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THE REACTION OF 2-HYDROXYGLYCAL ESTERS WITH ALCOHOLS IN THE PRESENCE OF *N*-IODOSUCCINIMIDE, STEREOSELECTIVE SYNTHESIS OF α ANOMERS OF ALKYL 3-DEOXYHEX-2-ENOPYRANOSIDES AND 3,4-DIDEOXYHEX-3-ENOPYRANOSID-2-ULOSES*

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ABSTRACT

Reaction of 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**; 2-hydroxyglucal tetraacetate) with 1.0–1.5 mol of primary, secondary, or tertiary alcohols, in the presence of 0.1–1.0 mol of *N*-iodosuccinimide (NIS) in acetonitrile as solvent, afforded the α anomers of alkyl 3-deoxyhex-2-enopyranosides in very good yields. The reaction proceeded more slowly, and with poorer yields, in the case of the tetrabenzoate corresponding to **1**. When **1** was treated with higher concentrations of 2-propanol, increasing proportions of a reaction by-product, 2-propyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose (**10**), were produced. Such sugar enones as **10** were more readily formed when the starting 2-hydroxyglycal acetate had the *lyxo* configuration. Thus, two cholesteryl α-hex-3-enopyranosid-2-ulose derivatives were each prepared in one step and with good yields. Remarkable stereoselectivity for the formation of the α anomers was observed in all of these reactions.

INTRODUCTION

Because 3-deoxyaldos-2-uloses and their enolic forms are involved in the acidic and basic degradation of carbohydrates, and in the Lobry de Bruyn–Alberda van Ekenstein transformations, their chemistry and the development of simple preparative routes have received considerable attention[1,2]. On the other hand, sugar enones[3,4] and sugar enolones[5] are currently the preferred precursors for the synthesis of branched chain, amino, and highly modified sugars. They also constitute appropriate building blocks for the construction of non-carbohydrate, natural products[4,5].

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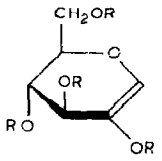
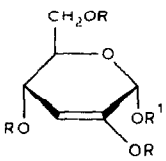
Alkyl 3,4-dideoxy-α- and -β-D-*glycero*-hex-3-enopyranosid-2-uloses have been prepared from enolic compounds[6], or from their anomeric fluorides[7], by acid-catalyzed elimination. These two are low-yielding methods, and the latter gave anomeric mixtures difficult to purify. A large-scale, multistep synthesis has been described[8]. We now report a convenient, stereoselective glycosidation of acylated 2-hydroxyglycals in the presence of *N*-iodosuccinimide (NIS) leading to the α anomers of alkyl 3,4-dideoxyhex-3-enopyranosid-2-uloses or their enolic precursors (alkyl 3-deoxyhex-2-enopyranosides) in high yields.

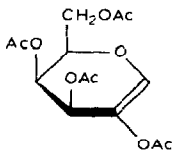
N-Bromosuccinimide[9] (NBS) and NIS[10] have been used for the glycosidation of glycal esters, affording selectively the α anomer of 2-deoxy-2-halogeno-glycosides. The reaction has been successfully applied in the preparation of anti-tumor-active, anthracycline antibiotics[11,12]. 2-Hydroxyglycal esters have shown a different behavior when treated with NBS and an alcohol. In this case (glycosyl bromide)uloses, instead of the expected 2-acyloxy-2-bromoglycosides, were obtained[13-15]. We have observed a different course of the reaction on replacing NBS by NIS.



