The Addition of *N*-Bromoacetamide to 2,3-Unsaturated Nitro Sugars, a New Approach to 2,3-Diamino Sugars. Synthesis of Derivatives of 2,3-Diamino-2,3-dideoxy-D-mannose and -D-talose[1]

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The methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitrohex-2-enopyranosides having the α-D-*erythro* (**1**), α-D-*threo* (**10**), β-D-*erythro* (**19**), and β-D-*threo* (**24**) configurations react smoothly with *N*-bromoacetamide (NBA) in the presence of sodium acetate in acetone or aqueous acetone. The main products are 2-acetamido-3-bromo-2,3-dideoxy-3-nitrohexose derivatives (**2**, **11**, **20**, **25**, and **26**). Depending on the amount of sodium acetate provided, varying proportions of 2-*O*-acetyl-3-bromo-3-deoxy-3-nitrohexose derivatives (**3**, **12**, and **21**) are formed also. The reactions are highly stereoselective in that the acetamido or acetoxy substituent appears to enter exclusively in the position *trans* to the anomeric methoxyl group. Generally the nitro group in the addition products appears to be oriented equatorially. An exceptional case is the reaction of **24**, which gives two C-3 epimers (**25** and **26**). Borohydride reduction of **3**, **12**, and **21** results in loss of the bromo and acetoxy substituents leading to known, saturated 2,3-dideoxy-3-nitro derivatives (**4**, **13**, and **23**). Compounds **2**, **11**, **20**, **25**, and **26** are debrominated by sodium borohydride to give vicinal acetamidonitro derivatives having the following configurations: α-D-*manno* (**5**, from **2**), α-D-*talo* (**14**, from **11**), β-D-*gluco* (**22**, from **20**), and β-D-*galacto* (**27**, from **25** and **26**). Compound **5** was converted by standard reaction sequences into methyl 2,3-diacetamido-2,3-dideoxy-α-D-mannopyranoside (**8**) and its 4,6-diacetate **9**. Compound **14** was similarly converted into the corresponding derivatives (**16** and **17**) of hitherto unknown 2,3-diamino-2,3-dideoxy-D-talose.

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Les méthyl-4,6-*O*-benzylidène-2,3-didéoxy-3-nitro-hex-2-ènopyranosides possédant les configurations α-D-*érythro* (**1**), α-D-*thréo* (**10**), β-D-*érythro* (**19**) et β-D-*thréo* (**24**) réagissent dans des conditions douces avec la *N*-bromoacétamide en présence d'acétate de sodium soit dans l'acétone ou l'acétone aqueuse. Les produits principaux de la réaction sont les dérivés 2-acétamido-3-bromo-2,3-didéoxy-3-nitro (**2**, **11**, **20**, **25** et **26**). Suivant la quantité d'acétate de sodium mise en jeu, des quantités variables des 2-*O*-acétyl-3-bromo-3-déoxy-3-nitro-hexopyranosides (**3**, **12** et **21**) sont aussi formés. Les réactions sont hautement stéréosélectives; les substituants acétamido ou acétoxyle semblent entrer exclusivement en position *trans* par rapport au groupe méthoxy anomérique. Dans les produits d'addition, le groupe nitro semble généralement en position équatoriale. Un cas exceptionnel est celui de la réaction du composé **24** qui conduit aux deux produits épimères en C-3 (**25** et **26**). La réduction des produits **3**, **12** et **21** par le borohydrure de sodium enlève les substituants bromo et acétoxyle conduisant ainsi aux dérivés saturés connus, les 2,3-didéoxy-3-nitro-hexopyranosides (**4**, **13** et **23**). La débromation, par le borohydrure de sodium, des composés **2**, **11**, **20**, **25** et **26** fournit des dérivés acétamido-nitro vicinaux ayant les configurations suivantes: α-D-*manno* (**5**, à partir de **2**), α-D-*talo* (**14**, à partir de **11**), β-D-*gluco* (**22**, à partir de **20**) et β-D-*galacto* (**27**, à partir de **25** et **26**). Le composé **5** a été converti par une suite de réactions standards en méthyl-2,3-diacétamido-2,3-didéoxy-α-D-mannopyranoside (**8**) et en son 4,6-diacétate (**9**). Le composé **14** a été converti de la même façon dans les dérivés correspondants (**16** et **17**) d'un sucre inconnu jusqu'ici, le 2,3-diamino-2,3-didéoxy-D-talose.

A preceding article (1) reported on syntheses of *gem*-halonitro sugars, for which *N*-bromoacetamide (NBA) was employed as an efficient reagent for bromination of saturated nitro glycosides. In conjunction with these studies, interest arose in the question as to how unsaturated nitro sugars would behave towards that reagent. It was found (2, 3) that α-nitroalkene groupings smoothly add NBA in the presence of sodium acetate, to give β-acetamido-α-bromo-α-nitroalkane systems. In the examples studied, which comprised 1-nitro-2-phenylethylene and a 5,6-unsaturated 6-nitrohexofuranose

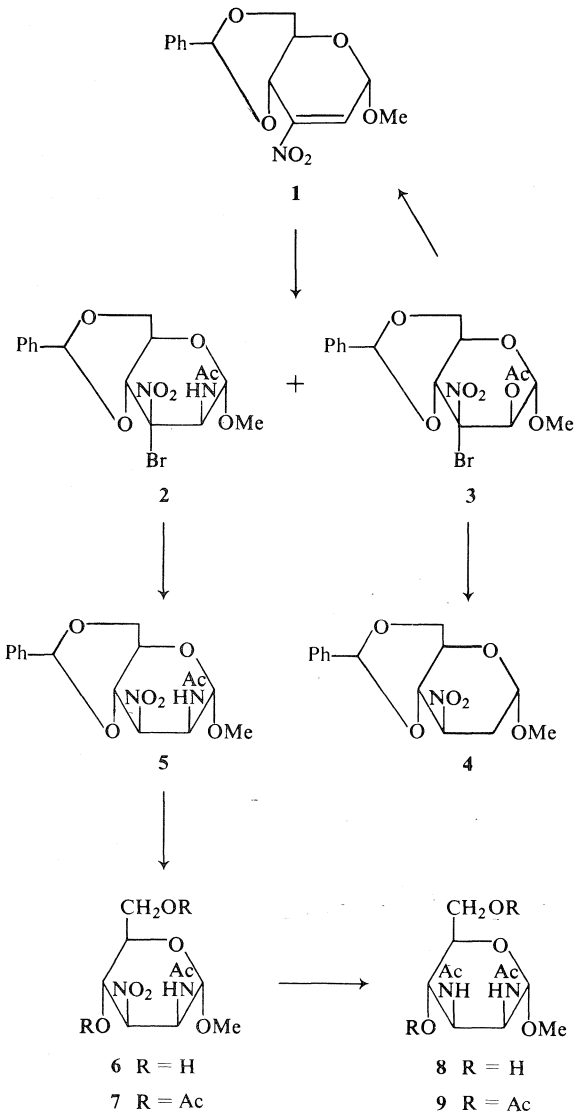
[1]Part XXXIII in a series on reactions of nitro sugars. For Part XXXII see ref. 3.

derivative, the nitro group was situated on a terminal carbon atom and NBA therefore proceeded to substitute the α-hydrogen atom present, producing β-acetamido-α,α-dibromo-α-nitro compounds. We now report applications of the NBA addition to carbohydrates containing an endocyclic α-nitroalkene moiety, *viz.*, 2,3-unsaturated 3-nitrohexopyranosides, in which such further substitution is of course not possible.

