cupric acetate (10 mg) in acetic acid (5 mL) was slowly heated until the evolution of nitrogen began (ca. 65 °C). The temperature was maintained at 65 °C for an additional 5 min and then the solvent was removed by freeze-drying. Thin layer chromatography (dichloromethane–ether, 4:1) of the oily product revealed a distinct spot at R_f 0.75, but with considerable streaking below it. The mixture (0.80 g) was chromatographed on silica gel (40 g in a 20 × 370 mm column) using dichloromethane–ether, 4:1, as the eluent. The major product, isolated in chromatographically pure form, was the one of R_f 0.75 (**17**, 0.32 g, 39%), which on standing for a month crystallized: mp 87–89 °C (lit.[13] 59–61 °C); IR (KBr) 1780 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{20}O_{11}$ (376.32): C, 47.87; H, 5.35. Found: C, 48.05; H, 5.50.

Decomposition of 15 in Acetic Acid. A solution of **15** (1.0 g) and cupric acetate (10 mg) in acetic acid (5 mL) was slowly heated until the evolution of nitrogen began (bath temperature 70 °C). The temperature was maintained at 70 °C for 5 min and the solution was concentrated in vacuo to give a white solid. The solid was recrystallized from ether to give the acyclic diketone **16** (1.0 g, 74%): mp 85–87 °C.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health, Grant No. AM-13551 and GM-19252, for support of this research. We thank Dr. Charles L. Watkins of this Department for providing us with some of the ^1H NMR spectra, and Drs. T. Phil Pitner and Jerry D. Glickson of the University of Alabama in Birmingham Comprehensive Cancer Center for their assistance in obtaining the theoretical ^1H NMR spectra.

Registry No.—**1**, 58-86-6; **13** acid chloride, 63181-62-4; sodium hydrogen tri-*O*-acetylxylarate, 63181-65-7; diazomethane, 334-88-3; glutaryl dichloride, 2873-74-7.

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δ-Dicarbonyl Sugars. 6. Preparation of an Unusual Trihaloheptulose from Xylaric Acid

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The formation of 3,4,5-tri-*O*-acetyl-6,7-anhydro-6-chloromethyl-1-deoxy-1-diazo-DL-*ido*-2-heptulose (**3**) as a by-product of the reaction of tri-*O*-acetylxylaryl dichloride (**1**) with diazomethane is described. Treatment of **3** with hydrogen bromide yielded 3,4,5-tri-*O*-acetyl-1,7-dibromo-6-chloromethyl-1,7-dideoxy-α-DL-*ido*-heptopyranos-2-ulose (**5**), which reacted with sodium azide to give a mixture of 3,4,5-tri-*O*-acetyl-2,7-anhydro-1-bromo-6-chloromethyl-1-deoxy-α-DL-*ido*-heptopyranos-2-ulose (**6**) and the 1-azido derivative **7**. The structure of **5** was determined by an x-ray crystallographic analysis.

In an earlier publication from this laboratory,[3] the acetate-induced cyclization of tri-*O*-acetyl-1,7-dibromo-1,7-dideoxy-*xylo*-2,6,-heptodiulose (**4**) was described.[4] This dibromide was prepared by treating crystalline tri-*O*-acetyl-1,7-bisdiazo-1,7-dideoxy-*xylo*-2,6-heptodiulose (**2**) with hydrogen bromide (Scheme I). On the basis of TLC it was deemed that the mother liquors of the reaction mixture that gave **2** were rich in this compound and when treated with hydrogen bromide would give additional **4**. When the crude product from this reaction failed to crystallize, the reaction mixture was treated with sodium azide to see if any bromide displacement might occur. This reaction yielded a crystalline compound whose IR spectrum had a moderately sized absorption due to an azido group, a strong carbonyl absorption, but no hydroxyl peak. Deacetylation gave a crystalline solid whose IR spectrum had the azide peak, a strong hydroxyl peak, but no carbonyl absorption. Reacetylation gave back the precursor acetate.