1 R = Ac
2 R = Bz



3 R = Ac, R^1 = CH_3CH_2-
4 R = Ac, R^1 = $(CH_3)_2CH-$
5 R = Ac, R^1 = $(CH_3)_3C-$
6 R = Ac, R^1 = cholesteryl
7 R = Bz, R^1 = $(CH_3)_2CH-$



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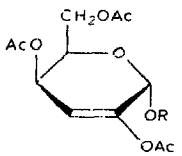
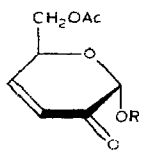
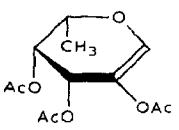


9 R = cholesteryl



10 R = $(CH_3)_2CH-$
11 R = cholesteryl



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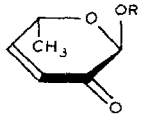

13 R = cholesteryl

RESULTS AND DISCUSSION

Acylated 2-hydroxyglycals were prepared by a modification of the procedure already described[16]. Elimination of hydrogen bromide from the acylated glycosyl bromides was carried out with 1,8-diazobicyclo[5.4.0]undec-5-ene (DBU) in 1,2-dichloroethane. The products were isolated from the reaction mixture in crystalline form, and with excellent yields. For example, 2-hydroxy-L-fucal triacetate (**12**) was prepared in ~85% yield from 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide.

The reaction of 2-hydroxyglycal esters with alcohols in the presence of NIS was performed under various conditions. When the procedure described by Lichtenthaler *et al.*[13,14] was followed, starting from **1** and methanol in dichloromethane, but using NIS instead of NBS, no reaction was observed. However, when acetonitrile was the reaction solvent, **1** was rapidly converted into a chromatographically faster-moving compound. The reaction took place with primary, secondary, and tertiary alcohols. The isopropyl derivative, which showed in t.l.c., good separation from the starting material **1**, was used for all of the following experiments.

When the reaction was carried out on a preparative scale, using equimolar amounts of NIS and **1**, and 2-propanol (1.5 mol per mol of **1**), a single product was obtained in 91% yield. Its structure was established as 2-propyl 2,4,6-tri-*O*-acetyl-3-deoxy-D-*erythro*-hex-2-enopyranoside (**4**), on the basis of its spectral data. The ^{1}H-n.m.r. spectrum of **4** (see Table I) showed signals characteristic of an isopropyl group (δ 3.91, H-2; and 1.25, 1.16, CH_3), a singlet at δ 5.12 that corresponded to the anomeric proton, and H-3 appeared as a doublet at δ 5.65 ($J_{3,4}$ 2.3 Hz). In the ^{13}C-n.m.r. spectrum of **4**, signals due to the two vinylic carbon atoms (δ 146.7 and 114.5), the anomeric carbon atom (δ 92.4), and C-4,5,6 (δ 65.5, 67.1, and 62.6) were observed (see Table II). A comparable pattern has been described for similar compounds[17]. The configuration of the anomeric center was determined

TABLE I

^{1}H-N.M.R. DATA FOR COMPOUNDS **3–7**, AND **9–13**

Compound	*H-1*	*H-3*	*H-4*	*H-5*	*H-6,6'*	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$
3	5.08(b.s)	5.73(d)	5.46(m)	4.22(m)	4.25(m)	2.2	8.0	—
4	5.12(b.s)	5.65(d)	5.40(dd)	←4.35–4.00(m)→		2.3	8.0	—
5	5.33(b.s)	5.69(d)	5.40(m)	4.23(m)	4.20(m)	2.3	8.2	—
6	5.20(b.s)	5.70(d)	5.40(dd)	←4.34–4.04(m)→		2.2	8.0	—
7	5.42(b.s)	6.04(d)	5.90(m)	←4.72–4.46(m)→		2.0	8.0	—
9	5.25(b.s)	5.92(d)	5.29(dd)	4.38(m)	4.22(m)	6.0	[a]	—
10	4.98(b.s)	6.16(dd)	6.97(dd)	4.78(m)	4.38; 4.23(dd)	10.8	1.8	2.7
11	5.01(b.s)	6.17(dd)	6.95(dd)	4.80(m)	4.36; 4.22 (dd)	10.5	1.3	2.5
12	6.61(d)	5.85(m)	5.33(dd)	4.31(m)	1.30(d)	5.0	1.2	0.9
13	4.96(b.s)	6.06(dd)	6.92(dd)	4.70(m)	1.37(d)	10.3	1.2	2.4

[a]Value uncertain.