The four stereoisomeric methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitrohex-2-enopyranosides having the α-D-*erythro* (**1**), α-D-*threo* (**10**), β-D-*erythro* (**19**), and β-D-*threo* (**24**) configurations readily reacted with NBA in aqueous acetone at room temperature when at least a catalytic amount of sodium acetate was provided. With one exception, a single acetamido adduct was obtained in high yield in each case, which indicated a high degree of stereoselectivity of the addition. These adducts, which possessed the structure of methyl 2-acetamido-4,6-*O*-benzylidene-3-bromo-2,3-dideoxy-3-nitrohexopyranosides (**2**, **11**, **20**, **25**, and **26**), were the main reaction products. Depending on the amount of catalyst employed, varying proportions of corresponding 2-acetoxy derivatives (**3**, **12**, and **21**) arose as by-products, which evidently was due to acetate ion competing with the reactive acetamido species for addition to the double bond. In every case the configuration generated at C-2 in the product proved to be governed by that of C-1 in the substrate, in such a way that a 1,2-*trans* arrangement was formed. Thus, in the α-D-glycosides **1** and **10** the acetamido (or acetoxy) group entered axially and in the β-D-glycosides **19** and **24**, equatorially. The configuration of the geminally substituted carbon atom C-3 could not be established rigorously. However, it is known that a nitro group situated at C-3 of a pyranose ring strongly prefers to assume the equatorial orientation in kinetically controlled nitronate protonation as well as when thermodynamic factors prevail (4) and we have argued on the basis of chemical and spectroscopic evidence that such preference very likely applies to the formation of 3-halogeno-3-nitro derivatives also (1). In the NBA additions here considered, the mechanism probably involves an initial nucleophilic attack of the acetamido moiety on C-2 which leads to intermediate anion formation at C-3; subsequent attack of Br^+ may occur from either direction (so that 2,3-*cis* or 2,3-*trans* addition can be the result) but will normally take place axially. The configurations depicted for, and names assigned to, most of the new bromonitro derivatives were therefore based on these assumed preferences. (The C-3 epimers **25** and **26** represented a special case; see later). The assignments received support from n.m.r. data.

Reaction of the α-D-*erythro* glycoside **1** with NBA in acetone solution containing a catalytic amount of sodium acetate gave in 76% yield the acetamido derivative **2**, which was termed[2] methyl 2-acetamido-4,6-*O*-benzylidene-3-bromo-2,3-dideoxy-3-nitro-α-D-altropyranoside. Only a trace of by-product was detected by t.l.c. but its proportion increased strongly when a large excess of sodium acetate was used. Under such conditions, 62.5% of **2** and 33.5% of the second product were isolated. The latter proved to be the known (1) methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-bromo-3-deoxy-3-nitro-α-D-altropyranoside (**3**). In this connection, further observations concerning the previously noted instability of **3** were made. Thus, attempted recrystallization of the compound from hot ethyl acetate regenerated **1** in reversal of the bromoacetoxylation. Treatment of **3** with sodium borohydride, which in similar instances had simply replaced the bromine by hydrogen (1, 5), produced the 2,3-dideoxy-3-nitro glycoside **4**. A likely explanation for this is that abstraction of bromine was followed by elimination of the acetoxy group to give intermediary **1** which is known (6) to be reduced to **4** rapidly. By contrast, action of sodium borohydride upon the acetamido derivative **2** removed the bromine without loss of the C-2 substituent, to give a high yield of methyl 2-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-3-

[2]Following a suggestion by Professor D. Horton, Columbus, Ohio, and pending adoption of an official international rule of nomenclature, we denote configurations of sugars that bear unequal geminal substituents on a ring carbon in this way: the substituent of a higher priority according to the Cahn–Ingold–Prelog rule (here Br) is thought of as replacing the hydroxyl group and the substituent of lower priority (here NO_2) is thought of as replacing the corresponding ring hydrogen, in a parent sugar, and the established configurational notation of the parent sugar so defined is used to describe the derivative (1). Hence the orientation of the nitro group in 3-bromo-3-deoxy-3-nitro-D-altrose is the same as in 3-deoxy-3-nitro-D-mannose although the absolute configuration of C-3 is reversed.

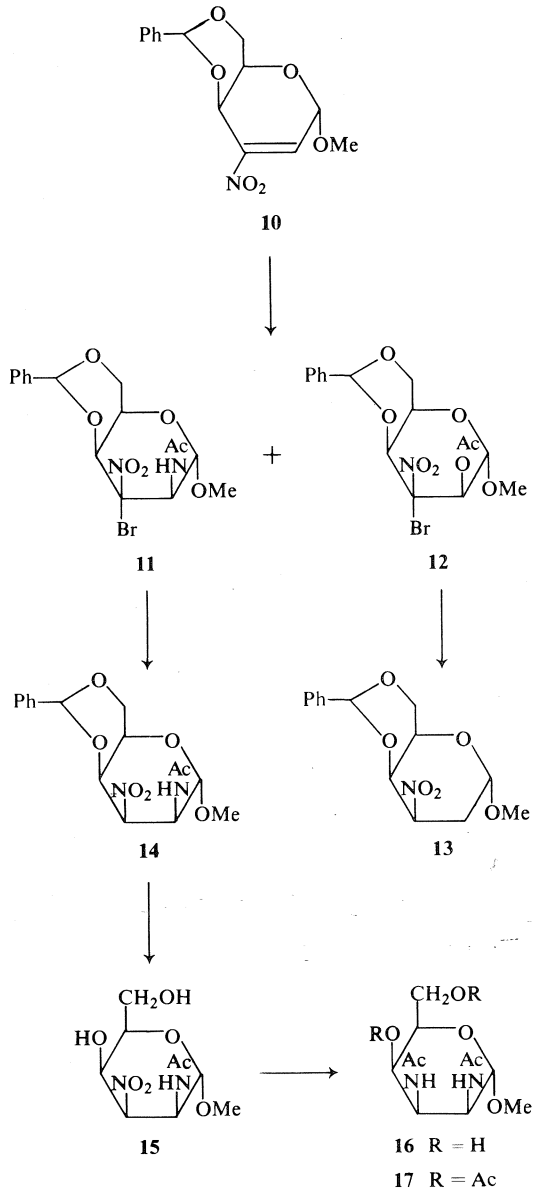


nitro-α-D-mannopyranoside (**5**).[3] Debenzylidenation of **5** with acid gave chromatographically homogeneous but amorphous methyl 2-acetamido-2,3-dideoxy-3-nitro-α-D-mannopyranoside (**6**) which was characterized by its crystalline 4,6-diacetate **7**. Catalytic hydrogenation of **6** in an acid medium followed in turn by *N*- and *O*-acetylation afforded methyl 2,3-diacetamido-2,3-dideoxy-α-D-mannopyranoside (**8**) and the known (8) 4,6-diacetate **9** thereof. The reaction sequence thus provided chemical proof for the configuration at C-2 in **2** as well as for the α-D-*manno* configuration of **5**–**8**.

