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3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose, an Acetamido-D-galactal Derivative, and the Mechanism of its Formation from 2-Acetamido-2-deoxy-D-galactose*

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The structure of an unsaturated amino sugar derivative, formed in low yield when 2-acetamido-2-deoxy-D-galactose is treated with boiling isopropenyl acetate containing a trace of *p*-toluenesulfonic acid, and formulated as 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-D-*threo*-hex-2-enopyranose(II) in an earlier publication, has been re-examined. Through a series of steps, including catalytic hydrogenation, the substance has been converted into a compound with an NMR spectrum which shows it to be 3,4,6-tri-*O*-acetyl-2-(*N*-acetylbenzamido)-1,5-anhydro-2-deoxy-D-talitol (X). This fact, together with a re-examination of its NMR spectrum, show the unsaturated compound to be 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose (III), a derivative of 2-acetamido-D-galactal (VI). The yield of III from 2-acetamido-2-deoxy-D-galactose has been substantially improved through isolation of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-galactopyranose (XIII) as an intermediate and III has been obtained in crystalline form. Evidence for the mechanism of its formation is presented.

Recent studies[1-4] have shown that the three 2-acetamido-2-deoxyaldohexoses of the D-*gluco*, D-*manno*, and D-*galacto* series behave in markedly diverse fashion when acetylated with boiling isopropenyl acetate containing a trace of *p*-toluenesulfonic acid. The D-*manno* isomer[2,3] gives a variety of substances which includes the unsaturated derivative 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (I). With this powerful acetylating agent, 2-acetamido-2-deoxy-D-galactose affords five products[4], and one of these, isolated as a syrup in 4.5% yield, proved to be an isomer of I. The NMR spectrum of the substance contained a low field doublet of spacing 1.6 Hz. This signal stood in contrast to the sharp singlet from H-1 of I and was assumed to represent the H-3 signal split by coupling with H-4 since a pair of doublets centered at τ 4.40 each showed a spacing of 1.6 Hz. Such couplings, albeit of

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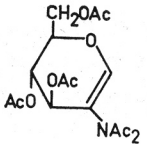
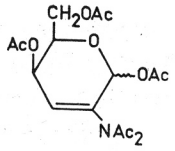
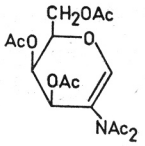
somewhat greater magnitude, have been observed in various diastereoisomeric methyl 3-deoxy-2,4,6-tri-*O*-methylhex-2-enopyranosides[5]. Treatment of the new unsaturated amino sugar derivative with sodium methoxide removed the *O*-acetyl and one of the *N*-acetyl groups to yield a crystalline compound which



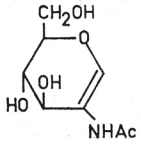
I



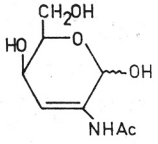
II



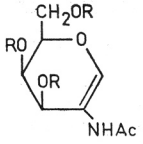
III



IV

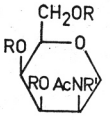


V



VI, R = H

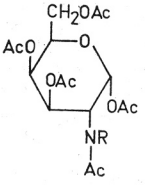
VII, R = Ac



VIII, R = R' = H

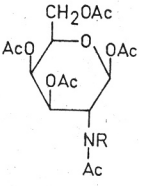
IX, R = Ac, R' = H

X, R = Ac, R' = CC_6H_5 (O)



XI, R = H

XII, R = Ac



XIII, R = H

XIV, R = Ac

gave a positive Fehling test; the corresponding derivative from I (IV) was stable toward Fehling solution. On the basis of these pieces of evidence, the new amino sugar derivative was assigned structure II and its deacetylation product structure V. In subsequent work we have succeded in crystallizing the acetylated unsaturated amino sugar derivative. A re-examination of the structure of this substance will now be described.

