of the test mixture supplied by C. Desaga, Heidelberg, Germany. The plates were prepared using a Desaga applicator set for a thickness of 0.25 mm.

2-Amino-2-deoxy-D-galactose hydrochloride was purchased from Pfanstiehl Laboratories, Waukegan, Ill. This material proved to be the β-form (see below).

2-[(Benzyloxycarbonyl)amino]-2-deoxy-D-galactose (I).[14]—2-Amino-2-deoxy-D-galactose hydrochloride (3.24 g.) was dissolved in 50 ml. of 6.6% aqueous sodium bicarbonate solution. While stirring at 0°, benzyl chloroformate (2.4 ml.) was added in two portions. Stirring was continued for 1 hr. at 0° and for an additional 2 hr. at room temperature. The product which precipitated as a crystalline mass was filtered by suction and extracted with hot ethyl acetate (100 ml.). The extract was dried over sodium sulfate and evaporated to dryness; the resulting product was crystallized from ethyl acetate: yield 2.2 g. (46%), m.p. 172–173°, $[\alpha]^{24}D$ +85.5° (5 min.) → 78 ± 0.7° (final, *c* 0.33, pyridine).

Anal. Calcd. for $C_{14}H_{19}NO_7$: C, 53.67; H, 6.11; N, 4.47. Found: C, 53.54; H, 6.33; N, 4.66.

2-[(Benzyloxycarbonyl)amino]-2-deoxy-6-O-*p*-tolylsulfonyl-D-galactose (II).—To a solution of I (0.7 g.) in dry pyridine (10 ml.) *p*-toluenesulfonyl chloride (0.6 g.) was added. The bright yellow reaction mixture was kept under seal for 14 hr. at room temperature. Water (0.5 ml.) was added and after 2 hr. the mixture was shaken with chloroform (100 ml.). The chloroform solution was washed with 10% hydrochloric acid (50 ml.), then with saturated sodium bicarbonate (50 ml.), and finally with water (20 ml.). The washings were successively re-extracted (in the same order) with chloroform (30 ml.). The chloroform solutions were combined, dried over sodium sulfate, and evaporated *in vacuo*. A white crystalline product resulted which was recrystallized from ethyl acetate–petroleum ether (b.p. 60–80°): yield 0.35 g. (33%); m.p. 132–134° dec.; $[\alpha]^{23}D$ + 38.3° (14 min.) → + 58 ± 1° (final, *c* 0.2, acetone); ultraviolet λ_{max} 259 mμ (ε 613), 263 (692), 268 (627), and 274 (475) (in dioxane).

Anal. Calcd. for $C_{21}N_{25}NO_9S$: C, 53.94; H, 5.39; N, 3.00; S, 6.86. Found: C, 53.96; H, 5.34; N, 3.24; S, 6.88.

1,3,4-Tri-O-acetyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-6-O-*p*-tolylsulfonyl-D-galactose (III).—Compound II (0.233 g.) was dissolved in dry pyridine (1.2 ml.), and acetic anhydride (0.35 ml.) was added while the reaction mixture was kept in an ice bath. After 0.5 hr. the mixture was removed from the bath and kept at room temperature overnight. Water was added (0.15 ml.) and after an additional 2 hr. the reaction mixture was extracted with chloroform (50 ml.). The chloroform solution was washed successively with 15% hydrochloric acid (20 ml.), saturated sodium bicarbonate (20 ml.), and water (10 ml.). The washings were re-extracted with chloroform (30 ml.); the combined chloroform extracts were dried over sodium sulfate and evaporated *in vacuo*. The residue, a colorless oil, was fractionated on silica gel (10 g.) using a column 1 cm. in diameter. After being charged with the oil, the silica column was washed with 1,2-dichloroethane (160 ml.) and the washings were discarded. The silica column was then eluted with a mixture of 1,2-dichloroethane–ethyl acetate (2:1, 45 ml.), and an eluate was obtained which, upon evaporation, yielded an oil which then solidified when dried in a desiccator: yield 0.227 g. (77%), $[\alpha]^{23}D$ +89.7 ± 3° (*c* 0.12, chloroform).

Anal. Calcd. for $C_{27}H_{31}NO_{12}S$: S, 5.40. Found: S, 5.64.