The addition of NBA to the α-D-*threo* glycoside **10** gave methyl 2-acetamido-4,6-*O*-benzylidene-3-bromo-2,3-dideoxy-3-nitro-α-D-idopyranoside (**11**) and methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-bromo-3-deoxy-3-nitro-α-D-idopyranoside (**12**) in yields of 83 and 15%, respectively. Treatment of **11** and **12** with sodium borohydride proceeded in full analogy to the previous series. Thus, the *O*-acetyl compound **12** suffered elimination and reduction leading to the 2,3-dideoxy-3-nitro glycoside **13** which had previously been obtained (6) by borohydride reduction of **10**, whereas the acetamido compound **11** was debrominated in high yield to furnish methyl 2-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-talopyranoside (**14**). Debenzylidenation of **14** gave the acetamidonitro glycoside **15**. The latter was catalytically hydrogenated under conditions of *N*-acetylation to produce methyl 2,3-diacetamido-2,3-dideoxy-α-D-talopyranoside (**16**), and *O*-acetylation of **16** gave the 4,6-diacetate **17**, the first derivatives of 2,3-diamino-2,3-dideoxy-D-talose to be recorded in the literature. Exhaustive hydrolysis of **16** with hydrochloric acid appeared to succeed according to spectroscopic evidence, but the reducing diamino sugar dihydrochloride failed to crystallize. *N*-Acetylation of the hydrolysis product likewise did not yield a crystalline derivative although i.r. and n.m.r. data of the product were consistent with a diacetamido sugar.

Since none of the products derived from **11** was known, structural proof was required. It was sufficient, however, to elucidate the steric arrangements at C-2 and -3 since those at the remaining centers were not in question. Hence, only the α-D-*talo*, α-D-*galacto*, α-D-*ido*, and α-D-*gulo* configurations had to be considered. Of these, the two last-mentioned ones could be regarded as highly unlikely as far as **14** and the subsequent products were concerned: they would comprise an axial C-3 substituent in the $_1C^4$ chair conformation (the more stable chair for

[3]Compound **5** proved identical with a minor by-product that had been obtained (7) in the reaction of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-α-D-glucopyranoside with ammonia. Some n.m.r. data and a chemical analogy had suggested the α-D-*manno* configuration for that by-product but a definitive assignment was held in abeyance. Unambiguous proof of configuration is furnished by the present work.



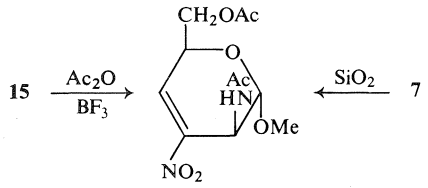
α-D-pyranosides) whereas, regardless of the original arrangement at the geminally substituted C-3 in **11**, reductive removal of the bromine atom by borohydride would most certainly lead to an equatorial nitro group.[4] The u.v. spectrum of the benzylidene acetal **14** in alcoholic 0.01 *N* KOH solution showed absorption at 250 nm with a very high intensity (ε 21 000) which was indicative of especially facile nitronate formation and hence pointed to the D-*talo* configuration, with two axial substituents flanking the nitro group (9). The n.m.r. spectrum of **14** was consistent therewith and it definitely ruled out the α-D-*galacto* configuration as no large splittings in the order of 10 Hz, that could have been attributed to 2,3-diaxial ring protons, were present in any of the signals. The α-D-*talo* configuration was further supported by the chemical shifts of the acetyl protons of **17**. In $CDCl_3$ solution the signals occurred at τ 7.88 7.98, 7.98, and 8.11 and were therefore attributable to an axial acetoxy, an axial acetamido, a primary C-6 acetoxy, and an equatorial acetamido group.[5] Final proof was obtained by chemical means. Boron trifluoride-catalyzed acetylation of **15** gave, instead of the 4,6-diacetate expected, an unsaturated monoacetate (**18**). The nitroolefinic nature of **18** was revealed by characteristic absorptions in the i.r. (ν_{max} 1530 cm^{-1}) and u.v. (λ_{max} 247 nm with ε 5000, in chloroform[6]). The n.m.r. spectrum demonstrated the presence of an olefinic proton (H-4, doublet at τ 2.64) and the remaining signals also agreed with the proposed structure. The ease with which **15** underwent elimination during acid-catalyzed acetylation was indicative of the *talo* configuration as it paralleled a similar tendency observed (10) in methyl 3,6-dideoxy-3-nitro-α-L-talopyranoside but had no counterpart in related compounds possessing other configurations. Finally, an identical nitroolefin **18** was obtained from the α-D-*manno* derivative **7** by dehydroacetoxylation with slightly basic silica gel in refluxing chloroform. This fact proved that **18** was methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-3-nitro-α-D-*threo*-hex-3-enopyranoside, and it showed that **7** and **15** had the same configuration at C-2. Conse-

[4]Compare the results of such debrominations recorded earlier (1) and later in the present article.

[5]This pattern was inconsistent with the α-D-*galacto* and α-D-*ido* configurations, though not with the α-D-*gulo* configuration. The acetyl proton signals of the isomer **9** appeared at τ 7.94, 7.96, 7.99, and 8.12 in accordance with the equatorial acetoxy, axial acetamido, primary C-6 acetoxy, and equatorial acetamido groups in the D-*manno* configuration. For references to the rule that permits such assignments and for a discussion of its applicability to other compounds described in this article, see a subsequent paragraph.

[6]Upon addition of 0.1*N* methanolic sodium methoxide (0.1 ml) to the $10^{-4}M$ solution of the sample (3 ml), a bathochromic shift to λ_{max}257 nm took place and the absorbance increased to 10 100. This is interpreted as resulting from nucleophilic addition of methoxide ion to give a saturated glycoside nitronate.

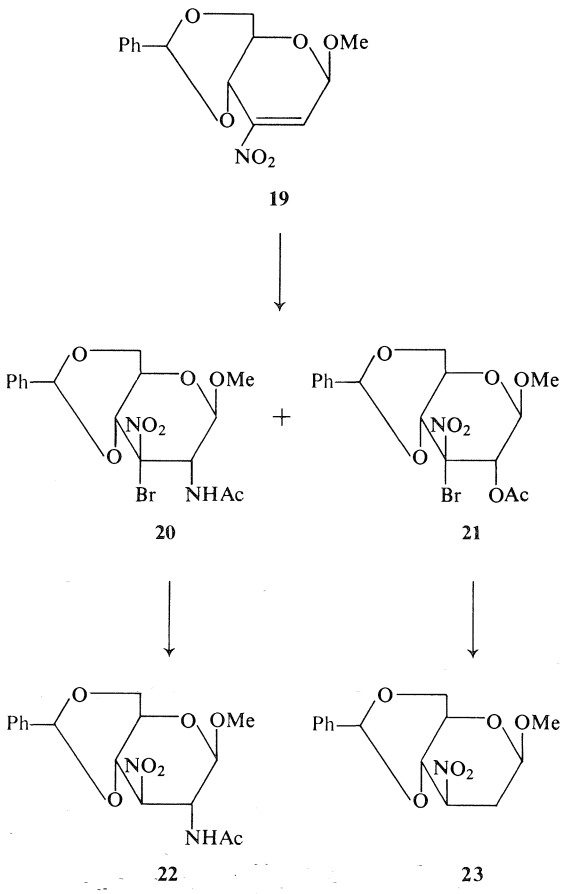
quently the α-D-*galacto* and α-D-*gulo* configurations were eliminated for **15**, and the α-D-*talo* configuration remained for **14**–**17** as the only one that was compatible with all the pieces of chemical and spectroscopic evidence accumulated.