In order to discover the origin of the acetylated azido compound, a reexamination of the diazomethylation mother liquors was necessary. Column chromatographic purification of a sample of the mother liquors after crystallization of **2** af-

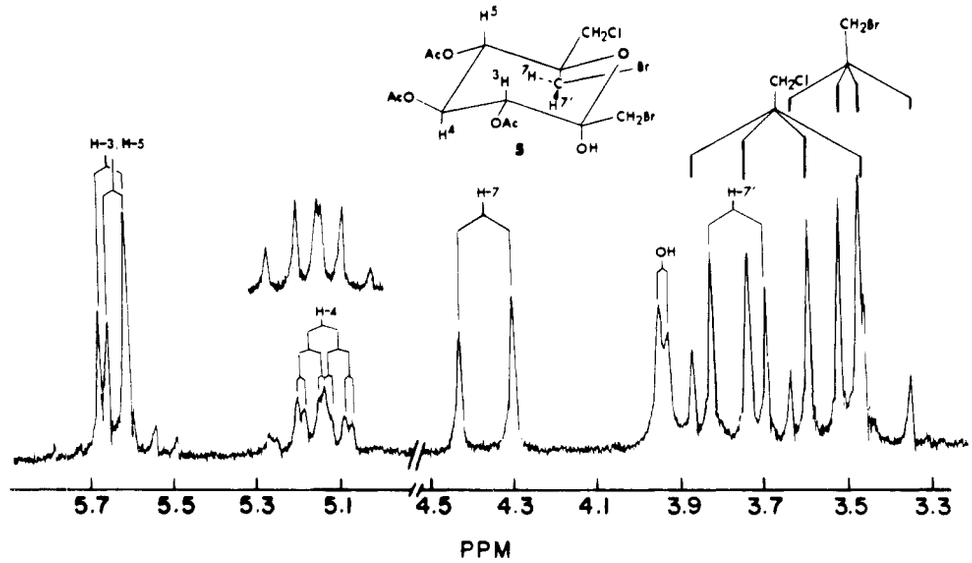
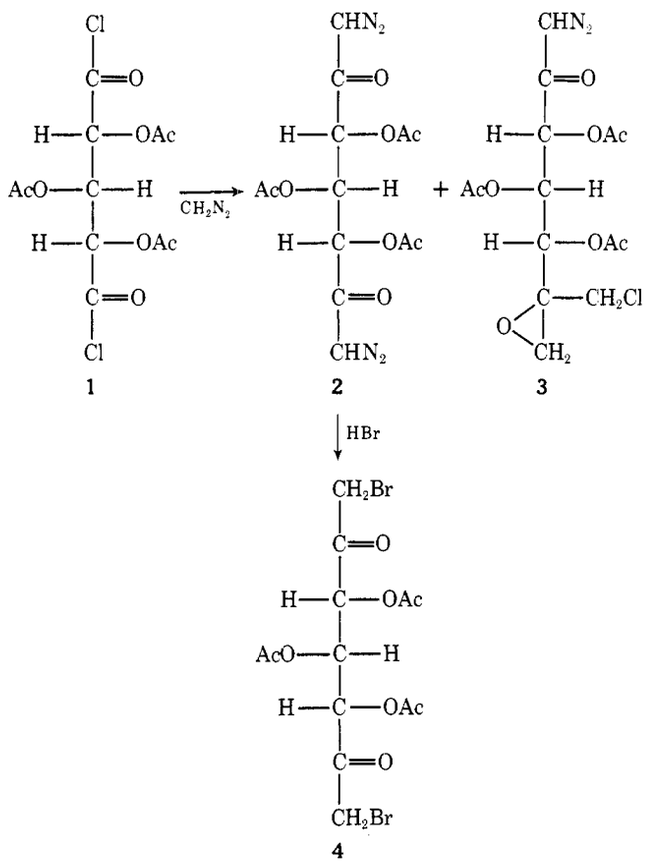
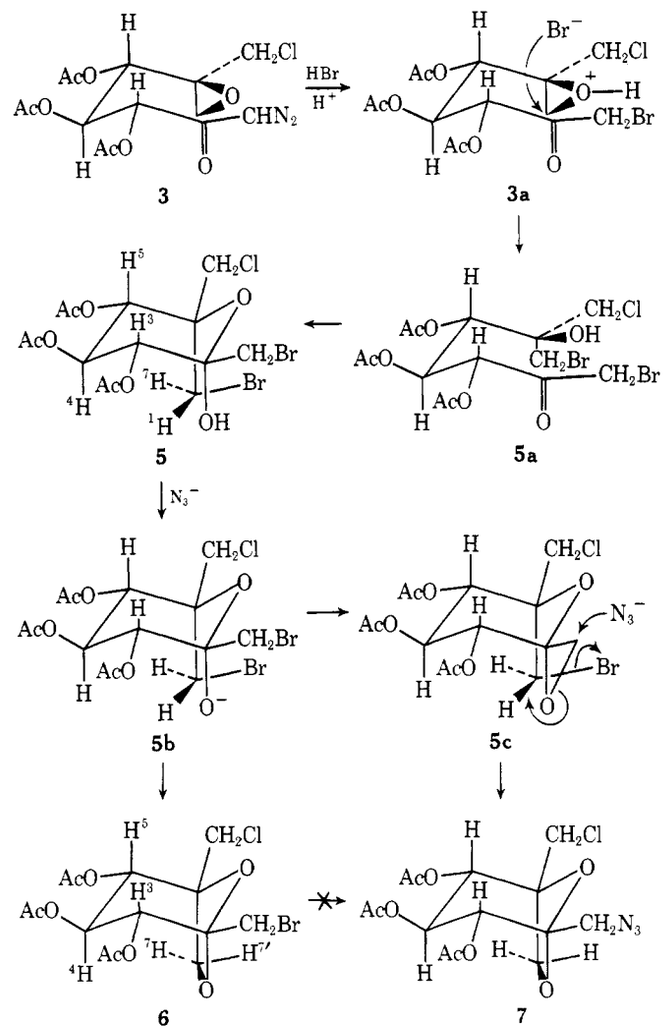