On further purification on a silica gel column (10 g., 1 cm. in diameter) that was first washed with 150 ml. of a mixture of 1,2-dichloroethane–ether (25:1) and then eluted with 100 ml. of the same mixture, the product had the following properties: $[\alpha]^{23}D$ +62.5 ± 2° (*c* 0.34, chloroform); ultraviolet λ_{max} 241 mμ (ε 608), 259 (660), 264 (696), 269 (597), and 274 (436).

Compound III was also obtained directly from I without the isolation of II. To a solution of I (2.18 g.) in dry pyridine (30 ml.) was added *p*-toluenesulfonyl chloride (1.8 g.). The reaction mixture was kept under seal at room temperature for 14 hr. It was then cooled in an ice bath, and acetic anhydride (5 ml.) was added. After 0.5 hr. the mixture was taken out from the bath and left standing overnight at room temperature. Water (3 ml.) was added, and after 2 hr. the solution was extracted with chloroform (500 ml.). The chloroform solution was washed successively with 15% hydrochloric acid (200 ml.) and saturated sodium bicarbonate (200 ml.). The washings were re-extracted with chloroform (300 ml.); the combined chloroform extracts were dried over sodium sulfate and evaporated *in vacuo*. An oil was obtained, which was purified on a silica gel column (100 g., 4 cm. in diameter). The column was first washed with 1,2-dichloroethane (500 ml.), then with 1,2-dichloroethane–ether (25:1, 250 ml.), and the desired product was eluted with 1,2-dichloroethane–ether (12:1, 250 ml.). Upon evaporation an oil was obtained, weighing 2.0 g. (50%). This oil was examined by thin layer chromatography on silica gel G using 1,2-dichloroethane–ether (3:1) as developer. The spots were revealed by a sulfuric acid spray followed by heating at 120° for 15 min. Four spots appeared, with R_{SR} values of 0.51, 0.61, 0.78, and 0.98. Material corresponding to the first two spots was eluted with ethyl acetate from a preparative thin layer chromatogram to which 50 mg. of the oil was applied, and which was run under the same conditions as above. Evaporation of the ethylacetate yielded 8 mg. of an oil, which, on the basis of its sulfur content, may have been a mixture of isomeric 3,6- and 4,6-di-O-*p*-tolylsulfonyl derivatives of II, with the empirical formula $C_{32}H_{35}NO_{13}S_2$.

Anal. Calcd. for $C_{32}H_{35}NO_{13}S_2$: S, 9.09. Found: S, 8.80.

A second fraction, isolated from the same preparative chromatogram (R_{SR} = 0.78, 32 mg.), represented the bulk of the applied material. It possessed properties corresponding to those of III: $[\alpha]^{25}D$ + 58 ± 0.5° (*c* 0.9, chloroform); ultraviolet λ_{max} 258 mμ (ε 652), 262 (709), 267 (622), and 273 (487).

Anal. Calcd. for $C_{27}H_{31}NO_{12}S$: C, 54.63; H, 5.26; N, 2.36; S, 5.40. Found: C, 54.44; H, 5.25; N, 2.68; S, 5.02.

The fast-moving product (R_{SR} = 0.98, 7 mg.) had a sulfur content corresponding also to that of a mono-*p*-tolylsulfonyl derivative.

Anal. Calcd. for $C_{27}H_{31}NO_{12}S$: S, 5.40. Found: S, 5.62.