18

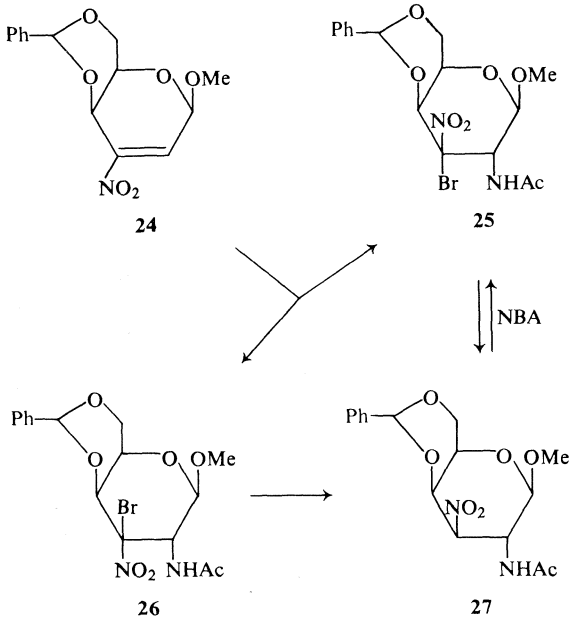
Addition of NBA to the β-D-*erythro* glycoside **19** in the presence of excess sodium acetate produced methyl 2-acetamido-4,6-*O*-benzylidene-3-bromo-2,3-dideoxy-3-nitro-β-D-allopyranoside (**20**) and its previously described (1) 2-acetoxy analog **21** in yields of 55 and 24%, respectively. For both products the equatorial orientation of the C-2 substituent was indicated by diaxial proton coupling (8 Hz) between H-1 and H-2. Reduction with sodium borohydride converted **20** into methyl 2-acetamido-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**22**), and **21**, into methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*arabino*-hexopyranoside (**23**), in complete analogy to the corresponding reactions mentioned earlier on. The known compounds **22** and **23**, which have served as useful intermediates in amino sugar syntheses, have been made in high yields from **19** by more direct methods (4*a*, 6, 11). No further work was therefore devoted to the reaction of **19** with NBA and the question of a possible influence of the sodium acetate concentration on the product ratio was not pursued. The highly stereoselective introduction of substituents at C-2 in the direction opposite to the aforedescribed examples, was, however, noted with interest.

Addition of NBA to the β-D-*threo* glycoside **24** also proceeded very smoothly. Only a catalytic amount of sodium acetate was applied in this case, and no acetoxybromo adduct was detected. The product consisted of approximately equal proportions of two acetamidobromo isomers which were isolated by column chromatography, each in about 45% yield. Both isomers exhibited an anomeric proton doublet with a splitting of 9 Hz, which indicated 1,2-*trans* diaxial ring hydrogen atoms and hence,



19 **20** **21** **22** **23**

an equatorial substituent at C-2. The stereoisomerism of the two adducts must therefore be due to different orientations at C-3, *i.e.*, the β-D-*gulo* (**25**) and β-D-*galacto* (**26**) configurations must hold. For reasons given below, the more slowly moving product was judged to be **25**, and the faster moving one was assigned formula **26**. Treatment of either compound with sodium borohydride led to the same product of debromination, namely, the known (12) methyl 2-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-galactopyranoside (**27**), which constituted chemical proof for configurational identity at C-2 and epimerism at C-3. Rebromination of **27** gave in 80% yield the slow-moving bromonitro compound (**25**) while only a trace of the fast-moving isomer (**26**) seemed to arise. It is a reasonable assumption supported by evidence that nitro glycosides of the type of **27** are brominated axially (1); the finding just mentioned thus provided grounds for the formula allocation made.



Discussion of Nuclear Magnetic Resonance Data

In addition to the n.m.r. parameters already mentioned, some further spectral features deserve comment. In the series of 4,6-*O*-benzylidene-3-deoxy-3-halo-3-nitro pyranosides studied previously it was noted that the chemical shift of the characteristic benzylidene methine proton singlet in the region of τ 4.2–4.5 is quite sensitive to the configurations at C-3 and -4. When compared with the position in the corresponding nonhalogenated compounds (all of which possess an equatorial nitro group at C-3), the methine signal upon halogenation at C-3 was moderately but significantly shifted downfield (by 0.1–0.2 p.p.m.) in some of the cases but remained virtually unaffected in others. This could be reconciled with all other considerations when the downfield shift was taken to indicate a *gauche* orientation between the C-3—halogen and the C-4—oxygen bonds while absence of such shift was taken to signify an *anti* orientation of these bonds (1). Similar observations were again made in the present series of compounds (Table 1). Thus, downfield shifts of 15, 12, and 21 Hz were found in the bromonitro compounds **2**, **20**, and **26** as compared to the bromine-free compounds **5**, **22**, and **27**, respectively. On the other hand, comparison of **11** and **25** with **14** and **27**, respectively, revealed only insignificant differences in the methine proton shifts. These findings reinforce the configurational assignments made for C-3.[7]

Another point of interest concerns the chemical shifts of acetyl proton resonances. In peracetylated pyranoses and aminopyranoses as well as their methyl glycosides, axial *O*-acetyl groups resonate at lowest field (τ 7.80–7.87), axial acetamido, equatorial *O*-acetyl, and primary (C-6) *O*-acetyl groups resonate in an intermediate range (τ 7.89–8.01), and equatorial acetamido groups give signals at highest field (τ 8.03–8.10 or sometimes slightly higher) in the most commonly employed solvent, chloroform-*d* (14–17). Better separation of signals is observed in dimethylsulfoxide-d_6 solution where the corresponding ranges have been reported (17) to be τ 7.86–7.89, 7.95–8.10, and 8.21–8.27. Very similar resonance ranges apply to peracetylated inositols, inosamines, and related cyclohexane derivatives (18, 19). The shift ranges have been verified on a multitude of examples in many laboratories and are now generally regarded as reliable stereochemical indicators for compounds of the types mentioned. We have used the principle to confirm the configurations of **9** and **17** (see above). Ambiguity may of course arise if acetyl signals happen to fall very close to range bounds. A case in point is the axial-acetamido signal (τ 8.02) of the nitro compound **7** which hardly differs from the equatorial-acetamido signal (τ 8.03) of the β-D-*gluco* isomer (11*b*) although normally a nitro group does not tend to cause serious deviations. However, certain functionalities such as free hydroxyl groups, halogens, sulfonate esters, and particularly, aryl substituents present in the molecule invalidate the aforementioned acetyl resonance ranges as a basis for ready stereochemical correlations (16–18). This is clearly illustrated by the benzylidenated nitro and bromonitro sugars listed here (Table 1) and earlier (Table 1 of ref. 1). Perusal of the tables will show that, although in several instances the signals do occur within the "normal" regions, they fall outside in many cases.

