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BASE-CATALYZED OLIGOMERIZATION OF LEVOGLUCOSENONE

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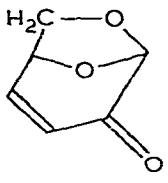
ABSTRACT

Heating levoglucosenone in aqueous triethylamine gives a dimer and two trimers in yields of 8, 18, and 56%, respectively. These compounds have been isolated crystalline, and their structures and stereochemistry have been investigated by ^{13}C- and ^{1}H-n.m.r. and other spectroscopic methods. These data indicate that the dimer is apparently formed by Michael addition to provide a C-3–C-4 linkage. Similar reactions provide a non-olefinic, C-3–C-4-linked, cyclic trimer and an olefinic, cyclic trimer containing two C-3–C-4 linkages and one C-2–C-3 linkage.

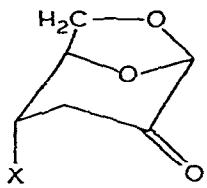
INTRODUCTION

Conversion of such cellulosic materials as waste paper and wood residues into chemical feedstock by pyrolytic methods has been the subject of extensive investigation in this laboratory[1–7]. The production of levoglucosenone (**1**, 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) by acid-catalyzed pyrolysis of waste paper has been developed into a practical laboratory synthesis[1], and many aspects of the chemistry of this multifunctional, reactive compound have been elucidated[1,4–7].

Facile, conjugate addition to the enone function of **1** occurs under base catalysis[1]. In the presence of triethylamine as catalyst, water, methanol, and benzenethiol add to **1**, to give the 1,6-anhydro-3-deoxy-β-D-hexopyranos-2-ulose derivatives **2–4**, respectively, in good yields. The D-*erythro* configuration of these products was assigned on the basis of chemical and n.m.r.-spectral evidence which showed that the substituent on C-4 was axial. By analogy, the primary products formed by conjugate addition of alkanethiols to bicyclo[3.2.1]oct-3-en-2-one, the carbocyclic analog of **1**, were shown to be the 4-*exo*(axial)-alkylthio derivatives, although, under basic conditions, these were rapidly equilibrated with the thermodynamically favored 4-*endo*-(equatorial) derivatives[8]. The carbohydrate products **2–4** must thus be formed in kinetically controlled reactions, with attack occurring exclusively at the *exo*-face of **1**; the *endo*-face is sterically hindered by the 1,6-anhydride bridge[1]. Subsequent equilibration of these products was not encountered.

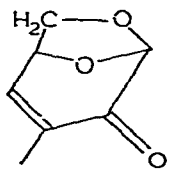


1



2 X = OH
3 X = OCH_3
4 X = SPh

5 X =



Preliminary attempts to use the same approach to add propan-2-ol and ethanol to **1** in aqueous media* revealed that a slower formation of the desired products (t.l.c. evidence) was accompanied by the precipitation of a yellow solid. Likewise, a yellow precipitate was observed in the preparation of **2** if the amount of Et_3N was increased, if the reaction time was extended, or if the temperature was raised. The reaction of **1** in aqueous Et_3N has now been investigated in further detail.

RESULTS AND DISCUSSION

In aqueous Et_3N at 80–85°, **1** was converted into three major products, namely, a dimer **5**, a non-olefinic trimer **6**, and an olefinic trimer **7**, together with a variety of minor, more-polar (t.l.c.) components. Product **7** precipitated from the solution as slightly impure, yellow needles (56%), and **5** and **6** were isolated from the filtrate by a combination of fractional crystallization and column chromatography in yields of 8 and 18%, respectively. Compounds **5** and **6** were also produced when **1** was heated with diethylamine in dry *N*,*N*-dimethylformamide, and were isolated in small yields (9 and 7%, respectively) by column chromatography.