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1,3,4-Tri-O-acetyl-2-[(benzyloxycarbonyl)amino]-2,6-dideoxy-6-iodo-D-galactose (IV).—Compound III (0.2 g.) was dissolved in acetone (3.4 ml.), sodium iodide was added (0.2 g.), and the mixture was put into a shaking autoclave. The reaction was carried out at 110° for 13 hr. The crystalline sodium *p*-toluenesulfonate which formed was removed by filtration and washed with a small amount of cold acetone. The combined acetone filtrates were evaporated at room temperature, and the resulting residue was extracted with chloroform (100 ml.). The extract was washed with 10% solution of sodium thiosulfate (20 ml.) and water (20 ml.), dried over sodium sulfate, and evaporated *in vacuo*. An oil was obtained which solidified on standing. The product contained only 53% of the expected amount of iodine. The crude material was fractionated twice on silica gel. The first column (10 g., 1 cm. in diameter) was washed with 1,2-dichloroethane (100 ml.) and eluted with 1,2-dichloroethane–ether (25:1, 160 ml.) to yield the desired product and some of the faster-moving starting material. This product was further purified on a second column of similar size by washing first with 1,2-dichloroethane–ether (50:1, 170 ml.) and eluting the product with the same solvent (200 ml.). Evaporation of the solvent mixture *in vacuo* at room temperature yielded an oil (IV): 73 mg. (42.5%); $[\alpha]^{24}D$ +56.2 ± 0.7° (*c* 0.12, chloroform); ultraviolet λ_{max} 254 mμ (ε 643), 259 (661), 264 (588), and 269 (437).

Anal. Calcd. for $C_{20}H_{24}INO_8$: I, 23.15. Found: I, 22.7.

2-[(Benzyloxycarbonyl)amino]-2,6-dideoxy-D-galactose (V). A. From the Natural Amino Sugar (VI).—D-fucosamine hydrochloride (40 mg.) from *C. violaceum*[15] was dissolved in water (1 ml.) and sodium bicarbonate (34 mg.) was then added. The solution was stirred with a magnetic stirrer, and cooled in an ice bath. Benzyl chloroformate was next added (0.02 ml.), and after 1 hr. the bath was removed and the mixture was stirred for 2 hr. at room temperature. The white precipitate which formed was filtered by suction and extracted with hot ethyl acetate (20 ml.); the ethyl acetate extract was dried over sodium sulfate. The ethyl acetate was removed *in vacuo* and the product was crystallized from ethyl acetate: yield 26 mg. (52%), m.p. 184° (turned brown few degrees above its melting point), $[\alpha]^{24}D$ +100° (14 min.) → +84 ± 1.3° (final, *c* 0.4, methanol).

Anal. Calcd. for $C_{14}H_{19}NO_6$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.40; H, 6.43; N, 4.81.

B. From IV.—Compound IV (0.239 g.) was dissolved in absolute methanol (5 ml.) and the solution was transferred to a hydrogenation flask which contained methanol (15 ml.), Raney nickel (25 mg.), and diethylamine (0.13 ml.) after equilibration with hydrogen. The consumption of hydrogen was 14.0 ml. and ceased after 1 hr. Following hydrogenation, the catalyst was removed by filtration and the solution was evaporated. The residue was dissolved in ethyl acetate (100 ml.) and the resulting solution was washed successively with 0.1 *N* hydrochloric acid (10 ml.), with saturated sodium bicarbonate (10 ml.), and finally with 20% sodium thiosulfate (10 ml.). The solution was then dried over sodium sulfate and the ethyl acetate was evaporated to give an oil. Hydrochloric acid, 10% (5 ml.), was added to the oil; the mixture was sealed in an ampule and heated at 110° for 3 hr. The cooled reaction mixture was extracted with ethyl acetate (150 ml. in two portions) and the ethyl acetate solution was re-extracted with water (5 ml.). The combined aqueous solution was kept for the isolation of 2-amino-2,6-dideoxy-D-galactose hydrochloride (VI, see below). The ethyl acetate solution was dried over sodium sulfate and treated with active charcoal. The solution was concentrated and petroleum ether was added until turbidity appeared. A crystalline precipitate was formed upon standing (V): yield 25.2 mg. (20%), m.p. 151–153°, $[\alpha]^{24}D$ +84.8° (7 min.) → +81.6 ± 1.6° (final, *c* 0.3, methanol); after recrystallization from ethyl acetate, m.p. 173°, $[\alpha]^{24}D$ +96.2° (6 min.) → +78 ± 1.3° (final, *c* 0.33, methanol). The material was found to be identical with 2-[(benzyloxycarbonyl)amino]-2,6-dideoxy-D-galactose prepared from the natural amino sugar as described above by mixture melting point and by having superimposable infrared spectra.

Anal. Calcd. for $C_{14}H_{19}NO_6$: N, 4.71. Found: N, 4.80.