Figure 1. 90-MHz ^{1}H NMR spectrum of **5** (excluding acetoxy proton signals) with decoupled signals at δ 5.16.

Scheme I



Scheme II



forded additional **2**, dimethyl tri-*O*-acetylxylarate, and a new compound, 3,4,5-tri-*O*-acetyl-6,7-anhydro-6-chloromethyl-1-deoxy-1-diazo-DL-*ido*-2-heptulose (**3**).[2] Treatment of **3** with hydrogen bromide gave crystalline **5**, which was then converted to the product with the azide group (Scheme II).

The ^{1}H NMR spectrum of **5** (Figure 1) was in good agreement with the structure eventually obtained by x-ray crystallographic analysis (Figure 2). The x-ray structure shows that the molecule in the crystalline state is in a regular chair conformation with the C-1 bromomethyl, chloromethyl, and three acetoxy groups all in equatorial positions. Although crystalline **5** is in a regular chair conformation with the H-3, H-4 and H-4, H-5 dihedral angles calculated to be approximately 175 and 170°, respectively, the conformation of the molecule in $CDCl_3$ solution appears to be somewhat skewed with these same dihedral angles considerably less than what they are in the crystalline state. The couplings between H-4 and its vicinal neighbors are 4.43 and 5.98 Hz, values which are lower than the normal 7–10 Hz associated with two vicinal anti-periplanar protons. H-4 also shows unusual long-range

coupling through five σ bonds with the C-2 hydroxyl proton ($J_{OH,H-4}$ = 1.8 Hz).[5] The fine splitting of the H-4 signal disappears with irradiation of the hydroxyl resonance (Figure 1) or deuterium exchange of the hydroxyl proton.

Although elemental analysis, TLC, and melting point range all indicate that **5** is a homogeneous substance, the ^{1}H NMR spectrum shows some impurities as reflected in the extraneous peaks accompanying the signals from the ring protons, particularly H-4. These impurities might include the β anomer of **5** and/or small amounts of the anomers resulting from bromide attack at the tertiary epoxide carbon of **3.** Excellent correlation between the observed coupled and decoupled spectra of **5** with their theoretical counterparts was obtained when these minor peaks were considered to be from impurities in the sample.

The product obtained from treating **5** with sodium azide was determined to be the bicyclo compound 3,4,5-tri-*O*-acetyl-2,7-anhydro-1-bromo-6-chloromethyl-1-deoxy-α-DL-*ido*-heptopyranos-2-ulose (**6**) contaminated with about 30% of the 1-azido derivative **7** (Scheme II). The mixture of **6** and **7** was separated by preparative TLC, but only with difficulty. However, pure **6** was easily obtained by preparative TLC after the mixture was catalytically hydrogenolyzed, presumably converting **7** to a more polar amine derivative.

The conversion of **5** to **6** was likely the result of a simple intramolecular nucleophilic displacement of the C-7 bromine with the azide-generated C-2 alkoxide ion **5b.** The structural assignment for **7,** and in particular the point of attachment of the azido group, is partially based on a comparison of the ^{1}H NMR spectra of **6** and **7.** The spectrum of **7** shows an upfield shift (0.1 ppm) of the C-1 methylene singlet, a result in keeping with displacement of the C-1 bromide with azide. In all other respects the two spectra are nearly identical.