[7]Unfortunately, for the new bromonitro 2-acetate **12** there exists no exact counterpart for comparison. However, its τ-value of 4.41, besides being very similar to that of **11**, is close also to those of the bromine-free compounds **13** (τ 4.43, ref. 1) and methyl 4,6-*O*-benzylidene-3-deoxy-3-nitro-α-D-talopyranoside (τ 4.42, ref. 13; all data refer to $CDCl_3$ solutions). This lends support to the assumed configuration.

TABLE 1. Chemical shifts (τ) of 100 MHz n.m.r. signals[a]

Compound	$PhCHO_2$	OCH_3	*O*—Ac	*N*—Ac	H-1	H-2	Other signals
2	4.21	6.64		8.04	5.33s	4.69d[b,c]	3.50d (N—H)
2*	4.19	6.68		8.19	5.30s	4.96d[b,c]	1.35d (N—H), 5.19d (8Hz, H-4?)
3	4.21	6.61	8.00		5.29s	4.35s	
5	4.36	6.61		8.01	5.32s		4.0m (N—H), 4.9m (H-2, -3)
5*	4.32	6.66		8.15	5.34s		1.6m (N—H), 4.94q (4, 10Hz, H-3)
7		6.60	7.90, 7.96	8.01	5.31s	~4.95	4.95 (H-3), 4.35t (10Hz, H-4)
9		6.63	7.94, 7.99	7.96, 8.12			5.12t (10Hz, H-4)
11	4.37	6.60		8.31	5.17s	4.81d[b,c]	3.27d (N—H), 5.17s (H-4), 5.7q (AB pattern, H-6, 6′), 5.82s (H-5)
12	4.41	6.59	8.03		5.08s	4.27s	5.22s (H-4), 5.5–5.9 (H-5, -6, 6′)
14	4.38	6.60		8.25	[d]	[d]	[d]
14*	4.24	6.67		8.31	[e]	[e]	[e]
17		6.63	7.88, 7.98	7.98, 8.11	5.40s		~3.75m (2N—H), ~4.6q (narrow, H-4)
18		6.56	7.92	8.03	5.12s	4.83d[b,f]	2.64d (2Hz, H-4), 4.2d (N—H), 5.3–5.8(H-5, -6, 6′)
20	4.38	6.54		8.02	5.49d	4.97q	4.0d[c] (N—H)
20*	4.15	6.60		8.19			
21	4.39	6.51	7.93		5.37d	4.47d	
22*	4.27	6.63		8.22	5.37d		4.99t (H-3)
25	4.32	6.56		7.93	5.38d	4.93q[c,g]	5.32s (H-4), 5.85q (AB pattern, H-6, 6′)
25*	4.30	6.62		8.15	5.52d		5.0-5.2 (H-2, -4), ~5.8 (H-5, -6, 6′)
26*	4.14	6.64		8.11			5.1–5.3 (H-1, -2, -4), 5.85 (H-6, 6′), 6.17 (H-5)
27*	4.35	6.64		8.24	5.5–5.8		4.72q (4, 11Hz, H-3), 5.24q (narrow, H-4)

[a]Data refer to $CDCl_3$ solutions except for compounds marked by an asterisk (*) which were measured in DMSO-d_6 solution. The substituent resonances were all singlets of the expected intensity. For ring protons, multiplicities are indicated as s (singlet, or apparent singlet in case of very small splitting), d (doublet), t (triplet), q (quartet), and m (multiplet).
[b]Singlet after D_2O exchange.
[c]$J_{2,NH}$ = 10 Hz.
[d]τ 3.05d (N—H); 4.99 and 5.14, centers of narrow 2-proton signals (H-1, -2, -3, -4); 5.7, center of 2-proton AB-quartet (H-6, 6′); 6.26s (H-5).
[e]τ 3.1d (N—H); 4.67q (narrow, H-3); 4.94d (~1 Hz, H-4); 5.25 (H-1 singlet over H-2 multiplet); 5.80s (H-6, 6′); 6.26s (H-5).
[f]$J_{2,NH}$ = 8 Hz.
[g]Doublet after D_2O exchange; $J_{1,2}$ = 8 Hz.

Especially striking examples are provided by **11** and **14** whose axial acetamido groups resonate upfield even of the "normal" equatorial-acetamido range, and by **25** and **26** whose equatorial acetamido groups, conversely, resonate below that range. Obviously a more detailed analysis is needed before the conformational significance of these data can be evaluated. On the other hand, the chemical shifts of the anomeric methoxyl signals do not appear to be subject to similar disturbances. In most of the compounds described here and earlier (1), these signals occur in the range τ 6.40–6.56 (β-glycosides) and τ 6.55–6.66 (α-glycosides) ($CDCl_3$ solutions),[8] in line with expectations (15).

[8]Exceptions exist in α-glycosides presumed to have an axial nitro group at C-3; an unusually high τ-value is observed (1).

Conclusion

Amination of the α- and β-D-*erythro* nitroolefins **1** and **19** (and of their preparative precursors, the corresponding saturated α- and β-D-glucopyranoside 2-acetates) with ammonia provides an excellent route to vicinal aminonitro sugars from which 2,3-diamino sugars can easily be prepared (4*a*, 7, 11*b*). However, in both anomeric series the predominant reaction products so obtainable possess the D-*gluco* configuration and only small proportions of D-*manno* isomers are formed.[9] The present work

[9]In remarkable contrast to this general steric course of the amination, addition of anthranilic acid to **19** under special reaction conditions yielded 56% of an adduct possessing the β-D-*manno* configuration, and this did provide the basis for a reasonably convenient synthesis of 2,3-diamino-2,3-dideoxy-D-mannose (20). Similar reaction of anthranilic acid with **1** gave only the α-D-*gluco* adduct (21).

has demonstrated that NBA lends itself as a vehicle for high-yielding aminations which in their stereoselectivity depend on the anomeric configuration of the substrate. Especially in view of the synthesis of the α-D-*manno* glycosides **5**–**9** the new approach represents a useful complement and improvement. The same pertains to the reactions of the D-*threo* nitroolefins **10** and **24**. Amination of the former with ammonia has never been tried, and the sequence here described provides a first access to hitherto unknown 2,3-diamino-2,3-dideoxy-D-talose. A modified procedure of amination of **24** had given, in 35–38% yield, the β-D-*galacto* derivative **27** which was subsequently converted into derivatives of 2,3-diamino-2,3-dideoxy-D-galactose (12). In the sequence **24** → **25** + **26** → **27** the overall yield was 85% (and might be even higher if separation of **25** and **26** is omitted), which clearly endows the new method with superior preparative appeal.