Like I, the unsaturated derivative from 2-acetamido-2-deoxy-D-galactose is resistant to catalytic reduction over palladium; steric factors are presumably responsible. The deacetylated derivative from it was, however, readily reduced, giving a single crystalline product in 96% yield; this was acetylated with acetic anhydride—pyridine to give a chromatographically homogeneous syrup. Elemental analysis and NMR clearly showed the presence of an *N*-acetyl group and three *O*-acetyl groups but other features were not readily apparent in the 60-MHz spectrum. As it has recently been shown[6] that the NMR spectra of some di-*N*-acyl derivatives are more readily interpretable than those of the corresponding *N*-acetyl compounds, we treated the acetate with benzoyl chloride, converting the acetamido group into an *N*-acetylbenzamido group. The resulting compound was a chromatographically homogeneous syrup with an elemental composition corresponding to $C_{21}H_{25}NO_9$. The NMR spectrum of the substance, measured at 100 MHz in deuterochloroform solution, is shown in Fig. 1. That only one ring proton appears as an octet (centered at τ 4.98) sug-

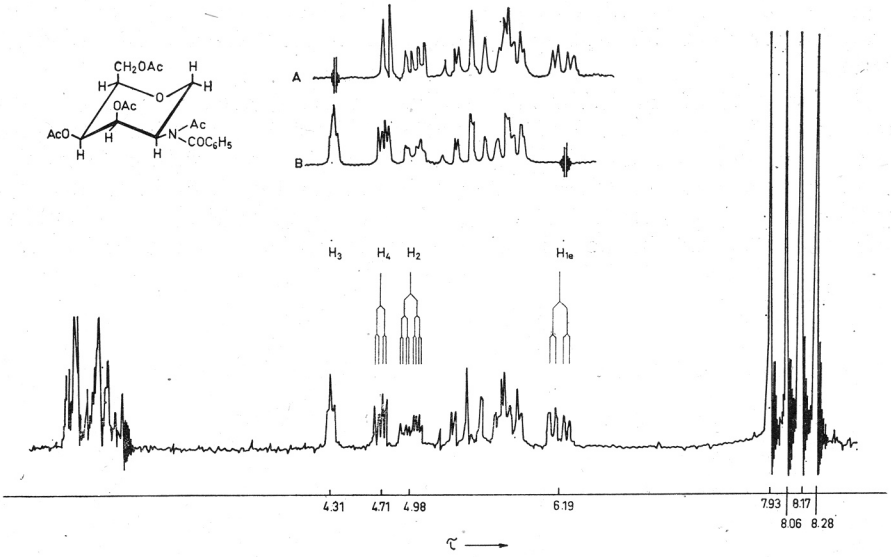


Fig. 1. NMR spectrum at 100 MHz of 3,4,6-tri-*O*-acetyl-2-(*N*-acetylbenzamido)-1,5-anhydro-2-deoxy-D-talitol (X) in $CDCl_3$ solution.

gests that H-2 is adjacent to geminal protons at C-1. Indeed, irradiation of the quartet centered at τ 6.19 caused the H-2 octet to collapse to a quartet and also caused a change in the spectrum around τ 5.50 (insert B in Fig. 1). The magnitude of the coupling constants (11.5 and 4.8 Hz) in the signal at τ 6.19 requires assignment of this quartet to the equatorial member of the geminal pair at C-1. The chemical shift for H-1a is in the neighborhood of τ 5.50, being overlaid with part of the H-5 signal. Precise assignment aside, H-1a is doubtless strongly deshielded so that it appears at lower field that H-1e. Although equatorial protons tend, in general, to give signals at lower field than axial ones[7], a reversal of this relationship is often found[6,8,9] when deshielding influences are present.[10]

The low field triplet of narrow spacing at τ 4.31 is ascribed to H-3. Irradiation at this position caused the H-4 quartet centered at τ 4.71 to collapse to a doublet and, as expected, the H-2 octet collapsed to a quartet (insert A in Fig. 1). The small coupling constants for H-3 and the adjacent protons suggest the gauche arrangement of the *talo* configuration.[7,11] The existence of a 10.0 Hz coupling in the H-2 octet indicates that H-2 must stand in a *trans*-diaxial relationship with one of the protons at C-1; with the D-*talo* configuration this indicates the *1C* conformation. Such a conformation may be preferred inasmuch as it places the bulky *N*-acetylbenzamido group in the equatorial position. In passing, it may be noted that the *O*- and *N*-acetyl signals appear at unusually high field. The NMR spectra of more examples of this type of structure must be examined before further comment on this phenomenon can be made.