Dimer **5** [*m/z* 252 ($M^{+\cdot}$, $C_{12}H_{12}O_6$)] contained both $\alpha\beta$-unsaturated and unconjugated carbonyl functionalities [λ_{max} 235 nm (ε 7,500), ν_{max} 1685 and 1730 cm^{-1}]. The structure of 1,6-anhydro-4-*C*-(1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulos-3-yl)-3,4-dideoxy-β-D-*erythro*-hexopyranos-2-ulose (**5**) was suggested by comparison of its ^{13}C-n.m.r. spectrum with those of **1**, **2**, and **4** (Table I). This revealed resonances typical of a 1,6-anhydrohex-3-enopyranos-2-ulose unit similar to **1**, but with the resonance for C-3 in **1** (126.5 p.p.m.) being shifted downfield to a singlet (137.1 p.p.m.) in **5**, indicating alkyl substitution at this position[9]. The bathochromic shift of the u.v. absorption maximum from 218 nm (ε 7,900) in **1**[1] to 235 nm (ε 7,500) in **5** is also consistent with α-substitution of the enone system[10]. Also present in the ^{13}C-n.m.r. spectrum of **5** were the resonances associated with a 1,6-anhydro-3-deoxyhexopyranos-2-ulose unit similar to **2** and **4**, but carrying a

*The addition of methanol to **1** surprisingly occurred more readily in 1:1 methanol–water than in absolute methanol.

TABLE I

^{13}C-N.M.R. DATA (p.p.m.) FOR THE 1,6-ANHYDRO-SUGAR DERIVATIVES[a]

Compound	*C-1*	*C-2*		*C-3*		*C-4*		*C-5*	*C-6*	*Solvent*
		Conj.	*Unconj.*	*Unsat.*	*Sat.*	*Unsat.*	*Sat.*			
1	102.3	189.8		126.5		150.7		72.7	67.2	$(CD_3)_2CO$
2	102.0		200.3		41.1		65.6	78.4	70.4	$(CD_3)_2CO$
4	102.3		198.6		38.3		49.3	76.5	68.1	$(CD_3)_2CO$
5	102.0 d	188.9 s		137.1 s		145.4 d		72.9 d	68.1 t	$(CD_3)_2CO$
	101.5 d		200.5 s		34.8 t		38.6 d	75.5 d	66.7 t	
6	100.8		202.4		36.9		42.4	73.9	67.0	$(CD_3)_2SO$
	97.8[b]		206.7[b]		37.9[b]		43.6[b]	74.4[b]	70.9[b]	

[a]See Experimental for ^{13}C-n.m.r. data for **7**. [b]Coincident signals for two carbon atoms.

TABLE II

^{1}H-N.M.R. DATA (270 MHz, $CDCl_3$) FOR DIMER **5**

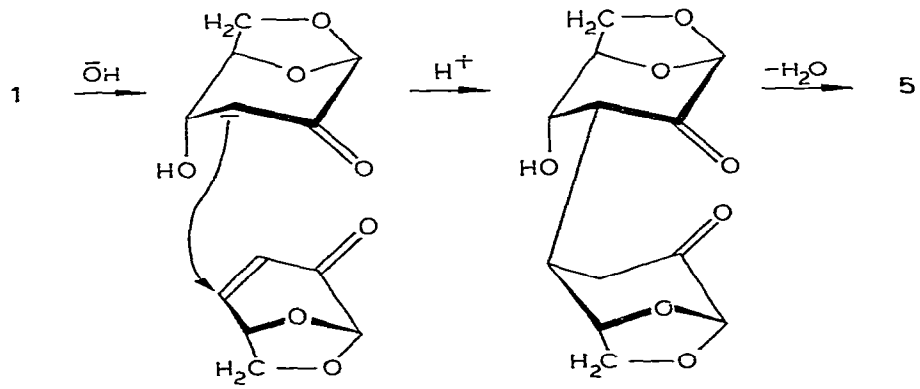
Assignment	*Chemical shift (δ)*	*Coupling constants (Hz)*
H-4′	7.08 d	$J_{4',5'}$ 5
H-1′	5.40 s	
H-1	5.11 s	
H-5′	5.06 dd	$J_{5',6'exo}$ 5.5
H-5	4.53 d	$J_{5,6exo}$ 5.5
H-6endo	4.15 d	$J_{6endo,6exo}$ 7.5
H-6exo	4.03 dd	
H-6′exo	3.89 dd	
H-6′endo	3.71 d	$J_{6'endo,6'exo}$ 6.5
H-4	3.43 d	$J_{4,5}$ small, $J_{3a,4}$ 9
H-3*a*	2.97 dd	$J_{3a,3e}$ 16
H-3*e*	2.23 d	$J_{3e,4}$ small

C–C-bonded substituent at C-4 (38.6 p.p.m.) rather than an oxygen (65.6 p.p.m. in **2**) or sulfur (49.3 p.p.m. in **4**) substituent at that position.