TABLE II

^{13}C-N.M.R DATA FOR COMPOUNDS **3–7**, AND **9–13**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*O–C of the anomeric substituent*
3	93.6	146.4	114.9	65.3	67.0	62.5	64.6
4	92.4	146.7	114.5	65.5	67.1	62.6	71.5
5	88.4	147.4	114.5	65.4	66.7	62.8	75.7
6	92.5	146.8	114.8	65.4	67.1	62.7	78.9
7	92.7	147.3	115.2	66.6	67.5	63.8	71.8
9	92.3	149.6	111.6	64.6	66.7	62.6	78.7
10	96.1	188.7	126.1	147.1	66.8	64.6	71.8
11	96.3	188.3	126.3	146.8	66.9	64.6	79.2
12	139.0	126.7	66.3[a]	64.3[a]	72.0	15.9	—
13	96.1	189.0	124.1	152.1	64.3	20.2	78.5

[a]Assignments may have to be interchanged.

undoubtedly by preparation of two crystalline 2-enopyranosides: the *tert*-butyl glycoside **5** (ref. 18) and the cholesteryl derivative **6** (ref. 19). The high stereoselectivity of the reaction must be pointed out. No traces of the β anomers were detected. In this respect, the synthetic route here reported betters the classical method of Ferrier[19,20] that led to anomeric mixtures of glycosides.

Although the reaction was much slower when smaller proportions of NIS (0.1, 0.3, and 0.5 mol per mol of **1**) were used, compound **4** was always obtained in very good yields. This observation would indicate that NIS plays a catalytic role during glycosidation.

The influence of larger proportions of 2-propanol was also evaluated. For all of the concentrations tested, compound **4** was always the main product, independent of the concentration of NIS used. However, an increase in the proportion of the alcohol produced significant amounts of a secondary product that was identified as **10**.

When the tetrabenzoate **2** (1 mol) was treated with NIS (1 mol) and 2-propanol (1.5 mol), the reaction proceeded slowly, and some starting material was recovered, even after 20 h. The product (**7**) was isolated in ~50% yield by column chromatography.

The 2-enopyranosyl glycosides (**3–6**) are the normal products of the acid-catalyzed allylic rearrangement of glycals[19,20], by a mechanism which involves an intermediate carbocation formed by elimination of the C-3 substituent[20,21]. Hence, the presence of catalytic amounts of an acid during the reaction of acylated 2-hydroxyglycals with alcohols and NIS would account for the resulting products. As NIS did not react with glycal derivatives in the absence of the alcohol, we could assume that the allylic rearrangement is promoted by the hydrogen iodide produced by oxidation of the alcohol[22,23] by NIS. Further reaction of hydrogen iodide with[24] NIS, would also explain the formation of iodine during glycosidation. The acid-

catalyzed mechanism of glycosidation proposed is supported by the fact that the reaction was inhibited when a base (triethylamine) was present. Furthermore, the lower yield of product **7**, as compared with its analog **4**, should be expected, as benzoylated derivatives of glycals isomerize by acid catalysis, more slowly than the corresponding acetates[25].

As already mentioned, the reaction here described is highly stereoselective, affording exclusively the α anomers of alkyl hex-2-enopyranosides. In accord, reports in the literature indicate that the formation of α anomers is strongly favored in the boron trifluoride[26] and stannic chloride[27] isomerization of glycals. It was established[28] that the anomeric equilibration is appreciably faster than the overall allylic rearrangement. Also, the high stereoselectivity can be understood if we accept that the incipient carbocation intermediate adopts, as does the final product[29], the $^{o}H_5$(D) conformation, in which the approach of the alcohol from the α face not only would be favored by the stereoelectronic effect of the ring-oxygen atom[30], but also because it would occur from the less-hindered side, opposite to the leaving acyloxyl group at C-3.