In considering the formation of **7** direct backside displacement of the C-1 bromide of either **5** or **6** is unlikely due to the steric shielding of this carbon by the C-2 oxygen. In fact, a mixture of **6** and **7** (**6**/**7** ca. 7:3) remains unchanged when treated with azide under those conditions that produced **7** from **5.** We have concluded that the anionic oxygen of **5b** in addition to forming the dioxolane system of **6** can also displace the C-1 bromide giving a transient epoxide **5c,** which is then opened with azide to give **7.**

The evidence for the stereochemistry of the epoxide in **5** is found in the proposed mechanism for the conversion of **3** to **5** with hydrogen bromide. Protonation of the epoxide oxygen to give **3a** is followed by ring opening with bromide at the sterically favored primary carbon, this step leading to **5** by way of its acyclic isomer **5a.**

Experimental Section

General Methods. All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer and proton magnetic resonance spectra were obtained on either a Varian Model EM-390 or HA-60IL spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded using a Hitachi-Perkin-Elmer Model RMU-7 double focusing mass spectrometer. All solvent evaporations were done using a flash evaporator at 20–40 mmHg and at a bath temperature of 35–40 °C. Analytical TLC was carried out on microscope slides coated with silica gel GF-254 (E. Merck, Darmstadt, W. Germany) and visualized by spraying with sulfuric acid and then charring. Preparative TLC was carried out on 20 × 20 cm plates precoated with a 1000-μm thickness of silica gel GF (Analtech, Inc., Newark, Del). Column chromatography was carried out using silica gel 60 (70–230 mesh, E. Merck, Darmstadt, W. Germany). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

3,4,5-Tri-*O*-acetyl-6,7-anhydro-6-chloromethyl-1-deoxy-1-diazo-DL-*ido*-2-heptulose (3). The diazomethylation of 2,3,4-tri-*O*-acetylxylaryl dichloride (**1**) was carried out as described in ref 2 to yield crystalline 3,4,5-tri-*O*-acetyl-1,7-bisdiazo-1,7-dideoxy-*xylo*-2,6-heptodiulose (**2**). The mother liquors from **2** were chromatographed affording syrupy **3** (2.1 g), which was homogeneous by TLC but possessed an ambiguous ^{1}H NMR spectrum. Upon dissolving this syrup in methylene chloride, diluting the solution with an equal volume of ether, seeding with crystals of **2,** presumably contaminated with **3,** and storing at −10 °C, crystalline **3** was obtained (300 mg, 1.7% based on **1**). An additional crop of **3** (255 mg, 1.5%) was obtained by concentrating the mother liquor to a syrup, dissolving it in ethanol, diluting with water to a very slight tubidity, and storing at −10 °C. Compound **3** had a mp of 90–92 °C [IR (KBr) 2115 (C=N=N), 1750 (C=O), and 1630 cm^{-1} (N=N); ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 6, two CH_3CO_2), 2.23 (s, 3, CH_3CO_2), 2.85 and 2.96 (both d, each 1, J_{gem} = 5 Hz, epoxide CH_2), 3.63 and 3.85 (both d, each 1, J_{gem} = 12 Hz, CH_2Cl), 5.38 (complex m, 3, three CHOAc), and 5.50 (s, 1, CHN_2); mass spectrum (70 eV) *m/e* 377 (M + 1) and 379 (M + 3) relative intensity ca. 3:1, monochlorine isotopic cluster].

Anal. Calcd for $C_{14}H_{17}O_8N_2Cl$ (376.76): C, 44.36; H, 4.55; Cl, 9.41; N, 7.44. Found: C, 44.56; H, 4.56; C l, 9.61; N, 7.33.