The ^{1}H-n.m.r. spectrum of **5** (Table II) was consistent with the assigned structure based on spectral data reported previously for **1**–**4** and related compounds[1,11]. Geminal coupling of 16 Hz permitted H-3*a* and H-3*e* to be discerned; these protons were coupled to H-4 ($J_{3a,4e}$ 9.0 Hz, and $J_{3e,4e}$ small). The *a,e*-assignment of this 9.0-Hz vicinal coupling contradicts the widely recognized rule that hexopyranose derivatives in chair conformations[12a], including 1,6-anhydrides[13], have $J_{a,e}$ in the range 2–6 Hz, and $J_{a,a}$ in the range 8–13 Hz. However, $J_{a,e}$ coupling in the range 5–9 Hz has been reported for bicyclo[3.2.1]octan-2-one derivatives[8,14,15] and their oxa[16,17] and dioxa analogs[1], which are related to **5**. In particular, the isomeric

4-phenylthiobicyclo[3.2.1]octan-2-ones were clearly differentiated by ^{1}H-n.m.r. spectroscopy[8], the 4-*exo*(axial) derivative having $J_{3,4}$ 7.0 (*a,e*) and 0.5 Hz (*e,e*), and the 4-*endo*(equatorial) derivative having $J_{3,4}$ 11.4 (*a,a*) and 6.8 Hz (*a,e*). Thus, the 9.0 Hz and small $J_{3,4}$ couplings in the ^{1}H-n.m.r. spectrum of **5** establish the axial nature of the substituent at C-4. Decreasing $J_{3a,4e}$ coupling in the series **5** (9.0 Hz), **4** (7 Hz), and **2** (5 Hz) is due to the increasing electronegativity of the atom bonded to C-4, *i.e.*, carbon, sulfur, and oxygen, respectively[12b].

A possible mechanism for the dimerization of **1** is shown in Scheme 1. Base-catalyzed hydration of **1** leads to the α-keto-stabilized carbanion of **2**, which can then attack the *exo*-face of **1**, in the stereospecific manner encountered in other addition reactions[1]. Subsequent dehydration leads to dimer **5**. T.l.c. of the initial reaction mixture showed the formation of the hydration product **2**.



Scheme 1

The mass spectrum of trimer **6** did not contain a molecular ion, but had a fragment ion at *m/z* 350 for $M^+ - CO$, where M is $C_{18}H_{18}O_9$. Compound **6** contained only saturated-ketone functionality (ν_{max} 1730 cm^{-1}), and its structure was determined on the basis of 360-MHz, ^{1}H-n.m.r. data (Table III) and ^{13}C-n.m.r. data (Table I). Resonances for three 1,6-anhydrohexopyranos-2-ulose residues with carbon-bearing substituents at positions 3 and 4 were observed in the ^{13}C-n.m.r. spectrum. Two of these residues had identical ^{13}C-chemical shifts, while the third was slightly different. The unsymmetrical nature of the trimer was also evidenced by three different singlets for anomeric protons. Initial, 100-MHz, spin–spin decoupling experiments confirmed that each C-3 (proton resonances at 2.7–3.7 p.p.m.) was linked directly to two C-4's (proton resonances at 1.4–2.5 p.p.m.). The stereochemistry around the central cyclohexane ring (*D*) of **6** was assigned on the basis of the six $J_{3,4}$ coupling constants; four of these are 12 Hz, consistent with *trans*-diaxial coupling. Only H-3*C* (3.66 p.p.m.) appeared to be equatorial, since its $J_{3,4}$ values of 6.1 and 4.3 Hz are both consistent with axial–equatorial coupling. There are two possible structures, both of which have five *trans*-diaxial protons and one H-3 in the equatorial position. One of these is **6** and the other is the same except for inversion