C. From Synthetic 2-Amino-2,6-dideoxy-D-galactose Hydrochloride (VI).—Compound VI (see below, 10 mg.) was treated with benzyl chloroformate according to A, yielding 5 mg. of crude product: after recrystallized from ethyl acetate, m.p. 181–182°, $[\alpha]^{24}D$ +106° (6 min.) → +85 ± 4° (final, *c* 0.06, methanol). The material was found to be identical with V prepared from the natural amino sugar by mixture melting point and by having superimposable infrared spectra.

2-Amino-2,6-dideoxy-D-galactose Hydrochloride (VI). A From IV.—The aqueous solution obtained in the preparation of V by hydrogenation of IV was evaporated at room temperature *in vacuo* and the residue was crystallized from water, methanol, and acetone: yield 25 mg. (40%), dec. pt. 192°, $[\alpha]^{23}D$ +117° (3 min.) → +92 ± 1.2° (final, *c* 0.2, water). The material moves on paper chromatograms as a single spot [R_{Gm} 1.82 (BEW), 1.78 (BAW)], similar to natural D-fucosamine [R_{Gm} 1.82 (BEW), 1.76 (BAW)]. It could be revealed by treatment of the paper with the ninhydrin or silver nitrate reagents.[20] The infrared spectra of the synthetic and natural compounds were indistinguishable.

Anal. Calcd. for $C_6H_{14}NClO_4$: N, 7.02. Found: N, 6.82.

B. From Synthetic 2-[(Benzyloxycarbonyl)amino]-2,6-dideoxy-D-galactose (V).—Compound V, (10 mg.) was dissolved in 22% hydrogen bromide in acetic acid (2 ml.). After 1 hr. dry ether (50 ml.) was added and the hygroscopic hydrobromide which precipitated was transferred with water (1 ml.) to a short column of Amberlite IR 120-H^+ (5 g., 1.5 cm. in diameter). The column was washed with water (50 ml.) and the eluate was discarded. The amino sugar was eluted by passage of 1 *N* hydrochloric acid (40 ml.). The eluate, evaporated to dryness *in vacuo*, yielded a small amount of material which failed to crystallize. Chromatography of this material on paper, followed by reaction with ninhydrin or silver nitrate, revealed a single spot [R_{Gm} 1.91 (BEW), 1.74 (BAW)] corresponding to 2-amino-2,6-dideoxy-D-galactose hydrochloride (R_{Gm} 1.93 (BEW), 1.74 (BAW)).

2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-galactopyranoside.—This material was prepared as described in the literature,[16] but in a greatly improved yield, using as starting material the β-anomer of 2-amino-2-deoxy-D-galactose hydrochloride: 2.0 g., dec. pt. 177°, $[\alpha]^{27}D$ + 55.6° (4 min.) → +94.5 ± 1° (final, *c* 0.85, water). The yield was 2.25 g. (62%) of material crystallized from ethyl acetate: dec. pt. 234–235°, $[\alpha]^{27}D$ +9.2 ± 0.9° (*c* 0.5, chloroform).

Anal. Calcd. for $C_{16}H_{23}NO_{10}$: C, 49.35; H, 5.95; N, 3.60. Found: C, 49.34; H, 5.94; N, 3.32.

Ethyl 2-Acetamido-2-deoxy-α-D-galactopyranoside (VII).—This compound was prepared from 2-acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-galactopyranoside as described in the literature.[16]

Ethyl 2-Acetamido-2-deoxy-6-O-*p*-tolylsulfonyl-α-D-galactopyranoside (VIII).—Compound VII (0.2 g.) was dissolved in dry pyridine (3 ml.). A soft gel was obtained, to which *p*-toluenesulfonyl chloride (0.3 g.) was added, and the mixture was shaken. A bright yellow color appeared immediately. The solution was kept at room temperature for 14 hr., water (0.2 ml.) was then added, and after an additional 2 hr. the reaction mixture was diluted with chloroform (60 ml.). The chloroform solution was washed successively with 10% hydrochloric acid (20 ml.), saturated sodium bicarbonate (20 ml.), and water (20 ml.). The chloroform was dried over sodium sulfate and evaporated *in vacuo*. The residue, a mixture of oil and solid, was crystallized from acetone–petroleum ether: yield 0.11 g. (35%); m.p. 144–145° dec.; $[\alpha]^{23}D$ +70.2 ± 0.2° (*c* 0.3, chloroform); ultraviolet λ_{max} 241 mμ (ε 465), 257 (457), 263 (607), 266 (567), 268 (560), and 274 (508).