3,4,5-Tri-*O*-acetyl-1,7-dibromo-6-chloromethyl-1,7-dideoxy-α-DL-*ido*-heptopyranos-2-ulose (5). Gaseous HBr was bubbled into a suspension of **3** (100 mg) in 5 mL of anhydrous ether while stirring. After about 2 min the solid went into solution and the effervescence stopped. More HBr was bubbled in for another 2 min and the reaction was allowed to stand for 10 min. The solution was then treated with a molecular sieve until it was no longer acid to litmus. The sieve was removed by filtration and the filtrate concentrated to a syrup and dried in vacuo (ca. 1 mmHg) for 3 h. The resulting froth was crystallized from ether and the solid formed was recrystallized from hot ethanol to yield **5** (100 mg, 74%) [mp 142–145 °C with softening at 140 °C; IR (KBr) 3500 (sharp, free OH), 3450 (broad, hydrogen-bonded OH), and 1750 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, Figure 1) δ 2.01, 2.05, 2.12 (each s, each 3, CH_3CO), 3.53 and 3.77 (both d, each 1, J_{gem} = 12.0 Hz, CH_2Cl), 3.42 and 3.54 (both d, each 1, J_{gem} = 10.5 Hz, equatorial CH_2Br), 3.75 (d, 1, $J_{H-7,H-7'}$ = 11.7 Hz, H-7'), 4.35 (d, 1, $J_{H-7,H-7'}$ = 11.7 Hz, H-7), 3.94 (d, 1, $J_{OH,H-4}$ = 1.8 Hz, OH confirmed by deuterium exchange), 5.16 (m, 1, H-4 coupled to H-3, H-5, and OH), and 5.65 and 5.66 (overlapping doublets, couplings with H-4 of 4.43 and 5.98 Hz, resonances attributed to, but not specifically assigned to, H-3 and H-5); mass spectrum (70 eV) *m/e* 509 (M + 1)]. The mass spectrum of **5** also exhibited the following isotopic clusters: weak, dibromine (M − CH_2Cl) at *m/e* 459, 461, and 463, relative intensity ca. 1:2:1; strong, monochlorine–monobromine (M − CH_2Br) at *m/e* 415, 417, and 419, relative intensity ca. 3:4:1; strong, dibromine (M − CH_2Cl, HOAc) at *m/e* 399, 401, and 403; and strong, monobromine (M − HCl, Br) at *m/e* 393 and 395, relative intensity ca. 1:1.

Anal. Calcd for $C_{14}H_{19}O_8Br_2Cl$ (510.58): C, 32.93; H, 3.75; Br, 31.30; Cl, 6.95. Found: C, 33.19; H, 3.88; Br, 30.94; Cl, 6.77.

For x-ray crystallographic analysis clear, rectangular, platelike crystals of **5** were obtained by room temperature crystallization from ethanol. Weissenberg and oscillation photographs showed that the crystals are monoclinic; the space group is $P2_1/c$, as indicated by the systematic absence of reflections $h0l$ with l odd and $0k0$ with k odd. A crystal with approximate dimensions of 0.4 × 0.3 × 0.2 mm was mounted along its a axis on a Picker FACS-1 diffractometer. Cell

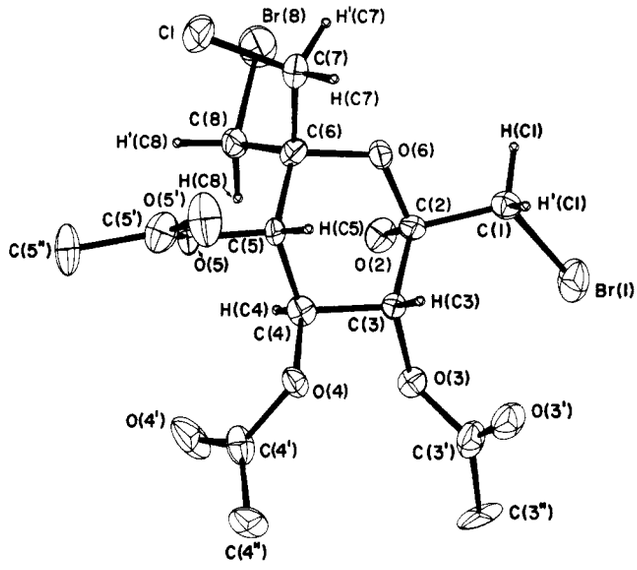


Figure 2. Stereoview of compound **5.**

dimensions, which were determined by a least-squares analysis of the 2θ values for 14 medium-angle reflections (Cu Kα, λ 1.5418 Å), are a = 6.060 (2), b = 13.193 (5), c = 24.688 (4) Å, and β = 102.21 (2)°.