The NMR evidence discussed above is fully consistent with formula X, 3,4,6-tri-*O*-acetyl-2-(*N*-acetylbenzamido)-1,5-anhydro-2-deoxy-D-talitol, and this structure clearly shows that III rather than II represents the unsaturated compound in question. In passing, it may be noted that models of both of the more probable conformers of VI clearly show steric features which should make the D-*talo* (rather than the D-*galacto*) configuration preponderate on catalytic reduction.

In the light of the evidence described above, it became necessary to reexamine the NMR spectrum of the unsaturated substance which was obtained directly from 2-acetamido-2-deoxy-D-galactose. In deuterochloroform at 100 MHz it gave a spectrum which is shown, in part, in Fig. 2. A simple decoupling experiment quickly demonstrated that the matching spacings of 1.6 Hz in the doublet at τ 3.39 and in the pair of doublets centered at 4.40 are, in fact, fortui-

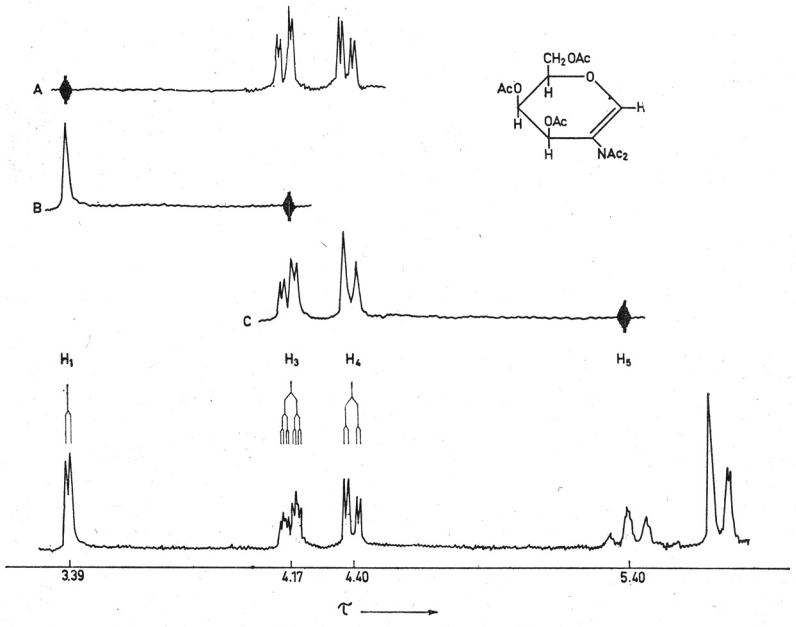


Fig. 2. NMR spectrum at 100 MHz of 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose (III) in $CDCl_3$ solution.

tous. Irradiation of the low field doublet at τ 3.39 did not affect the pair of doublets at 4.40 but caused the pair of quartets at 4.17 to collapse to a pair of doublets (insert A in Fig. 2); conversely, irradiation of the pair of quartets at 4.17 sharpened the low field doublet at 3.39 to a singlet (insert B in Fig. 2). This pattern of signals is most readily rationalized on the basis of structure III, the low field doublet representing H-1 coupled at long range with H-3 whose signal at τ 4.17 shows couplings with protons further around the ring. Confirmation of these assignments came through irradiation of the signal centered at 5.40. The H-3 signal at 4.17 collapsed to a quartet with spacings of $J_{1,3} = 1.6$ and $J_{3,4} = 4.2$ Hz; the quartet from H-4, centered at 4.40, also collapsed to a doublet (insert C in Fig. 2). It is apparent, then, that H-3 is coupled at long range to H-5 which gives the signal centered at 5.40. Thus, NMR data fully support structure III.