TABLE III

^{1}H-N.M.R. DATA [360 MHz, $(CD_3)_2SO$] FOR NON-OLEFINIC TRIMER **6**

Assignment[a]		*Chemical shift (δ)*	*Coupling constants (Hz) (based on assignment set 1)*
Set 1	*Set 2*		
H-1[b]		5.23 s	
H-1[b]		5.21 s	
H-1[b]		5.12 s	
H-5*A*	H-5*C*	4.99 dd	
H-5*B*		4.81 dd	$J_{5B,6Bexo}$ 3.3
H-5*C*	*H-5A*	4.64 dd	$J_{5C,6Cexo} \sim 3.5$, $J_{4C,5C}$ 3.0
H-6*A*endo	H-6*C*endo	4.25 d	$J_{6Aendo,6Aexo}$ 7.8
H-6*A*exo	H-6*C*exo	3.95 dd	$J_{5A,6Aexo}$ 5.3
H-6*B*endo		3.75 d	$J_{6Bendo,6Bexo}$ 6.6
H-3*C*		3.66 m	
H-6*B*exo		3.63 m	
H-6*C*endo	H-6*A*endo	3.52 d	$J_{6Cendo,6Cexo}$ 6.8
H-6*C*exo	H-6*A*exo	3.49 dd	
H-3*B*	H-3*A*	3.06 dd	$J_{3B,4B}$ 12.0, $J_{3B,4C}$ 12.0
H-3*A*	H-3*B*	2.76 dd	$J_{3A,4A}$ 12.0, $J_{3A,4B}$ 12.0
H-4*A*[c]	H-4*C*	2.46 ddd	$J_{3C,4A}$ 6.1, $J_{4A,5A}$ 1.6
H-4*B*		1.53 ddd	$J_{4B,5B}$ 2.8
H-4*C*	H-4*A*	1.43 ddd	$J_{3C,4C}$ 4.3

[a] *A*, *B*, and *C* refer to the pyranoid rings in formula **6**. [b] H-1*A*,1*B*,1*C* not specifically assigned. [c] Partially merged with solvent resonance.

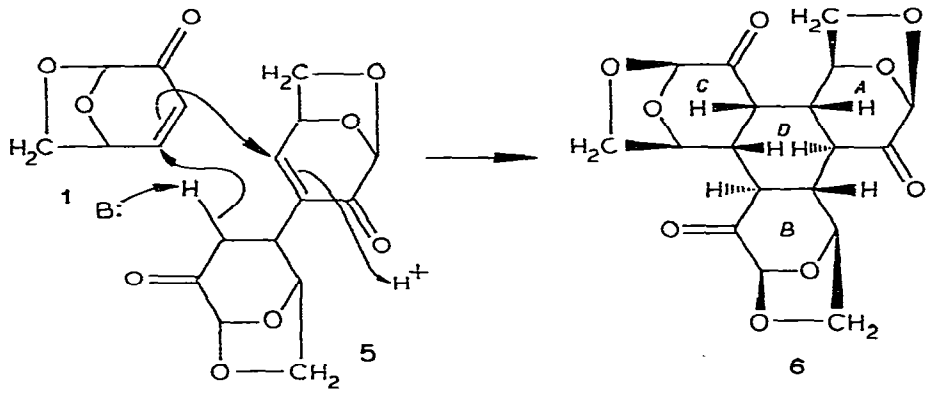
at all six of the carbons comprising ring *D*. Molecular models revealed severe steric problems with the latter model, which was thus eliminated. These models also showed that the structure shown for **6*** would have rings *A* and *B* in the boat form, and rings *C* and *D* in the chair form. Thus, residues *A* and *B* could account for the similar set of ^{13}C resonances, and residue *C* for the dissimilar set.

To fully interpret the ^{1}H-n.m.r. spectrum, complete, 360-MHz, spin–spin decoupling experiments were carried out. However, the cyclic nature of **6** made an unambiguous interpretation impossible, despite stereochemical knowledge of the structure. These experiments could not distinguish between assignment-sets 1 and 2 (Table III), which can be viewed as related to each other by a mirror plane passing through the unambiguously assigned H-3*C* and H-4*B*. All 360-MHz decoupling experiments were fully consistent with both interpretations.