On the other hand, the formation of the by-product during the glycosidation of **1**, **8**, and **12** in the presence of NIS, when large proportions of alcohols were used, would suggest an allylic rearrangement from the 2-enopyranosides (**4** and **9**), by attack of the alcohol on the enolic ester, generating a carbonyl group at C-2, and inducing the elimination of the acetoxyl group at C-4. The attack of the alcohol on the 2-acetoxyl group is supported by the fact that acetylcholesterol was isolated from the reaction mixture when cholesterol was the alcohol employed. The structure of the resulting alkyl hexenopyranosid-2-uloses was established on the basis of their spectral data. Thus, the ^{1}H-n.m.r. spectrum of **10** showed the anomeric proton as a broad singlet (δ 4.98), and the vinylic H-3 and H-4 appeared shifted downfield (δ 6.16 and 6.97, respectively) with a large coupling constant ($J_{3,4}$ 10.8 Hz), as reported for similar compounds[6]. The ^{13}C-n.m.r. spectrum of **10** showed the signal for the 2-carbonyl group at δ 188.7. The signals for C-3 and C-4, which were not differentiated for related compounds[17], were determined undoubtedly by single-frequency decoupling of H-3 and H-4, respectively. The lower-field signal (147.1 p.p.m.) corresponds to C-4, in agreement with the assignment of the β-carbon atoms in α,β-unsaturated ketones[31].

The formation of alkyl hex-3-enopyranosid-2-uloses takes place more readily in the 2-enopyranosyl glycosides having the *threo* configuration, in which the axially oriented substituent at C-4 is eliminated. Compounds **10** and **11** were obtained in very good yields starting from **8**. Also, **13** was the only product when **12** was treated with NIS and an excess of cholesterol. The sugar enones, readily accessible by the route here described, are currently used as starting materials in several synthetic transformations[18], including the preparation of unsaturated keto nucleosides[32] possessing significant antitumor activity.

EXPERIMENTAL

General methods. — Melting points were determined in a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter. Silica gel 60 (230–400 mesh, E. Merck, Darmstadt, G.F.R.) was used for column chromatography. T.l.c. was performed on plastic sheets precoated with silica gel 60F (E. Merck), with the following solvent systems: (*A*) 2:1 hexane–ethyl acetate, and (*B*) 4:1 toluene–ethyl acetate. Detection was effected by spraying the plates with 5% H_2SO_4 in ethanol, with subsequent heating. I.r. spectra were recorded with a Perkin–Elmer Model 421 spectrophotometer. N.m.r. spectra (^1H- and ^{13}C-) were recorded with a Varian XL100 spectrometer at 100.1 and 25.2 MHz, respectively, for solutions in chloroform-*d*. Chemical shifts refer to an internal standard of tetramethylsilane (δ 0.00); signal multiplicities are given as: b.s, broad singlet; d, doublet; and m, multiplet.

*2,3,4-Tri-*O*-acetyl-1,5-anhydro-6-deoxy-*L*-lyxo-hex-1-enitol* (**12**). — Crystalline 2,3,4,6-tetra-*O*-acetyl-α-L-fucopyranosyl bromide[33] (3.0 g, 8.5 mmol) dissolved in 1,2-dichloroethane (5 mL) was chilled at −20°, and 1,5-diazobicyclo[5.4.0]-undec-5-ene (DBU; 1.45 g, 9.5 mmol) was added dropwise. The solution was stirred for 0.5 h in the dark, and allowed to warm to room temperature. T.l.c. examination showed a single spot (R_F 0.42, solvent *A*) with a mobility lower than that of the starting material (R_F 0.46). The reaction mixture was diluted with dichloromethane (100 mL), washed successively with 5% hydrochloric acid, water, and saturated sodium hydrogencarbonate, and dried (magnesium sulfate). Compound **12** crystallized spontaneously upon evaporation of the solvent (1.95 g, 85%). Recrystallized from ethanol, it had m.p. 133–134°, $[\alpha]_D^{25}$ −8° (*c* 1, chloroform).