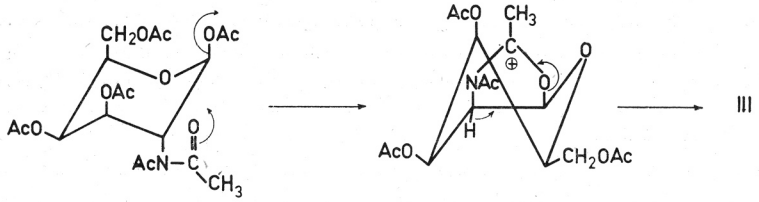
The 2,3,4,6-tetra-*O*-acetyl-1-deoxy-hex-1-enopyranoses of the D-*arabino* and D-*lyxo* configurations (»2-hydroxy-D-glucal tetraacetate« and »2-hydroxy-D--galactal tetraacetate«) may be regarded as analogs of I and III in which the diacetamido group at C-2 has been replaced by an acetoxy group. It is, therefore, interesting to note that the vinyl proton of the D-*arabino* isomer gives a sharp singlet at 3.35 while H-1 of the D-*lyxo* isomer gives a doublet with a spacing of 1.3 Hz centered at 3.36.[12] Since vinyl—allylic proton couplings reflect spatial relationships[13], it is apparent that I and III (as well as their hydroxyhexal tetraacetate analogs) exist in different conformations.

While the present investigation was in progress, wholly independent evidence for structure III was obtained in the Bethesda laboratories.[14] On heating in tetramethylurea solution containing a trace of *p*-toluenesulfonic acid, the 4,5-(3,4,6-tri-*O*-acetyl-2-deoxy-hexopyrano)-2-methyl-2-oxazolines with the D-*gluco* and D-*manno* configurations were found to rearrange to the tri-*O*--acetyl derivative of IV. That a similar rearrangement of the corresponding oxazoline with the D-*galacto* configuration, followed by de-*O*-acetylation, gave the unsaturated compound which we described earlier[4], further confirms structure VI and, hence, III. It was also found that highly purified samples of VI appear to be devoid of reducing power toward hot Fehling solution.

With the dual objective of making III more readily available for further research and of providing some evidence bearing on the mechanism of its formation, we have examined the behavior of the two anomeric 2-acetamido--1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-galactoses[15] (XI and XIII) with isopropenyl acetate containing a trace of *p*-toluenesulfonic acid. When the α anomer (XI) was treated in this fashion for 48 hrs., 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-galactopyranose (XII) was obtained in 96% yield, no III being detected. It is possible that an earlier report[4] of the formation of III in low yield (3.9%) in this reaction arose through the presence of some XIII as an impurity in the XI which was used. The β anomer XIII gave III in 69% yield and XII in 9% yield. When the reaction time was shortened to 1 hr., however, the main product from XIII proved to be 1,3,4,6-tetra-*O*-acetyl-2-(*N*--acetylacetamido)-2-deoxy-β-D-galactopyranose[4] (XIV). Monitoring the progress of the reaction with thin layer chromatography revealed that on long boiling XIV decreases as III increases. Treatment of pure XIV with isopropenyl acetate in a separate experiment gave III in 42% yield. The formation of a small proportion of XII on treatment of XIII may be due to a $\beta \rightarrow \alpha$ anomerization

although earlier studies[3] appeared to indicate that neither of the anomeric 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-mannopyranoses were anomerized under these conditions.

The evidence here clearly indicates that III is formed from XIV and a mechanism analogous to that suggested earlier[3] for a parallel case in the D-*manno* series is presumed to be operative. It is to be noted that, while XIV was



XIV

isolable from the reaction mixture, no trace of 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-mannopyranose, the corresponding intermediate in the D-*manno* series, was ever detected.[2,3] It is likely that the penultimate step in the formation of compounds such as I and III involves a *trans* diaxial attack of one of the *N*-acetyl groups on the acetoxy group at C-1. As the precursor in the D-*manno* series presumably affords the required *trans* diaxial arrangement in its normal conformation, the D-*manno* intermediate mentioned above may have but a transient existence. In the D-*galacto* series, attack may involve the *1C* conformation (XIV) and the energy barrier in going from the normal *C1* conformation of XIV through to III may explain the presence of XIV in the earlier stages of the reaction. As mentioned earlier, acetylation of 2-acetamido-2-deoxy-D-glucose with isopropenyl acetate produces 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-glucopyranose. To place the required groups of this compound in the *trans* diaxial orientation would require an intermediate with all groups axial and it is, therefore, perhaps not surprising that no trace of I has been detected when 2-acetamido-2-deoxy-D-glucose is treated with isopropenyl acetate—*p*-toluenesulfonic acid.