A possible mechanism for the formation of **6** is shown in Scheme 2. It involves the overall condensation of three units of **1**, by way of dimer **5**, which, on formation of its α-keto-stabilized carbanion in basic medium, could undergo intermolecular condensation with **1** followed by intramolecular ring-closure to give **6**. These Michael additions are shown as one step for convenience and are similar to that postulated

*This structure has now been confirmed by X-ray crystallography. Details will be published later.

to occur in the dimerization of **1**→**5** (Scheme 1), and the formation of **2**–**4**, where each C-4 has an *exo*-substitution pattern. However, the C-3 substitution pattern of **6** is variable, indicating that the carbanion can attack either face of the ring or, alternatively, that epimerization occurs *via* keto-enol tautomerism, yielding the thermodynamically favored product.



Scheme 2

The olefinic trimer **7** has very low solubility in such volatile organic solvents as chloroform and acetone. This made t.l.c. difficult, but a minor impurity could be detected in the sample initially isolated. A purer sample of **7** was obtained (42%) by converting **1** into **2** under mild conditions (room temperature, 0.007 mol. equiv. of Et_3N), and subsequently completing the condensation at 75° with additional Et_3N.

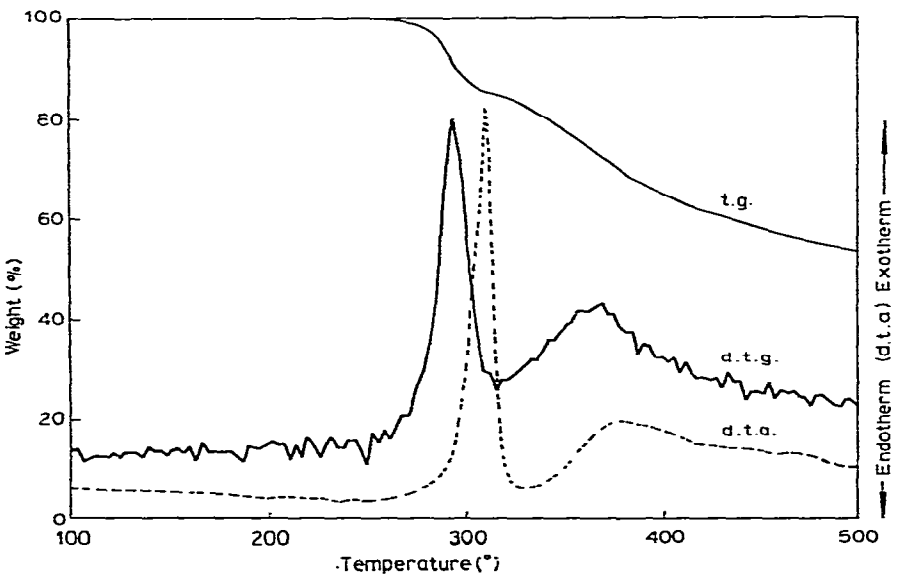


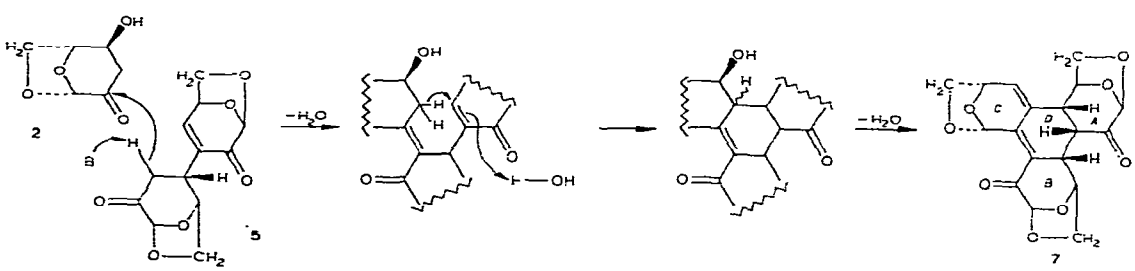
Fig. 1. Thermal gravimetry (t.g.), differential thermal gravimetry (d.t.g.), and differential thermal analysis (d.t.a.) of **7**.