Experimental

For general preparative techniques and instruments used see preceding articles of this series (*e.g.*, refs. 1, 6, 7, 10, 13). Optical rotations were measured at room temperature, and unless otherwise indicated, the solvent was chloroform (*c*, 0.5–1). Infrared data refer to Nujol mulls. Column chromatography was performed on silica gel (70–325 mesh, a product of E. Merck AG, Darmstadt), and the following solvent systems (v/v) were employed: A, chloroform–acetone (7:3); B, carbon tetrachloride – ethyl acetate (7:3); C, the same (4:3); D, chloroform–methanol (4:1); E, the same (8:1).

*Methyl 2-Acetamido-4,6-O-benzylidene-3-bromo-2,3-dideoxy-3-nitro-α-D-altropyranoside (**2**) and Methyl 2-O-Acetyl-4,6-O-benzylidene-3-bromo-3-deoxy-3-nitro-α-D-altropyranoside (**3**)*

(a) Reaction with Catalytic Amount of Sodium Acetate

A 50-mg sample of the nitro olefin **1** (ref. 22; see also footnote 9 in ref. 21), NBA (35 mg), and sodium acetate (2 mg) were stirred in acetone (4 ml), at room temperature. After 2 h the mixture was processed by the addition of water (6 ml) and evaporation of most of the acetone. A white precipitate was collected, washed with cold water, and dried. Thin-layer chromatography with solvent A showed a main product spot (**2**) and only traces of a faster moving product (presumably **3**). Two recrystallizations from ethyl acetate – petroleum ether gave **2** (56.5 mg, 76%) melting at 125–126° and at 127–129° after another recrystallization from ethanol–water; $[\alpha]_D$ +46°, ν_{max} 3260 (NH), 1660, 1530 (amide), and 1560 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{19}BrN_2O_7$ (431.3): C, 44.60; H, 4.44; N, 6.51; Br, 18.50. Found: C, 44.32; H, 4.59; N, 6.63; Br, 18.68.

(b) Reaction with Excess Sodium Acetate

A solution of **1** (293 mg) in acetone (20 ml) was mixed with a solution of NBA (200 mg) in aqueous, saturated sodium acetate (15 ml), and the mixture was vigorously stirred for 7 h. Water (30 ml) was then added, and removal of acetone by partial evaporation gave a white solid (dry weight 425 mg) that showed two strong spots (**2** and **3**) on t.l.c. with solvent A. The products were separated on a 20-g silica gel column by use of solvent A. The fast-moving fractions gave crystalline **3** (145 mg, 33.5%); m.p. 152–153°; $[\alpha]_D$ +10.5°; ν_{max} 1760 (OAc) and 1570 cm^{-1} (NO_2). Comparison of spectra and physical constants established the identity with **3** described earlier; reported (1), m.p. 152–153°; $[\alpha]_D$ +12.3°. Recrystallization of the product from hot ethyl acetate converted it into **1**, m.p. 181–182°; $[\alpha]_D$ −97.5°; ν_{max} 1525 cm^{-1} (nitroalkene) without carbonyl band (lit. (22) m.p. 183°; $[\alpha]_D$ −93° (in ethyl acetate)).

The slow-moving fractions eluted from the above column gave 270 mg (62.5%) of **2**, m.p. 127–129° upon recrystallization from ethanol–water.

*Methyl 4,6-O-Benzylidene-2,3-dideoxy-3-nitro-α-D-arabinohexopyranoside (**4**)*

A solution of **3** (100 mg) and sodium borohydride (30 mg) in ethanol (20 ml) was stirred in an ice bath for 1 h and then acidified with 2 *N* acetic acid. Upon addition of water (20 ml) and partial evaporation of the ethanol a white precipitate was obtained, which was washed with water. Recrystallization from ethanol–water gave 59.5 mg (87%) of **4**; m.p. 109–110°, unchanged on admixture of authentic **4** (6, 22). The identity was ascertained by comparison of i.r. spectra.

*Methyl 2-Acetamido-4,6-O-benzylidene-2,3-dideoxy-3-nitro-α-D-mannopyranoside (**5**)*

A mixture of **2** (150 mg), sodium borohydride (150 mg), and ethanol (10 ml) was stirred at room temperature for 1 h. Acidification with 2 *N* acetic acid, dilution with water (20 ml), and partial evaporation produced a white solid which was washed with cold water, dried, and recrystallized from chloroform – *n*-pentane. There was obtained 112 mg (91%) of **5**; m.p. 121–123°; $[\alpha]_D$ +14.8°; ν_{max} 3300–3200 (NH), 1665 (amide I), 1560–1530 cm^{-1} (NO_2 and amide II). The i.r. spectrum was identical in every detail with that of a product previously obtained and referred to (7) as "by-product **6**" (m.p. 123–125° and $[\alpha]_D$ +16° for a sample shown to contain some chloroform of crystallization; the exhaustively dried compound melted at 186–187° and gave correct microanalytical data for $C_{16}H_{20}N_2O_7$).

*Methyl 2-Acetamido-4,6-di-O-acetyl-2,3-dideoxy-3-nitro-α-D-mannopyranoside (**7**)*

Compound **5** (600 mg) was stirred with 90% trifluoroacetic acid (5 ml) for 30 min at room temperature. Evaporation with successive additions of several portions of water, and eventually ethanol, gave the debenzylidenated compound (**6**) as a colorless syrup which exhibited a single, slow-moving spot on t.l.c. (solvent A). All attempts at crystallization failed. Part of the material (100 mg) was acetylated with acetic anhydride (3 ml) by use of 3 drops of boron trifluoride etherate as a catalyst (30 min at ambient temperature). The reaction mixture was poured into ice water to give an amorphous precipitate which was filtered off, washed with cold water, and dried. Reprecipitation from ethyl acetate

solution with petroleum ether gave chromatographically pure **7** showing $[\alpha]_D$ +38°; ν_{max} 3300 (NH), 1745 (OAc), 1665 (amide I), 1560 (NO_2), and 1535 cm^{-1} (amide II).

Anal. Calcd. for $C_{13}H_{20}N_2O_9$ (348.3): C, 44.83; H, 5.79; N, 8.05. Found: C, 44.75; H, 5.89; N, 8.19.

*Methyl 2,3-Diacetamido-2,3-dideoxy-α-D-mannopyranoside (**8**)*

A solution of syrupy **6** (300 mg; see the preceding section) and platinum dioxide (200 mg) in water (50 ml) and 0.1 *N* hydrochloric acid (11.6 ml) was shaken for 2.5 days at 25° with hydrogen under pressure (4 atm). Removal of the catalyst, evaporation of the solution, and evaporation of several portions of added ethanol from the residue gave a colorless syrup. For *N*-acetylation, the syrup was dissolved in water (10 ml), and methanol (1 ml), acetic anhydride (0.5 ml), and Dowex-1 × 8 (carbonate form) were added. The mixture was stirred at room temperature for 90 min. Evaporation of the filtered solution gave a colorless syrup which crystallized from ethanol–ether to afford **8** (243 mg, 77%); m.p. 248–250°; $[\alpha]_D$ +4.8° (*c* 0.4, in water); ν_{max} 3520, 3470, 3300 (NH, OH), 1640 and 1540 cm^{-1} (amide).

Anal. Calcd. for $C_{11}H_{20}N_2O_6$ (276.3): C, 47.82; H, 7.30; N, 10.14. Found: C, 47.55; H, 7.43; N, 9.97.