EXPERIMENTAL

Melting points are uncorrected. Specific rotations were measured at 20—23°. Thin layer chromatography was conducted on silica gel G (E. Merck) using the solvent system specified, components being detected by spraying with 10% sulfuric acid and heating at 100°. Column chromatography was conducted on silica gel (0.2—0.5 mm, E. Merck), 10-ml fractions being collected. The NMR spectra were obtained in chloroform-*d* solution using Varian A-60A, Varian HA-100, and JEOL JNM-4-H-100 spectrometers and tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin Elmer Model 137 instrument.

*Catalytic Reduction of 2-Acetamido-1,2-dideoxy-*D-lyxo-*hex-1-enopyranose* (VI) *to 2-Acetamido-1,5-anhydro-2-deoxy-*D-*talitol* (VIII)

Crystalline VI (350 mg., formerly designated[4] as 2-acetamido-2,3-dideoxy-D-*threo*-hex-2-enose) was dissolved in glacial acetic acid (10 ml.); palladium black catalyst (300 mg.) was added and the suspension was shaken with hydrogen at room temperature until absorption of the gas had ceased (7 hr.). The catalyst was removed

by filtration and the filtrate was concentrated *in vacuo* (40° bath) to a colorless syrup which was dried *in vacuo* over sodium hydroxide. TLC of the resulting syrup showed the presence of two components and it was chromatographed on a column of silica gel (20 g.) using ether—methanol (3 : 1, v/v) for elution.

Fractions 11 to 23 contained the major product which was obtained as a syrup (338 mg., 96%) which solidified on standing. All attempts to crystallize the substance failed. For analysis, the 2-acetamido-1,5-anhydro-2-deoxy-D-talitol (VIII) was dried at 60°: m. p. 110—112°, $[\alpha]_D$ —76.8° (c 1.01, H_2O). IR absorption (KBr) was observed at 3300 (OH and NH), 1630 and 1520 $cm.^{-1}$ (NHAc).

Anal. $C_8H_{15}NO_5$ (205.22) calc'd.: C 46.82; H 7.37; N 6.83%
found: C 46.74; H 7.48; N 7.12%

*2-Acetamido-3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-*D*-talitol* (IX)

2-Acetamido-1,5-anhydro-2-deoxy-D-talitol (VIII, 200 mg.) was acetylated with acetic anhydride (3 ml.) and pyridine (5 ml.), the mixture being stored at room temperature overnight. After removal of excess reactants, a syrup (310 mg.) was obtained and this was chromatographed on a column of silica gel (22 g.) using ether—methanol (9 : 1, v/v) as eluent. A colorless syrup, homogeneous on TLC, was obtained: 245 mg. (76%); $[\alpha]_D$ —13.9° (c 1.08, $CHCl_3$). IR absorption (neat) at 3300 (NH), 1750 (OAc), 1680 and 1540 $cm.^{-1}$ (NAc). NMR peaks at τ 3.56 (broad doublet, NH), 4.60 (doublet, J = 3.6 Hz, 1H), 4.88 (quartet, J = 3.6 and 4.8 Hz, H-4), 5.40—6.40 (multiplet, 6H), 7.79, 7.93, 7.96 (OAc) and 7.91 (NAc). The chemical shift of the *N*-acetyl group falls in the range reported by Lichtenthaler and Emig[16] for axial acetamido groups.