Compound 7 decomposed at 290° without melting. Thermal analysis (Fig. 1) revealed a sharp exotherm peaking at 315°, associated with a rapid, 12% loss of weight. The residue then underwent gradual decomposition at higher temperatures. The thermal properties of this compound are quite different from those of other carbohydrates, which are generally dominated by endothermic transitions associated with cleavage at the glycosidic linkage to form volatile products[18]. These data show that the C–C-bonded units in this compound are not readily cleaved.

The molecular formula of 7 was established as $C_{18}H_{16}O_8$ (mol. wt. 360) on the basis of elemental analysis and molecular weight determination [357 by vapor pressure osmometry; *m/z* 360 ($M^{+\cdot}$, minor), 330 ($M^+ - CH_2O$, base peak)]. Thus, 7 must be formed from the condensation of three molecules of **1** with the overall loss of one molecule of water.

The structure shown for 7 was deduced primarily from the ^{13}C-n.m.r. data, the multiplicities of the signals being determined by off-resonance decoupling (see Experimental). Five distinct sets of resonances were observed: two ketonic carbons (2 s), four olefinic carbons (3 s, 1 d), three acetal carbons (3 d), six ether carbons (3 d, 3 t), and three sp^3-hybridized, unoxygenated carbons (3 d). I.r. absorptions at 1683 and 1746 cm^{-1} confirm that only one of the two carbonyl groups is conjugated. The u.v. absorption at 314 nm (ε 11,900) and the presence of only one olefinic-carbon doublet indicate a tetrasubstituted dienone group. The nine acetal and ether carbons correspond to C-1,5,6 of the three 1,6-anhydro-sugar units, and their chemical shifts are consistent with those found in related compounds (Table I).

The relative stereochemistry of the three adjacent, sp^3-hybridized, unoxygenated carbons, *C-3A*, *C-4A*, and *C-4B*, in 7 could not be determined from the proton–proton coupling data. For this reason, the X-ray crystallographic study described in the following paper was undertaken[19]. This study confirmed the postulated partial structure and determined that the three methine protons in question were all on the same side of the molecule, as shown for 7 in Scheme 3.



Scheme 3

The ^1H-n.m.r. spectral data for 7 are given in Table IV. The assignments were deduced from 360-MHz decoupling experiments. The sole olefinic proton is observed as a broadened doublet of doublets at 6.80 p.p.m., with vicinal (4.6 Hz) coupling, and four-bond (1.5 Hz) and six-bond (small) allylic coupling. The anomeric protons are singlets at 7.10, 5.21, and 5.04 p.p.m. The remarkable downfield shift (2 p.p.m.)

TABLE IV

^{1}H-N.M.R. DATA [360 MHz, $(CD_3)_2SO$] FOR OLEFINIC TRIMER 7

Assignment[a]	*Chemical shift (δ)*	*Coupling constants (Hz)*
H-1*C*	7.10 s	
H-4*C*	6.80 m[b]	$J_{4A,4C} \sim 1.5$, $J_{4B,4C}$ small
H-1[c]	5.21 s	
H-5*A*	5.19 dd	$J_{4A,5A}$ small
H-1[c]	5.04 s	
H-5*C*	5.00 dd	$J_{4C,5C}$ 4.6, $J_{5C,6Cexo}$ 4.5
H-5*B*	4.73 d	$J_{5B,6Bexo}$ 4.2
H-6*A*endo	4.27 d	$J_{6Aendo,6Aexo}$ 7.8
H-6*A*exo	3.95 dd	$J_{5A,6Aexo}$ 5.2
H-6*B*endo	3.81 d	$J_{6Bendo,6Bexo}$ 6.9
H-3*A*	3.71 dd	$J_{3A,4A}$ 6.9
H-6*C*exo	3.67 dd	
H-6*C*endo	3.63 d	$J_{6Cendo,6Cexo} \sim 7$
H-6*B*exo	3.60 dd	
H-4*A*	3.28 br d	
H-4*B*	2.63 d	$J_{3A,4B}$ 4.1

[a]*A*, *B*, and *C* refer to the pyranoid rings in formula 7. [b]Irradiation of H-4*B* causes this resonance to sharpen to a dd. [c]H-1*A*,1*B* not specifically assigned.

of H-1*C* at 7.10 p.p.m., compared with the expected ~5.2 p.p.m. value found for anomeric protons in related 1,6-anhydro derivatives[1], is considered to be due to its being both allylic and in the proximity of, and co-planar with, a γ-related carbonyl group. The latter, specific deshielding (the *peri*-effect) can cause[12c,20] downfield shifts of up to 1.8 p.p.m. The upfield shift for H-4*B* at 2.6 p.p.m., when compared with H-4*A* at 3.3 p.p.m., is believed to be caused by its proximity to the carbonyl group of residue *A* where the C-H bond lies in the shielding region of the C=O plane[21] with the hydrogen atom thrust away from the oxygen.