*Methyl 2,3-Diacetamido-4,6-di-O-acetyl-2,3-dideoxy-α-D-mannopyranoside (**9**)*

The compound **8** (100 mg) was treated with acetic anhydride (1 ml) in pyridine (4 ml) for 16 h at 25°. Azeotropic evaporation with toluene and ethanol, followed by crystallization of the residue from benzene – petroleum ether, furnished 109 mg (83%) of **9**; m.p. 199–201°; $[\alpha]_D$ +84°; ν_{max} 3300 (NH), 1745 (OAc), 1640, and 1545 cm^{-1} (amide) (lit. (8) m.p. 200–202°; $[\alpha]_D$ +89.2°).

*Methyl 2-Acetamido-4,6-O-benzylidene-3-bromo-2,3-dideoxy-3-nitro-α-D-idopyranoside (**11**) and Methyl 2-O-Acetyl-4,6-O-benzylidene-3-bromo-3-deoxy-3-nitro-α-D-idopyranoside (**12**)*

A 200-mg sample of the nitro olefin **10** (13) dissolved in acetone (16 ml) was added to a solution of NBA (200 mg) and sodium acetate (10 mg) in water (10 ml). The reaction mixture was stirred at room temperature for 2.5 h during which a white precipitate appeared. Addition of water (25 ml) and subsequent removal of acetone by partial evaporation produced further quantities of precipitate. The material was isolated, washed with cold water, dried, and shown by t.l.c. (solvent C) to consist of two easily separable, main components. They were separated on a 20-g silica gel column using solvent A. The fast-moving, minor component (**12**) was obtained as crystals (46 mg, 15.6%) melting at 225–226°; $[\alpha]_D$ +31.5°; ν_{max} 1760 (OAc) and 1565 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{18}BrNO_8$ (432.3): C, 44.50; H, 4.20; Br, 18.45. Found: C, 44.63; H, 4.01; Br, 18.74.

The slow-moving, major component (**11**) was isolated as crystals (245 mg, 83%) melting at 175–176°; $[\alpha]_D$ +19.1°; ν_{max} 3460 (NH), 1705, 1500 (amide I and II), 1570 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{19}BrN_2O_7$ (431.3): C, 44.60; H, 4.44; Br, 18.50. Found: C, 44.74; H, 4.56; Br. 18.37.

*Methyl 4,6-O-Benzylidene-2,3-dideoxy-3-nitro-α-D-lyxo-hexopyranoside (**13**)*

Treatment of **12** (165 mg) with sodium borohydride (40 mg) in ethanol (30 ml) for 30 min at 0° was followed by work-up as described for the preparation of the isomer **4**. It yielded 95 mg (85%) of **13**, m.p. 103–105°. Identity with an authentic sample (6, 22) was established by a mixture melting point and comparison of the i.r. spectra.

*Methyl 2-Acetamido-4,6-O-benzylidene-2,3-dideoxy-3-nitro-α-D-talopyranoside (**14**)*

Compound **11** (80 mg) was treated with sodium borohydride (20 mg) in ethanol (10 ml) at 0°. The debromination appeared complete after 5 min (t.l.c. with solvent A). After 10 min the mixture was worked up as described for the isomer **5**. Recrystallization of the product from chloroform – petroleum ether gave 55 mg (85%) of **14**; m.p. 205°; $[\alpha]_D$ +55.3°; ν_{max} 3450 (NH), 1695, 1510 (amide I and II), 1560 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{20}N_2O_7$ (352.3): C, 54.54; H, 5.72; N, 7.95. Found: C, 54.39; H, 5.74; N, 7.80.

*Methyl 2-Acetamido-2,3-dideoxy-3-nitro-α-D-talopyranoside (**15**)*

Compound **14** (220 mg) was debenzylidenated with trifluoroacetic acid in the same manner as **5**. The product crystallized on trituration with ether to give 153 mg (93%) of **15**; m.p. 119–120°, raised to 120–121° by recrystallization from chloroform–ether; $[\alpha]_D$ +52.5° (*c* 0.6, water); ν_{max} 3400, 3200 (NH, OH), 1655, 1540 (amide I and II), 1540 cm^{-1} (NO_2).

Anal. Calcd. for $C_9H_{16}N_2O_7$ (264.2): C, 40.90; H, 6.10; N, 10.60. Found: C, 40.95; H, 5.94; N, 10.77.

*Methyl 2,3-Diacetamido-2,3-dideoxy-α-D-talopyranoside (**16**)*

A solution of **14** (400 mg) in methanol (40 ml) was hydrogenated in the presence of acetic anhydride (2.4 ml) with prereduced platinum oxide (400 mg) as the catalyst. Ordinary temperature and pressure was used. Hydrogen consumption ceased after 5 h and work-up then afforded a syrup that crystallized from ethanol–ether. The product was purified by passage over a small silica gel column using solvent D as the eluent, and subsequently recrystallized from ether. The yield was 289 mg (69%); m.p. 218–219°; $[\alpha]_D$ +11.8° (*c* 0.8, water).

Anal. Calcd. for $C_{11}H_{20}N_2O_6$ (276.3): C, 47.82; H, 7.30; N, 10.14. Found: C, 47.68, H, 7.29; N, 9.98.

*Hydrolysis of **16***

The glycoside **16** (150 mg) was refluxed with half-concentrated hydrochloric acid (15 ml) for 16 h. The dark brown solution was evaporated, and water was evaporated repeatedly from the residue in order to remove remnant acid. The dark syrup was then dissolved in water, and the solution was decolorized with acid-washed activated charcoal and evaporated to give a colorless, hygroscopic syrup that could not be crystallized. It reduced Fehling solution strongly, gave a ninhydrin positive spot ($R_{glucosamine\text{-}HCl}$ 0.86) in paper chromatography (23) and exhibited no methoxyl and acetyl signals in an n.m.r. spectrum in D_2O. One may, therefore, assume that complete hydrolysis of **16** to 2,3-diamino-2,3-dideoxy-D-talose dihydrochloride had taken place.

Part of the syrup (50 mg) was *N*-acetylated by the usual procedure (24); compare the preparation of **8**, above. The syrupy product was chromatographed on a column of silica gel (20 g) with chloroform–methanol (1:1). A material (35 mg) was eluted which was homogeneous on t.l.c. but failed to crystallize. It reduced Fehling solution, showed strong amide i.r. bands at 1650 and 1530 cm^{-1} (neat film), and exhibited 2 strong n.m.r. signals attributable to *N*-acetyl groups (60 MHz spectrum in D_2O).

*Methyl 2,3-Diacetamido-4,6-di-O-acetyl-2,3-dideoxy-α-D-talopyranoside (**17**)*

Compound **16** (100 mg) was acetylated with acetic anhydride (1 ml) and pyridine (4 ml) at room temperature. The reaction mixture was evaporated with added toluene and ethanol, and the syrupy product was passed over a small silica gel column by means of solvent E and then crystallized from benzene – petroleum ether. The yield was 99 mg (76%); m.p. 85–89°; $[\alpha]_D$ +107.5°. The n.m.r. spectrum revealed benzene of crystallization to be present in the sample, and the microanalysis was acceptable assuming this amounted to 0.5 mol/mol.