Anal. Calc. for $C_{12}H_{16}O_7$: C, 52.94; H, 5.92. Found: C, 53.19; H, 5.76.

Similarly, the following 2-hydroxyglycal esters[26,34] were prepared: 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**, 83%), 1,5-anhydro-2,3,4,6-tetra-*O*-benzoyl-D-*arabino*-hex-1-enitol (**2**, 93%), and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*lyxo*-hex-1-enitol (**8**, 89%).

*Ethyl 2,4,6-tri-*O*-acetyl-3-deoxy-α-*D*-erythro-hex-2-enopyranoside* (**3**). — To a solution of glycal **1** (0.66 g, 2.0 mmol) in acetonitrile (2 mL) were added absolute ethanol (0.18 mL, 3.0 mmol) and *N*-iodosuccinimide (0.45 g, 2.0 mmol). The mixture was stirred in the dark for 0.5 h with external cooling (ice–water) and then for 2.5 h at room temperature. The brownish-red solution was diluted with dichloromethane (150 mL), successively washed with 10% aqueous sodium thiosulfate, saturated sodium hydrogencarbonate, and water, and dried (magnesium sulfate). Ethyl 2,4,6-tri-*O*-acetyl-3-deoxy-α-D-*erythro*-hex-2-enopyranoside (**3**) was obtained as a colorless syrup (0.58 g, 92%) showing a single spot in t.l.c. (R_F 0.46, solvent *B*), faster-moving than the starting glycal **1** (R_F 0.40, solvent *B*). It showed $[\alpha]_D^{25}$ +81° (*c* 1, chloroform).

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.37; H, 6.66.

*2-Propyl 2,4,6-tri-*O*-acetyl-3-deoxy-α-*D*-erythro-hex-2-enopyranoside* (**4**). —

(*a*) The procedure described for the preparation of **3** was employed, starting from glycal **1** (0.66 g, 2 mmol), *N*-iodosuccinimide (0.45 g, 2.0 mmol), and 2-propanol (0.23 mL, 3.0 mmol) in acetonitrile (2 mL). Compound **4** was isolated as a syrup (0.60 g, 91%) that had $[\alpha]_D^{25}$ +57° (*c* 1, chloroform); R_F 0.50 (solvent *B*).

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.55; H, 6.67. Found: C, 54.75; H, 6.88.

(*b*) Smaller amounts of *N*-iodosuccinimide (0.1, 0.3, and 0.5 mol per mol of **1**) were used. Thus, starting from **1** (0.20 g, 0.6 mmol), 2-propanol (0.07 mL, 0.9 mmol), and *N*-iodosuccinimide (13.5 mg, 0.06 mmol) in acetonitrile (1 mL), the reaction was accomplished after 20 h of stirring in the dark at room temperature. The product **4** was isolated from the reaction mixture in 87% yield (0.17 g).

(*c*) A solution of **1** (33 mg, 0.1 mmol), NIS (25 mg, 0.11 mmol), and 2-propanol (0.01 mL, 0.12 mmol) in dichloromethane (1 mL) was stirred at room temperature. Glycal **1** remained unreactive; the reaction was monitored by t.l.c. for 20 h.

(*d*) Triethylamine (0.015 mL, 0.1 mmol) was added to a solution of **1** (33 mg, 0.1 mmol), NIS (23 mg, 0.1 mmol), and 2-propanol (0.01 mL, 0.12 mmol) in acetonitrile (0.3 mL). The only compound detectable, even after 20 h, was the starting glycal **1**.

(*e*) A solution of glycal **1** (33 mg, 0.1 mmol) and *N*-iodosuccinimide (25 mg, 0.11 mmol) in acetonitrile (0.5 mL) was stirred in the dark at room temperature. No reaction occurred in the absence of the alcohol.