Anal. $C_{14}H_{21}NO_8$ (331.33) calc'd.: C 50.75; H 6.39; N 4.23%
found: C 51.02; H 6.18; N 4.47%

*3,4,6-Tri-*O*-acetyl-2-(*N*-acetylbenzamido)-1,5-anhydro-2-deoxy-*D*-talitol* (X)

2-Acetamido-3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-talitol (IX, 700 mg.) was dissolved in dry pyridine (6 ml.) and the solution, cooled to 0°, was treated with freshly distilled benzoyl chloride (0.8 ml.). After storage at room temperature for four days it was poured into ice-water and the product was extracted with chloroform. The combined extracts were washed successively with 2 *N* hydrochloric acid, saturated sodium bicarbonate solution, and water; moisture was removed with sodium sulfate and the solution was concentrated *in vacuo* to give a crude product which was chromatographed on a column of silica gel (60 g.) using ether as eluent. From fractions 18 to 29 the product (600 mg., 65%) was obtained as a syrup. Prior to analysis, the substance was rechromatographed on silica gel using the same solvent: $[\alpha]_D$ + 94.3° (c 1.025, $CHCl_3$); IR absorption spectrum (neat) at 1740 (OAc), 1700 (C = O), 1660 (NAc), and 1600 $cm.^{-1}$ (phenyl); NMR signals at τ 4.31 (triplet, J = 2.6 Hz, H-3), 4.71 (quartet, J = 3.0 and 6.1, H-4), 4.98 (octet, $J_{1a,2}$ = 10.0, $J_{1e,2}$ = 4.8, $J_{2,3}$ = 2.8 Hz, H-2), 5.25—5.90 (multiplet, 4H), 6.19 (quartet, $J_{1e,2}$ = 4.8, $J_{1a,1e}$ = 11.5 Hz, H-1e), 7.93, 8.06, 8.17, and 8.28 (OAc and NAc, 12H).

Anal. $C_{21}H_{25}NO_9$ (435.44) calc'd.: C 57.92; H 5.79; N 3.22%
found: C 57.76; H 6.04; N 3.12%

*Behavior of 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-*D*-galactopyranose* (XI) *with Isopropenyl Acetate*

Compound XI had m. p. 174—175° and $[\alpha]_D$ + 107°; Stacey[15] reported m. p. 178° and $[\alpha]_D$ + 102° for this compound. One gram of the substance was added to isopropenyl acetate (10 ml.) containing *p*-toluenesulfonic acid (15 mg.) and the mixture was boiled under reflux for 48 hr. The solvent was removed *in vacuo* and the crystalline residue was treated with ether to yield 1,3,4,6-tetra-O-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-galactopyranose (XII, 1.06 g., 96%). Recrystallized from ethanol, the product had m. p. 115—116° either alone or in admixture with an authentic sample.[4]

2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-galactopyranose (XIII)

A modification of the procedure which Stacey[15] used for the preparation of XIII from 2-amino-2-deoxy-D-galactose hydrochloride was employed with 2-acetamido-2-deoxy-D-galactose as a starting material.

A mixture of 2-acetamido-2-deoxy-D-galactose (6.0 g.), acetic anhydride (25 ml.) and anhydrous zinc chloride (2.0 g.) was shaken at room temperature overnight and then poured into ice-water. The crystalline XIII that precipitated was removed by filtration and leached with hot ethanol (15 ml.) to remove traces of the α anomer of XIII and dried: 5.2 g. (49%), m. p. 236—237°. Stacey[15] reported m. p. 235°.

Behavior of 2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-galactopyranose (XIII) *with Isopropenyl Acetate. A. To give 3,4,6-tri-O-acetyl-2-(N-acetylacetamido)-1,2-dideoxy-D-lyxo-hex-1-enopyranose* (III)

A mixture of XIII (1.0 g.) and isopropenyl acetate (15 ml.) containing *p*-toluenesulfonic acid (20 mg.) was boiled under reflux for 24 hr., the progress of the reaction being followed by TLC using ether. The first product to appear was 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-galactopyranose (XIV) and, after 1 hr., III could be detected. As the reaction progressed further, the intensity of the spots of XIV decreased while those due to III increased. At the termination of the reaction a third, slower-moving component was detected.