Intensity data were collected with the diffractometer, by use of nickel-filtered copper radiation, a scintillation counter, and a θ–2θ scanning technique. Measurements were made for the 3199 reflections with $2\theta \leq 128°$. The scanning speed was 1°/min for the $h \geq 0, \geq 0, l \geq 0$ sector of reciprocal space. However, the crystal began to show signs of decomposition, and the scanning speed was increased to 2°/min for the remainder of the data collection. The intensities of three reference reflections (200, 020, and 001) that were monitored periodically during the data collection decreased continuously to about 75% of their original values. The intensity values were scaled by a least-squares procedure in which the intensities of the standard reflections were used to calculate scale factors as a function of crystal exposure time. Intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correctional term $(0.03S)^2$, S being the scan count. The intensities and their variances were corrected for Lorentz and polarization factors, absorption corrections were applied by using the computer program ORABS,[8] and the data were scaled by means of a Wilson[7] plot.

A trial structure was obtained by the heavy-atom method as follows: coordinates for one bromine atom were determined from a sharpened Patterson map; coordinates for the second bromine atom were determined from a sum-function superposition of sharpened Patterson maps translated to the first bromine atom position; and the remaining nonhydrogen atoms were located in a Fourier map that was calculated by using phase angles derived from the two atoms. The trial structure was refined by using a modified version of the full-matrix least-squares program ORFLS.[9,10] The quantity minimized was $\Sigma w[(F_o^2 - F_c^2)/k^2]^2$, where k is a scale factor and weight w is equal to $1/\sigma^2(F_o^2)$. Scattering factors for the nonhydrogen atoms were from the "International Tables for X-Ray Crystallography",[11] anomalous dispersion correction factors for these atoms were from Cromer and Liberman,[12] and hydrogen atom scattering factors were from Stewart, Davidson, and Simpson.[13] Coordinates for those hydrogen atoms bonded to carbon atoms (excluding methyl groups) were calculated by assuming tetrahedral coordination around the carbon atoms and C–H bond distances of 0.95 Å. The hydrogen atoms were assigned the isotropic temperature factors of the carbon atoms to which they are bonded, and were included in the calculation of structure factors, but not in the least-squares refinement. The nonhydrogen atom positional parameters, the anisotropic temperature parameters, and Zachariasen's[14] isotropic extinction parameter g (as formulated by Coppens and Hamilton[15]) were included in the refinement.

The final R index ($\Sigma\|F_o| - |F_c\|/|F_o|$) is 0.130, and the goodness-of-fit $\{[\Sigma w[(F_o^2 - F_c^2)/k^2]/(m-s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined$\}$ is 1.38. During the last cycle of refinement, no parameter shifted more than one-fourth of its estimated standard deviation. A final difference Fourier map showed several peaks and troughs of magnitudes ranging from 0.6 to 1.1 e/Å in the vicinities of the bromine atoms; there were no other peaks or troughs in excess of 0.6 e/Å^3.

3,4,5-Tri-*O*-acetyl-2,7-anhydro-1-bromo-6-chloromethyl-1-deoxy-α-DL-*ido*-heptopyranos-2-ulose (6) and 3,4,5-Tri-*O*-acetyl-2,7-anhydro-1-azido-6-chloromethyl-1-deoxy-β-DL-*ido*-heptopyranos-2-ulose (7). A solution of **5** (200 mg, 0.39 mmol) in 5 mL of anhydrous acetone was stirred at room temperature with NaN_3 (500 mg, 1.3 mmol) overnight. Analysis of this reaction mixture by TLC (6:1, benzene–ether) showed the absence of starting material and only one spot of greater R_f value than the starting material. The mixture was diluted with 100 mL of chloroform and concentrated to a paste. This paste was triturated with chloroform and the resulting solid and liquid mixture was washed twice with water. The chloroform layer was dried and decolorized over a mixture of $CaCl_2$ and decolorizing carbon and after filtration of the mixtures and concentration of the filtrate the product was crystallized from ether. The solid was filtered and washed with ether to yield 100 mg of a slightly yellow-tinted material (mp 122–125 °C) subsequently determined to be a mixture of **6** contaminated with ca. 30% of **7**. No change in the ratio of these compounds, as evidenced by ^{1}H NMR spectroscopy, was observed when the mixture was treated overnight with azide as described. A mass spectrum of this mixture exhibited a parent ion (m/e 428) for **6** and a parent ion (m/e 391) for **7** along with several isotopic clusters: strong, monobromine (from **6**, M − Cl) at m/e 393 and 395, relative intensity ca. 1:1; strong, monochlorine–monobromine (from **6**, M − OAc) at m/e 369, 371, and 373, relative intensity ca. 3:4:1, and strong, monochlorine (from **7**, M − OAc) at m/e 332 and 334, relative intensity ca. 3:1.