Anal. Calcd. for $C_{17}H_{25}NO_8S$: N, 3.47; S, 7.95. Found: N, 3.40; S, 8.31.

Ethyl 2-Acetamido-3,4-di-O-acetyl-2-deoxy-6-O-*p*-tolylsulfonyl α-D-galactopyranoside (IX).—Compound VIII (0.1 g.) in dry pyridine (0.5 ml.) was treated with acetic anhydride (0.15 ml.) at 0° and left overnight at room temperature. Water was added (0.1 ml.) and the mixture was left for 2 hr. It was then extracted with chloroform (50 ml.). The chloroform solution was washed successively with 10% hydrochloric acid (20 ml.), saturated sodium bicarbonate (20 ml.), and water (20 ml.). The solution was dried over sodium sulfate and evaporated *in vacuo*. The residue was an oil: yield 0.104 g. (86%); $[\alpha]^{22}D$ +76.4 ± 1.2° (*c* 0.4, chloroform); ultraviolet λ_{max} 258 mμ (ε 473), 263 (605), 266 (569), 269 (575), and 274 (518).

Anal. Calcd. for $C_{21}H_{29}NO_{10}S$: N, 2.93. Found: N, 2.35.

Ethyl 2-Acetamido-3,4-di-O-acetyl-2,6-dideoxy-6-iodo-α-D-galactopyranoside (X).—The acetylated *p*-tolylsulfonyl compound (IX, 0.15 g.) was reacted with sodium iodide (0.15 g.) in the manner described for IV. The oil obtained upon evaporation of the chloroform solution was fractionated by means of a silica gel column (20 g., 1.5 cm. in diameter). The column was

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first washed with 1,2-dichloroethane–ethyl acetate (9:1, 250 ml.), the washings were discarded, and the product was eluted with 1,2-dichloroethane–ethyl acetate (1:1, 200 ml.): yield 52 mg. (37%) of oil, $[\alpha]^{23}D$ +84.3 ± 0.2° (*c* 2, chloroform), ultraviolet λ_{max} 256 mμ (ε 497).

Anal. Calcd. for $C_{14}H_{22}INO_7$: I, 28.63; CH_3CO, 29.13. Found: I, 27.42. Found (in another fraction): I, 31.00; CH_3CO, 26.9.

2-Amino-2,6-dideoxy-D-galactose Hydrochloride (VI).—The iodo derivative X (50 mg.) was dissolved in methanol (10 ml.) containing Raney nickel (10 mg.) and diethylamine (0.02 ml.), and was reduced under pressure for 1 hr. The reaction mixture was treated as described under the preparation of V from IV. The oil obtained upon evaporation of the ethyl acetate solution still contained 8.6% of iodine. The oil was hydrolyzed by treatment with 2 *N* hydrochloric acid (0.3 ml.) in a sealed ampule for 2.5 hr. at 110°. In the hydrolysate the major product was 2-amino-2,6-dideoxy-D-galactose hydrochloride as revealed by ninhydrin and by silver nitrate [R_{Gm} 1.81 (BEW), 1.78 (BAW)]. There appeared three additional spots, one of which had R_{Gm} 0.90 (BEW), 0.88 (BAW) and corresponded to 2-amino-2-deoxy-D-galactose hydrochloride [R_{Gm} 0.90 (BEW), 0.87 (BAW)] (probably resulting from the hydrolysis of the small amount of iodo compound left). The other two had R_{Gm} 2.67 and 3.00 (BEW), 2.44 and 2.82 (BAW). The material having R_{Gm} 1.78 (BAW) was eluted from a preparative chromatogram on Whatman No. 3 paper (BAW) by water (50 ml.) and methanol (20 ml.). Hydrochloric acid, 1 *N* (2 ml.), was added and the combined solutions were partially evaporated *in vacuo*. Addition of acetone gave rise to a crystalline product: yield 2.83 mg. (7%), dec. pt. 174–176°, $[\alpha]^{25}D$ +99.4° (5 min.) → +81 ± 1° (final, *c* 0.24, water).