The solvent was removed *in vacuo* and the residue was chromatographed on a column of silica gel (35 g.) using ether. Fractions 6 to 11 contained 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose (III) which was obtained in crystalline form: 600 mg., 69%. Recrystallized from ethanol, the substance had m. p. 98—99° and $[\alpha]_D + 13.0°$ (c 0.98, $CHCl_3$). Its chromatographic behavior, IR spectrum, and NMR spectrum were indistinguishable from those of the syrup of $[\alpha]^{20}_D + 16.0°$(c 0.90, $CHCl_3$) described earlier[4] as 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-D-*threo*-hex-2-enopyranose. NMR signals at τ 3.39 (doublet, $J_{1,3} = 1.6$ Hz, H-1), 4.17 (pair of quartets, $J_{3,4} = 4.2$, $J_{1,3} = 1.6$, $J_{3,5} = 1.0$ Hz, H-3), 4.40 (quartet, $J_{3,4} = 4.2$, $J_{4,5} = 1.6$ Hz, H-4), 5.40 (H-5), 7.61 (NAc, 6H), 7.88, 7.92, and 8.02 (OAc, 9H).

Anal. $C_{16}H_{21}NO_9$ (371.36) calc'd.: C 51.75; H 5.70; N 3.77%
found: C 51.79; H 5.45; N 3.93%

Fractions 12 and 13 contained a mixture of III, XIV, and a third component (80 mg.). From fractions 14 to 20 the third component was isolated in crystalline form (100 mg., 9%); its chromatographic behavior, m. p., and m. m. p. identified it as 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-galactopyranose (XII).

B. To give 1,3,4,6-Tetra-O-acetyl-2-(N-acetylacetamido)-2-deoxy-β-D-galactopyranose (XIV)

The reaction described in *A* above was repeated but stopped after 1 hr. of refluxing. The solvent was removed *in vacuo* and the crystalline residue was recrystallized from ethanol to yield XIV: 750 mg., 68%. After another recrystallization, the substance showed m. p. 168—169°. Its IR and NMR spectra were superimposable with those of an authentic specimen.[4] TLC of the original mother liquors revealed the presence of a trace of III.

Reaction of 1,3,4,6-Tetra-O-acetyl-2-(N-acetylacetamido)-2-deoxy-β-D-galactopyranose (XIV) *with Isopropenyl Acetate*

A sample (1.0 g.) of XIV, anomerically pure by NMR[4], was dissolved in isopropenyl acetate (10 ml.) containing *p*-toluenesulfonic acid monohydrate (15 mg.) and the solution was boiled under reflux for 24 hr. The solvent was removed *in vacuo* and the dark residue was chromatographed on a column of silica gel (35 g.) using ether for elution.

Fractions 8 to 13 were pooled and evaporated to yield III (360 mg., 42%). Fractions 14 to 16 contained unchanged XIV as well as III and XII (250 mg.). Fractions 17 to 20 gave crystalline XII (250 mg., 25%, m. p. 114—116°); its IR spectrum was identical with that of an authentic sample.[4]

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IZVOD

Mehanizam nastajanja 3,4,6-tri-*O*-acetil-2-(*N*-acetilacetamido)-1,2-dideoksi-D-*likso*-heksen-1-piranoze iz 2-acetamido-2-deoksi-D-galaktoze

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Ponovno je ispitana struktura nezasićenog amino-šećera, koji nastaje u niskom iskorištenju u reakciji 2-acetamido-2-deoksi-D-galaktoze s izopropenil acetatom i *p*-toluensulfonskom kiselinom. Supstancija je bila prevedena preko nekoliko reakcionih stupnjava u spoj čiji NMR spektar pokazuje slijedeću strukturu: 3,4,6-tri-*O*-acetil-2-(*N*-acetilbenzamido)-1,5-anhidro-2-deoksi-D-talitol (X). Ova činjenica i ponovno detaljno ispitivanje NMR spektra nezasićenog amino-šećera pokazala je da je struktura tog spoja 3,4,6-tri-*O*-acetil-2-(*N*-acetilacetamido)-1,2-dideoksi-D-*likso*-heksen-1-piranoza (III). Izneseni su dokazi za mehanizam nastajanja supstancije III i bitno je poboljšano iskorištenje preko 2-acetamido-1,3,4,6-tetra-*O*-acetil-2-deoksi-β-D-galaktopiranoze (XIII) kao intermedijera.

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