The mixture (100 mg) of **6** and **7** dissolved in 10 mL of ethanol containing 0.2 mL of 6 N HCl was hydrogenated over Pt (from 100 mg of PtO_2) for 2 h at atmospheric pressure. A TLC (1:1, benzene–ether) of this reaction mixture showed one spot of identical R_f value with that of the starting mixture and another spot at the origin. After customary workup, the major component, the one not at the origin, was recovered by preparative TLC (9:1, benzene–ether). The crystalline product was recrystallized from hot ethanol to yield pure **6** (55 mg, 33% from **5**) [mp 136–138 °C; IR (KBr) 1755 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.98, 2.03, 2.15 (each s, each 3, CH_3CO_2), 3.47 (s, 2, CH_2Br), 3.68 (s, 2, CH_2Cl), 3.83 (d, 1, J_{gem} = 8.0 Hz, H-7′), 4.34 (d, 1, J_{gem} = 8.0 Hz, H-7), and 5.28 (unresolved m, 3, H-2, H-3, and H-4)].

Anal. Calcd for $C_{14}H_{18}BrClO_8$ (429.66): C, 39.13; H, 4.22; Br, 18.60; Cl, 8.25. Found: C, 39.29; H, 4.24; Br, 18.70; Cl, 8.49.

Another sample of the mixture of **6** and **7** (100 mg) was separated by preparative TLC (developing with 9:1 benzene–ether and visualizing with iodine vapor) into three fractions: the head, middle, and tail of a broad band. The head fraction was found to still contain a small amount of azide **7** (IR band at 2100 cm^{-1}), so it was chromatographed again on a preparative TLC plate. Again, the head fraction of this band was scraped off and extracted with acetone to give 15 mg of pure **6**. The tail fraction of the first chromatogram was also chromatographed again and the tail of this band yielded 5 mg of **7** [mp 125–128 °C; IR (KBr) 2110 (N_3) and 1750 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3, CH_3CO_2), 2.04 (s, 6, two CH_3CO_2), 3.37 (s, 2, CH_2N_3), 3.68 (s, 2, CH_2Cl), 3.84 (d, 1, J_{gem} = 8.0 Hz, H-7′), 4.33 (d, 1, J_{gem} = 8.0 Hz, H-7), and 5.27 (unresolved m, 3, H-2, H-3, and H-4)].

Deacetylation of the Mixture of 6 and 7. A 200-mg sample of the mixture of **6** and **7** was suspended in 5 mL of absolute methanol and sodium methoxide was added in small amounts while stirring until the solid dissolved. The reaction was stirred for an additional 5 min and a TLC (6:1, benzene–ether) at this point showed the absence of starting material and only one spot at the origin. The reaction mixture was treated with acid ion-exchange resin until neutral and then allowed to stand over decolorizing carbon for 10 min. The resin and charcoal were removed by filtration and the filtrate was concentrated to a syrup. This syrup crystallized upon standing overnight. The solid was recrystallized by dissolving it in several drops of absolute methanol, diluting with 25 mL of $CHCl_3$, and then concentrating just until crystallization began to occur. This yielded 50 mg of a solid of mp 135–139 °C. An IR of this solid showed a strong, broad hydroxyl absorption at 3340 cm^{-1}, a small sharp azide peak at 2100 cm^{-1}, but no carbonyl absorption. Its ^{1}H NMR spectrum, taken in both acetone-d_6 and D_2O, showed the absence of any acetate groups, a complex multiplet centered at about δ 3.8, and a broad peak for the hydroxyl protons at about δ 4.5.

This solid and its mother liquor were combined and concentrated to a syrup. The syrup was dissolved in 2 mL of pyridine and 1.5 mL of acetic anhydride and allowed to stand for 3 h. TLC (6:1, benzene–ether) showed the complete disappearance of starting material and only one spot of identical R_f value as that of the original mixture of **6** and **7**. Standard workup of the reaction mixture yielded 35 mg of a solid (mp 123–125 °C), identified as the mixture of **6** and **7** by its IR and NMR spectra.

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Supplementary Material Available: Tables of hydrogen and nonhydrogen atomic parameters with estimated standard deviations and a table of selected bond angles (4 pages). Ordering information is given on any current masthead page.