Anal. Calcd. for $C_{15}H_{24}N_2O_8 \cdot 0.5C_6H_6$ (399.4): C, 54.13; H, 6.81, N, 7.01. Found: C, 53.76; H, 7.09; N, 7.10.

*Methyl 2-Acetamido-6-O-acetyl-2,3,4-trideoxy-3-nitro-α-D-threo-hex-3-enopyranoside (**18**)*

*(a) From **15***

To a mixture of **15** (100 mg) and acetic anhydride (3 ml) was added boron trifluoride etherate (3 drops). The reaction mixture was kept at ambient temperature for 30 min and then poured into ice water whereby solid **18** separated. The product was isolated, washed well with cold water, and dried: yield, 93 mg (85%); m.p. 159–161°, raised to 162–163° by recrystallization from ethyl acetate – petroleum ether; $[\alpha]_D$ +82.5°.

Anal. Calcd. for $C_{11}H_{16}N_2O_7$ (288.3): C, 45.85; H, 5.59; N, 9.71. Found: C, 45.72; H, 5.64; N, 9.91.

*(b) From **7***

A solution of **7** (30 mg) in dry chloroform (10 ml) was refluxed for 1 h in the presence of 30 mg of silica gel (from a fresh supply, "for column chromatography", p*H* of aqueous slurry ~7–7.5). The filtered solution was evaporated to give a syrup which crystallized from ethyl acetate – petroleum ether, affording 15 mg of **18**, m.p. 162–163°. The i.r. and n.m.r. spectra of the products obtained from **7** and **15** were identical.

*Methyl 2-Acetamido-4,6-O-benzylidene-3-bromo-2,3-dideoxy-3-nitro-β-D-allopyranoside (**20**) and Methyl 2-O-Acetyl-4,6-O-benzylidene-3-bromo-3-deoxy-3-nitro-β-D-allopyranoside (**21**)*

A solution of 293 mg of the nitro olefin **19** (11*a*, 25) in acetone (20 ml) was mixed with a saturated, aqueous sodium acetate solution (15 ml) containing NBA (200 mg). The mixture was stirred at room temperature for 5 h, then diluted with water (20 ml), and partially evaporated to remove acetone. The white precipitate was washed with water and dried (393 mg). It contained two components that were readily separable on a silica gel column (20 g) with solvent A. The faster moving component (**21**) was isolated as crystals (102 mg, 24%), m.p. 224–225° after recrystallization from ethyl acetate – petroleum ether. An undepressed mixture m.p. and comparison of i.r. and n.m.r. spectra proved the identity of the product with previously prepared **21**, (lit. (1) m.p. 223–225°).

The slower fractions from the column yielded 237 mg (55%) of crystalline **20**. After recrystallization from ethyl acetate – petroleum ether it melted at 205–206° and showed $[\alpha]_D$ −70°; ν_{max} 3300 (NH), 1645, 1545 (amide I and II), 1560 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{19}BrN_2O_7$ (431.3): C, 44.60; H, 4.44; H, 6.51; Br, 18.50. Found: C, 44.67; H, 4.56; N, 6.32; Br, 18.78.

*Methyl 2-Acetamido-4,6-O-benzylidene-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**22**)*

Debromination of **20** (50 mg) using sodium borohydride (50 mg) in ethanol (10 ml) yielded, after 30 min at room temperature, the known glycoside **22** (36 mg, 88%); m.p. 309–311° as reported (11*b*). The i.r. and n.m.r. spectra were identical with those of an authentic sample.

*Methyl 4,6-O-Benzylidene-2,3-dideoxy-3-nitro-β-D-arabino-hexopyranoside (**23**)*

Reaction of **21** (100 mg) with sodium borohydride (50 mg) in ethanol (20 ml) for 1 h at room temperature afforded 65 mg (96%) of **23** melting at 144–146°, undepressed upon admixing an authentic sample (6, 11*a*). The i.r. spectrum of the product was identical with that of the sample.

*Methyl 2-Acetamido-4,6-O-benzylidene-3-bromo-2,3-dideoxy-3-nitro-β-D-gulopyranoside (**25**) and -β-D-galactopyranoside (**26**)*

To a solution of 293 mg of the nitro olefin **24** (25, 26) in acetone (20 ml) was added NBA (300 mg) and sodium acetate (10 mg) in water (5 ml). The reaction mixture was stirred overnight at room temperature. Two new, more slowly moving products were formed (t.l.c. with solvent A). Dilution of the mixture with water (30 ml) and evaporation of the acetone produced a white precipitate which was washed with cold water and dried (441 mg). Chromatography on silica gel (20 g) with solvent A effected separation of the two products, the faster moving one being **26** (196 mg, 45.5%) and the slower one, **25** (187 mg, 43.4%).

Recrystallized from ethanol, the β-D-*gulo* isomer **25** showed m.p. 190–191°; $[\alpha]_D$ −20.5° (*c*, 0.4 in dimethylformamide); ν_{max} 3320 (NH), 1670, 1525 (amide I and II), 1565 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{19}BrN_2O_7$ (431.3): C, 44.60, H, 44.44; N, 6.51; Br, 18.50. Found: C, 44.43; H, 4.59; N, 6.36; Br, 18.38.

The β-D-*galacto* isomer **26** was recrystallized from ethyl acetate – petroleum ether; m.p. 188–189° decomp.; $[\alpha]_D$ +86.6° (*c*, 0.9 in chloroform); ν_{max} 3320 (NH), 1670, 1540 (amide I and II), 1570 cm^{-1} (NO_2).

Anal. Calcd. for $C_{16}H_{19}BrN_2O_7$ (431.3): C, 44.60, H, 4.44; N, 6.51; Br, 18.50. Found: C, 44.90; H, 4.62; N, 6.38; Br, 18.33.

*Methyl 2-Acetamido-4,6-O-benzylidene-2,3-dideoxy-3-nitro-β-D-galactopyranoside (**27**)*

Compounds **25** and **26** (64 mg each) were separately reduced in like manner, with sodium borohydride (50 mg) in ethanol (10 mg) in an ice bath. Processing of the reaction mixtures as described previously gave

crystalline products (51 and 50 mg, 97 and 95%) that were identical according to t.l.c., i.r. spectra (ν_{max} 3300, 1655, 1550–1545 cm^{-1}), decomposition points of 288–289° (after recrystallization from nitromethane), and $[\alpha]_D$ values of +34.5° and +36.7° (*c* 0.5, in dimethylformamide). The i.r. spectra were identical with that obtained from an authentic sample of **27** (12).

For *rebromination*, a solution of **27** (40 mg) in acetone (15 ml) was stirred for 10 min at room temperature with NBA (40 mg) and saturated aqueous sodium acetate solution (1 ml). Thin-layer chromatography with solvent A revealed complete disappearance of **27** and formation of a product having the same R_f value as **25**. Work-up of the reaction mixture and recrystallization of the crude product from ethanol furnished 39.5 mg (80.5%) of **25**, m.p. 188–191°, unchanged on admixture of **25** from **24**. The identity was confirmed by i.r. spectra.

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