(*f*) Larger proportions of 2-propanol (2.0, 2.5, and 3.0 mmol per mol of **1**) were used. Thus, when glycal **1** (0.61 g, 1.85 mmol) was treated with *N*-iodosuccinimide (0.42 g, 1.85 mmol) and 2-propanol (0.35 mL, 4.63 mmol) in acetonitrile (2.0 mL) for 20 h in the dark, two products were detected by t.l.c., one with the same R_F as **4** (0.50, solvent *B*), and the other of R_F 0.52. The mixture was separated by column chromatography with increasing concentrations of ethyl acetate in benzene. Fractions containing the faster-moving component were pooled and evaporated, affording a syrup (0.10 g, 24%) identified as 2-propyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose (**10**) that had $[\alpha]_D^{25}$ +3° (*c* 1, chloroform).

Anal. Calc. for $C_{11}H_{16}O_5$: C,57.89; H, 7.06. Found: C, 58.35; H, 7.12.

From later fractions from the column was isolated compound **3** (0.42 g, 69%).

tert-*Butyl 2,4,6-tri*-O-*acetyl-3-deoxy*-α-D-erythro-*hex-2-enopyranoside* (**5**). — To a solution of **1** (0.33 g, 1.0 mmol) in acetonitrile (2 mL) were added *tert*-butanol (0.15 mL, 1.5 mmol) and *N*-iodosuccinimide (23 mg, 0.1 mmol). The mixture was stirred for 60 h in the dark at room temperature. A single spot, R_F 0.59 (solvent *B*), was then detected by t.l.c. The mixture was treated as described for **3**, and then purified by column chromatography, affording 0.23 g (66%) of **5**. Recrystallization from water gave pure **5**, m.p. 58–60°, $[\alpha]_D^{25}$ +78° (*c* 0.5, chloroform), in good agreement with values reported in the literature[18].

Cholesteryl 2,4,6-tri-O-*acetyl-3-deoxy*-α-D-erythro-*hex-2-enopyranoside* (**6**). — Compound **1** (0.33 g, 1.0 mmol), cholesterol (0.46 g, 1.2 mmol), and *N*-iodo-

succinimide (23 mg, 0.1 mmol) were dissolved in a mixture of benzene (2 mL) and acetonitrile (2 mL). The solution was stirred in the dark at room temperature until no starting glycal **1** was detectable by t.l.c. (20 h); purification of the mixture was performed as already described. The syrup crystallized from ethanol; yield 0.33 g. A second crop of crystals was obtained from the mother liquors (0.15 g, total yield 73%). Compound **6**, recrystallized from the same solvent, had m.p. 125–126°, $[\alpha]_D^{25}$ +69° (*c* 0.6, chloroform), in agreement with values reported in the literature[19].

*2-Propyl 2,4,6-tri-*O*-benzoyl-3-deoxy-α-*D-erythro-*hex-2-enopyranoside* (**7**). — To a solution of compound **2** (1.16 g, 2.0 mmol) in acetonitrile (4 mL) were added 2-propanol (0.23 mL, 3.0 mmol) and *N*-iodosuccinimide (0.45 g, 2.0 mmol). The solution was stirred for 20 h in the dark, when examination by t.l.c. showed some starting material (R_F 0.52, solvent *A*) and another component of higher mobility (R_F 0.58). The mixture was purified as before, and separated by column chromatography with 4:1 hexane–ethyl acetate. Compound **7** was isolated as a syrup (0.51 g, 49%), that crystallized upon standing for several weeks. On recrystallization from ethanol, it had m.p. 91–93°, $[\alpha]_D^{25}$ +73° (*c* 1, chloroform).

Anal. Calc. for $C_{30}H_{28}O_8$: C, 69.70; H, 5.46. Found: C, 69.91; H, 5.54.