Anal. Calcd. for $C_6H_{14}ClNO_4$: N, 7.02. Found: N, 6.83.

2-Acetamido-2,6-dideoxy-D-galactose. A. From D-Fucosamine of *C. violaceum*.—This compound was prepared according to the method of Kuhn, *et al.*[4]: m.p. 196–197° dec., $[\alpha]^{23}D$ +129° (4 min.) → + 92 ± 0.1° (final, *c* 2, water).

Anal. Calcd. for $C_8H_{15}NO_5$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.49; H, 7.40; N, 6.62.

B. From Synthetic 2-Amino-2,6-dideoxy-D-galactose Hydrochloride.—The mother solution of VI was evaporated and the residue was dissolved in a minimal amount of water. Methanol (0.5 ml.), triethylamine (0.02 ml.), and acetic anhydride (0.02 ml.) were added at room temperature and the mixture was left overnight. The whole reaction mixture was spotted on paper and chromatographed in BAW. A single spot could be detected which gave positive reaction with silver nitrate and which moved the same distance as an authentic sample of 2-acetamido-2,6-dideoxy-D-galactose A. Both compounds had an R_{Gm} of 2.68 (BAW). No material reacting with ninhydrin could be detected in the chromatograms.

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A Re-examination of the Polymerization of Sterculic Acid. II. Ozonolysis of the Sterculic Acid Polymer

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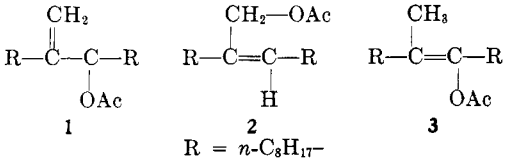
The sterculic acid polymer was ozonized to yield formaldehyde, 2-decanone, 2-keto-1-decanol, azelaic acid, 9-ketodecanoic acid, nonanoic acid, and a mixture of 9-keto-10-hydroxy- and 9-hydroxy-10-ketostearic acids. These products are in accord with the two allyl ester structures (**1a** and **b**, and **2a** and **b**) in the polymer as well as the enol ester structure (**3a** and **b**).

In part I it was shown that 1,2-di-*n*-octylcyclopropene reacts with acetic acid to form the allyl esters **1** and **2** plus smaller amounts of the enol ester **3**.[1]



1 **2** **3**

R = *n*-C_8H_{17}–

Sterculic acid (**4**) polymerizes in a similar fashion with opening of the cyclopropene ring and formation of a polyester.[2-4] Permanganate–periodate oxidations of the acetylated acids from hydrolysis of the polymer showed the two allyl ester structures (**1a** and **b** and **2a** and **b**) to be present, but no chemical or spectroscopic evidence for **3a** and **b** could be found.[4] The olefinic carbon atoms in **4** and its reaction products are starred (Chart I).

The ratios of the various repeating units in this structure do not correspond to those in the polymer; the structure is illustrative only of the types of units that are present in the polymer. When a mixture of **1** and **3** was oxidized with permanganate–periodate in the presence of *t*-butyl alcohol,[5] nonyloin acetate (from **1**) and unchanged **3** were obtained.[1] Ozonolysis of the same mixture yielded the cleavage products expected from both compounds.[1] Although the permanganate–periodate reagent is able to cleave mono-,[6] di-,[5,6] and trisubstituted[4] olefins, it was unable to attack the tetrasubstituted derivative **3**. Ozone, on the other hand, cleaves the tetrasubstituted olefins 1,2-dimethylcyclopentene[7] and 2,3-diphenylindene[8] as well as **3**,[1] and the presence of **3a** and **3b** in the sterculic acid polymer could be revealed by ozonolysis and identification of 2-decanone (from **3a**) and 9-ketodecanoic acid (from **3b**).

Sterculic acid was polymerized at 110° for 3 hr. and the polymer was extracted with methanol to remove low molecular weight material.[4] Its average degree of polymerization by titration was 12.8 sterculic acid residues per chain. It was saponified (sapon. equiv.: calcd., 294.5; found, 296 and 295) to a mixture of acids

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