The formation of 7 from **1** in aqueous Et_3N (Scheme 3) is assumed to proceed by way of **5** and an aldol condensation with **2**, giving an intermediate that could undergo ring closure by a Michael addition to form the 6-membered, carbocyclic nucleus of 7. Elimination of water, extending the conjugation, completes the transformation.

The absolute stereochemistry at C-3*A*, C-4*A*, and C-4*B* in 7 is also compatible with this postulated mechanism. Center 4*B* has the geometry expected for it to have originated from C-4 in **5**. Also, centers 3*A* and 4*A* are consistent with the closure of the central cyclohexene ring (*D*) of 7 by Michael addition to the enone function of ring *A*; the carbanionic site on ring *C* has approached the sterically less-hindered face of ring *A* (*i.e.*, *exo* or opposite to the 1,6-anhydro bridge), and the proton has been added in a *trans*-diaxial manner at C-3*A*.

The oligomerizations of levoglucosenone (**1**) reported here represent a new reaction pathway for enones under basic conditions. Base-catalyzed reactions that

have previously been reported for monocyclic enones in the hexopyranose[22] and cyclohexane[23] series are initiated by abstraction of protons from carbons adjacent to the enone system. However, H-1 and H-5 of **1** are not acidic, because resonance stabilization of the associated anions is prevented by the bicyclic nature of the molecule.

EXPERIMENTAL

General. — Thermal analysis (t.g., d.t.g., and d.t.a.) was conducted[24] in loosely covered aluminum pans under nitrogen at 15°/min. Solvents used for chromatography were *A*, 3:2 ethyl acetate–1,2-dichlorethane; and *B*, 5:4:1 acetone–ethyl acetate–water. T.l.c. data was obtained as described previously[1]. The molecular weight determination was performed by ARRO laboratories (Joliet, Illinois, U.S.A.). Mass spectra were recorded on a Varian Mat III instrument at 80 eV. Compounds **1–4** had been prepared previously[1].

Base-catalyzed condensation of levoglucosenone (**1**). — (*a*) *In aqueous medium.* A solution of **1** (2.70 g) and Et_3N (0.02 ml) in water (175 ml) was kept for 24 h at room temperature. T.l.c. (solvent *A*) then indicated that **1** (R_F 0.55) had largely been converted into 1,6-anhydro-3-deoxy-β-D-*erythro*-hexopyranos-2-ulose (**2**, R_F 0.25). The solution was then heated to 75° and more Et_3N (1.0 ml) was added, causing the color of the solution to darken to orange. The olefinic trimer **7** precipitated within 15 min as yellow platelets (1.07 g, 42%) and was collected by filtration. Compound **7** decomposed without melting at 290°. Recrystallized from dimethyl sulfoxide–ethanol, it had $[\alpha]_D$ −383° (*c* 0.68, dimethyl sulfoxide); molecular weight (vapor pressure osmometry, *N*,*N*-dimethylformamide) 357; ν_{max}^{KBr}: 3465*, 2958, and 2886 (CH), 1796 (C=O sat.), 1683 (C=O conj.), 1609 (w), and 1576 cm^{-1} (C=C conj.); λ_{max} (95% EtOH): 314 nm (ε 11,900); mass spectrum (*m*/*z*): 360 ($M^{+}\cdot$, minor), 330 (M − CH_2O, base peak), 302 (M − CH_2O − CO), 285 (M − CH_2O − HCOO), 257, 243, and 229; ^{13}C-n.m.r. [$(CD_3)_2SO$, internal Me_4Si]: δ 200.5 s and 193.5 s (carbonyl), 145.5 s, 134.6 d, 129.7 s, and 122.0 s (olefinic), 102.3 d, 99.9 d, and 95.4 d (anomeric), 74.95 d, 74.89 d, 71.6 (superimposed d and t), 69.6 t, and 67.0 t (-CH_2O- and >CHO-), 45.3 d, 42.9 d, and 38.8 d (aliphatic**).