From later fractions from the column was recovered unreacted glycal **6** (0.30 g).

*2-Propyl 6-*O*-acetyl-3,4-dideoxy-α-*D-glycero-*hex-3-enopyranosid-2-ulose* (**10**). — To a solution of compound **8** (0.33 g, 1.0 mmol) in acetonitrile (2 mL) were added 2-propanol (0.12 mL, 1.57 mmol) and *N*-iodosuccinimide (23 mg, 0.10 mmol). The solution was stirred in the dark at room temperature. No starting material was detected by t.l.c. after 48 h. The mixture was purified as described for **3**, and the syrup obtained was chromatographed on a column of silica gel by eluting with 3:97 ethyl acetate–benzene. From the first fractions was isolated compound **10** (0.14 g, 61%). It showed the same physical constants as compound **10** prepared (see preparation *f*) from 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**).

*Cholesteryl 2,4,6-tri-*O*-acetyl-3-deoxy-α-*D-threo-*hex-2-enopyranoside* (**9**) *and cholesteryl 6-*O*-acetyl-3,4-dideoxy-α-*D-glycero-*hex-3-enopyranosid-2-ulose* (**11**). — A solution of glycal **8** (0.33 g, 1.0 mmol), cholesterol (0.46 g, 1.2 mmol), and *N*-iodosuccinimide (0.23 g, 1.0 mmol) in 1:3 acetonitrile–benzene (4 mL) was stirred for 24 h in the dark. The mixture showed (by t.l.c.) two main components, R_F 0.65 and 0.73 (solvent *B*). After the usual extractions, the solid residue was applied to a column, and eluted with 3:97 ethyl acetate–toluene. Fractions containing the product (R_F 0.73) were pooled and evaporated, affording crystalline **11** (0.13 g, 24%). Recrystallized from ethanol, it had m.p. 111–112°, $[\alpha]_D^{25}$ +7° (*c* 1, chloroform).

Anal. Calc. for $C_{35}H_{54}O_5$: C, 75.77; H, 9.81. Found: C, 75.66; H, 10.05.

Crystalline compound **9** (0.15 g, 23%) was obtained from later fractions from the column. Recrystallized from ethanol, it had m.p. 171–173°, $[\alpha]_D^{25}$ −46° (*c* 1, chloroform).

Anal. Calc. for $C_{39}H_{60}O_8$: C, 71.25; H, 9.21. Found: C, 71.34; H, 9.03.

When glycal **8** (0.13 g, 0.4 mmol) was treated with cholesterol (0.31 g, 0.8 mmol) under the same conditions as before, complete conversion into **11** was observed. Chromatographic purification (3:97 ethyl acetate–toluene) afforded crystalline **11** (0.134 g, 60%).

*Cholesteryl 3,4,6-trideoxy-α-*L*-glycero-hex-3-enopyranoside-2-ulose.* (**13**). — Compound **12** (0.18 g, 0.66 mmol), cholesterol (0.46 g, 1.2 mmol), and *N*-iodosuccinimide (0.16 g, 0.7 mmol) were dissolved in 1:1 (v/v) benzene–acetonitrile (4 mL), and the solution was stirred in the dark at room temperature. When **12** was completely consumed (20 h), the mixture was processed as usual, and purified by column chromatography with toluene. The component having R_F 0.55 (toluene) was isolated crystalline and identified as acetylcholesterol; m.p. 111–112°, $[\alpha]_D^{25}$ −42° (*c* 0.7, chloroform), in good agreement with values reported in the literature[35]. Fractions containing the product having R_F 0.33 (toluene) were evaporated, affording crystalline **13** (0.27 g, 55%). Recrystallized from ethanol, it had m.p. 152–153°, $[\alpha]_D^{25}$ −60° (*c* 1, chloroform).

Anal. Calc. for $C_{33}H_{52}O_3$: C, 79.79; H, 10.55. Found: C, 79.65; H, 10.43.

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