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Synthesis of Cholest-5-ene-3β,11α,15β-triol-7-one. A Model for the Steroid Nucleus of Oogoniol, a Sex Hormone of the Water Mold *Achlya*

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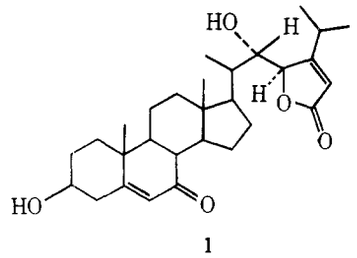
The synthesis of cholest-5-ene-3β,11α,15β-triol-7-one (**4**), a compound containing the nuclear functionalities of oogoniol, is described. Starting from a relatively unfunctionalized steroid, 7-dehydrocholesterol benzoate, oxygen functions were introduced into rings B, C, and D. The first stage of the synthesis was the oxygenation of C-15 through the hydroboration of cholesta-7,14-dien-3β-ol (**7b**) to give cholest-7-ene-3β,15α-diol (**8**). Then the 11α-alcohol and C-7 ketone functions were introduced via the Δ^7 double bond by a series of reactions first developed in the early 1950s to oxygenate C-11 of ring C unsubstituted steroids for corticosteroid syntheses. The resulting cholestane-3β,11α,15α-triol-7-one (**12a**) was selectively acetylated at C-3 and C-11 and the Δ^5 double bond was introduced through a bromination–dehydrobromination sequence. The final stage of the synthesis was the inversion of the C-15 alcohol to generate the desired β configuration. The 15α-alcohol was oxidized to the ketone and subsequent hydride reduction yielded predominantly the 15β-alcohol. This reduction also reduced the unsaturated C-7 ketone which was then oxidized with manganese dioxide. Saponification of the 3β- and 11α-acetates produced the desired cholest-5-ene-3β,11α,15β-triol-7-one (**4**), which proved to be biologically inactive.

Sexual reproduction in the water mold *Achlya* has been thoroughly studied and the involvement of sex hormones regulating this process has been conclusively demonstrated.[2] Sexual reproduction in *Achlya bisexualis* is initiated by the secretion of antheridiol (**1**) by the female strain which induces the formation of antheridial branches in the male strain. Antheridiol, isolated as a crystalline compound[3] and shown to have structure **1**,[4] was the first steroidal sex hormone to be identified in the plant kingdom and several syntheses have been reported.[5] After stimulation by anteridiol, the sexually activated male strain releases a second hormone, hormone B, which causes the female strain to develop oogonial branches. From a hermaphroditic strain of *Achlya heterosexualis* which produces hormone B without prior stimulation by anteridiol, McMorris and co-workers have recently isolated and characterized two crystalline compounds having hormone B activity.[6] They have named these compounds oogoniol-1 and -2 and have proposed structures **2a, 2b,** and **2c,** respectively, for these two compounds plus a third closely related compound, oogoniol-3, which was obtained as part of a noncrystalline mixture.



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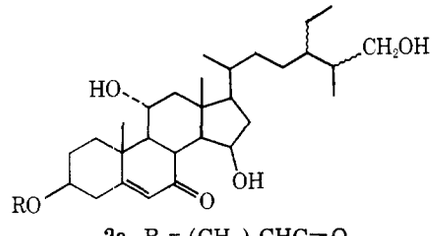

2a, R = $(CH_3)_2CHC{=}O$
2b, R = $CH_3CH_2C{=}O$
2c, R = Ac
2d, R = H

The oogoniols are therefore the second example of steroidal plant sex hormones to be identified, and confirmation of the structure assignment by synthesis is desirable. Even more importantly, structural modification would permit an evaluation of the structural specificity of the biological activity associated with the different functionalities of structure **2.** Oogoniol-1, -2, and -3 (**2a, 2b,** and **2c**) differ only in the kind of ester group present at C-3. The parent tetraol **2d,** which will be referred to here simply as oogoniol, has been shown to be even slightly more biologically active than **2a** and **2b.**[6] It was therefore decided to devise a synthesis of oogoniol (**2d**) rather than any of the C-3 esterified compounds **2a, 2b,** and **2c.**

Any synthesis of oogoniol utilizing a steroidal starting material can be logically divided into two parts. One part is the construction of the side chain, which ideally should be stereospecific so that the stereochemistry and absolute configuration at C-24 and C-25 can be determined. The other part