Anal. Calc. for $C_{18}H_{16}O_8$: C, 60.0; H, 4.5. Found: C, 60.1; H, 4.6.

In a second experiment, Et_3N (1.0 ml) was added to a solution of **1** (1.30 g) in warm water (30 ml), and the mixture was immediately heated at 80–85° for 15 min. Yellow needles (0.69 g, 56%) were rapidly formed, and were collected by filtration. T.l.c. (solvent *B*) showed this product to contain a small proportion of a non-u.v.-

*This band may be due to the enol tautomer of the unconjugated ketone. A small, ^{1}H-n.m.r. singlet (<0.3 H) at 8.3 p.p.m. was also present on a few occasions, supplying additional evidence for the formation of an enol.

**The 42.9 and 38.8 p.p.m. resonances occur in the region of the solvent resonances [$(CD_3)_2SO$], and were assigned as doublets on the basis of an experiment in which the fully decoupled spectrum was digitally substracted from the ORCW spectrum, thereby eliminating the solvent peaks.

absorbing component (R_F 0.45) in addition to **7** (R_F 0.60), and this could not be removed by recrystallization.

The filtrates remaining after removal of **7** were shown by t.l.c. (solvent *A*) to contain two main components, R_F 0.60 (u.v.-absorbing, brown) and 0.50 (non-u.v.-absorbing, blue). The filtrate from the second experiment was evaporated to dryness, and the residue was taken up in acetone, from which the non-olefinic trimer **6** soon separated as a white solid (0.11 g). Fractionation of the residual material by column chromatography on silica gel with ethyl acetate–light petroleum (1:4→1:2) yielded 1,6-anhydro-4-*C*-(1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulos-3-yl)-3,4-dideoxy-β-D-*erythro*-hexopyranos-2-ulose (**5**; 0.10 g, 8%) and **6** (0.12 g; total yield, 18%).

Recrystallization of **5** from ethyl acetate–light petroleum gave colorless plates, m.p. 170–172°, $[\alpha]_D$ −482° (*c* 0.3, acetone); ν_{max}^{KBr}: 1730 (C=O sat.) and 1685 cm^{-1} (C=O conj.); λ_{max} (95% EtOH): 235 nm (ε 7,500); mass spectrum (*m/z*): 252 ($M^{+\cdot}$, 5%), 224 ($M^+ - CO$), 207 ($M^+ - HCOO$), 206, 196 ($M^+ - CO - CO$), 195, 194, 179 ($M^+ - CO - HCOO$), 178, 177, 166, 160, 150, 149, 135, 121, and 105 (base peak).

Anal. Calc. for $C_{12}H_{12}O_6$: C, 57.1; H, 4.8. Found: C, 57.4; H, 4.9.

The trimer **6**, when recrystallized from ethyl acetate, had m.p. 324°, $[\alpha]_D$ −86° (*c* 0.46, *N*,*N*-dimethylformamide); ν_{max}^{KBr}: 1730 cm^{-1} (C=O sat.); mass spectrum (*m/z*): 350 ($M^{+\cdot} - CO$), 322, 304, 291, 276, 231, 230, 203, 202, 201, 157, 156, 149, 143, 141, 131, 129, 128, 117, 115, 105, 91, 77, 58, and 43 (base peak).

Anal. Calc. for $C_{18}H_{18}O_9$: C, 57.1; H, 4.8. Found: C, 57.4; H, 5.0.

(*b*) *In* N,N-*dimethylformamide*. Freshly distilled Et_2NH (5.0 ml) was added to a solution of **1** (0.5 g) in *N*,*N*-dimethylformamide (10 ml, dry), and the solution was heated under reflux for 14 h. The solvent was then evaporated at 40° (0.3 Torr) and the residue was fractionated by column chromatography on silica gel with 1:2 ethyl acetate–light petroleum, to give crystalline samples of dimer **5** (45 mg, 9%) and trimer **6** (35 mg, 7%).

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