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SOME REACTIONS OF LEVOGLUCOSENONE

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ABSTRACT

The role of the major variables in the pyrolytic production of levoglucosenone from acid-treated cellulose and paper has been established Reduction, oxidation, acid- and base-catalyzed addition, acetolysis, and rearrangement reactions of this product have been investigated These reactions proceed with considerable stereoselectivity to give a variety of novel compounds Nucleophilic addition to the double bond provides a facile method for the synthesis of 4-thio and other 4-substituted sugar derivatives

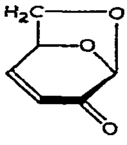
INTRODUCTION

The tremendous amount of municipal, and industrial, solid waste in this country contains mainly containers, newsprint, wrappings, disposable items, and other materials produced from pulp and paper[1] This colossal waste challenges the ingenuity of carbohydrate chemists to find a better method for management of natural resources Development of the thermal, catalytic, and hydrocracking processes by petroleum chemists[2] provides a lead for utilization of these and other wasted cellulosic materials

This article indicates some of the technical possibilities for catalytic pyrolysis of cellulosic materials to levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **1**), which can be converted into a variety of potentially useful compounds Production of these compounds from **1** involves interesting reactions, including selective reduction, addition to the double bond and the carbonyl group, and ring contraction and opening

RESULTS AND DISCUSSION

Pyrolytic production of levoglucosenone (**1**) — Pyrolysis of cellulose involves a complex series of concurrent and consecutive reactions that provide a variety of products discussed in previous reports from this laboratory[3–11] Among these products, levoglucosenone (**1**) and 1,4 3,6-dianhydro-α-D-glucopyranose (**2**) are formed by a combination of transglycosylation and dehydration reactions of the



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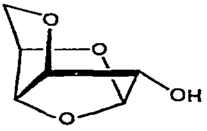

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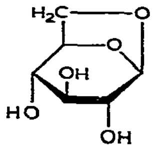

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TABLE I

PYROLYTIC PRODUCTION OF LEVOGLUCOSENONE (1), 1,4 3,6-DIANHYDRO-α-D-GLUCOPYRANOSE (2), AND LEVOGLUCOSAN (3)

Substrate	*H_3PO_4 (%)*	*Sample weight (g)*	*Oven temp (°C)*	*Pressure (torr)*	*Percent yield from substrate*				
					Char	*Tar*	**1**	**2**	**3**
Effect of pressure									
Cellulose	1 5	1	340	760	39	15	7	1 2	0 5
	1 5			1 5	42	14	4	0 7	4 5
	1			150	45	16	6	0 8	
	5			1 5	44	5	1 7	0 2	
Effect of oven temperature									
	1	1	275	760	52	8	4	0 4	
			300		47	11	7	0 6	
			325		43	13	8	0 8	
			350		42	14	7	0 6	
			400		35	20	8	1 1	
			425		32	19	6	1 1	
Effect of acid concentration									
	0 5	1	360	760	36	26	7	0 8	
	1				38	20	8	0 8	
	5				43	10	5	0 3	
	10				45	9	2 5	0 1	
Effect of scale									
	5	0 005	350	760	—	—	11 1	—	
	1	1	350		41	16	8	0 8	
	1	10	~370		35	14	2 2	1 0	
	1	20	~370		37	11	2 0	0 7	
	1	50	~370		38	10	2 0	0 8	
Production from paper									
Kraft paper	1 7	0 5	345	760	43	21	6	0 9	
	2 9	0 5			45	15	6	0 7	
	5 6	0 5			46	11	5	0 4	

D-glucosyl residues in cellulose, and are partly converted into other products, or charred by ensuing reactions[4–6] In order to obtain optimal yields, it is necessary to determine the conditions that promote the desirable reactions and minimize degradation of the product

High yields of levoglucosan (1,6-anhydro-β-D-glucopyranose, **3**) are obtained on vacuum pyrolysis at 300–500° in the absence of any catalyst[7]. Under these conditions, transglycosylation reactions dominate over dehydration and fission reactions, and rapid evaporation and removal of levoglucosan and other anhydro sugars limit their further conversion into oligosaccharides, or decomposition to other volatile compounds and char. However, the presence of an acid catalyst promotes the dehydration and charring reactions that produce **1**, other unsaturated compounds, and char, at the expense of **3** and related, transglycosylation products[11]. The effects of pressure, temperature, acid concentration, and the scale of production, which are conceived as the principle variables in the production of **1**, have been investigated and are summarized in Table I.

These data indicate that better yields of **1** are obtained on acid-catalyzed pyrolysis at atmospheric pressure, in contrast to the production of **3**, which is enhanced under vacuum. The pressure, however, has little or no effect on the total amount of tar and char, so that the increased production of **1** under atmospheric conditions is at the expense of **3**. Moreover, it is seen that increasing the acid concentration from 1.5 to 5% further decreases the yield of **1** on vacuum pyrolysis, and that the use of an intermediate vacuum (150 torr) is of no advantage. Thus, the rest of the pyrolysis experiments were conducted at atmospheric pressure, which is preferred over vacuum for the production of **1**.

Increasing the oven temperature from 300 to 400° decreases the yield of char and increases the yield of tar and of **2**, but has little effect on the yield of **1**, which is consistently within the range of 7 to 8%. Thus, it appears that, at higher temperatures, any increased synthesis of **1** is offset by its increased degradation and conversion into char and other tar components. The acid-catalyzed pyrolysis and evaporation of the volatile products is highly endothermic. Therefore, increased oven temperature, as noted before[7,8], seems to increase the rate of heat transfer rather than the temperature of the reacting substrate. It was noted that the pyrolysis of small samples at temperatures above 300° was always complete within 10 min, therefore, the exact pyrolysis time was not determined.

It has already been shown[4,11] that Arrhenius acids are preferable as catalysts, because such Lewis acids as zinc chloride could enhance further decomposition and charring of levoglucosenone (**1**). In these experiments, phosphoric acid was used as a standard catalyst, because of its lower volatility than that of sulfuric acid or hydrochloric acid. Increasing the phosphoric acid concentration from 0.5 to 10% by weight results in increased formation of char and decreased yields of tar. Better yields (7–8%) of **1** are obtained with acid concentrations of 0.5–1%, whereas pyrolysis in the presence of 10% of acid provides only a 2.5% yield. An intermediate concentration of acid (~5%) was found to be advantageous, because of the high concentration of **1** in the tar fraction.

As noted before[7,8], heat transfer is an important factor in pyrolysis experiments. In previous experiments[4] using 5-mg samples, ~11% yields of **1** were recorded by direct pyrolysis–g.l.c. methods. In this study, the yields obtained from 1-g samples

TABLE II

RELATIVE PROPORTIONS OF LEVOGLUCOSENONE (**1**), 2-FURALDEHYDE, 1,4 3,6-DIANHYDRO-α-D-GLUCOPYRANOSE (**2**), AND 5-(HYDROXYMETHYL)-2-FURALDEHYDE (**4**) IN PYROLYSIS TARS

Substrate[a]	H_3PO_4 (%)	*G l c peak area ratio*			
		1	*2-Furaldehyde*	**2**	**4**
Cellulose	2	100	12	9	4
Kraft paper	2 0	100	23	7	4
Newsprint	3 2	100	20[b]	8	3

[a]Pyrolysis of 0 5-g samples at 350° and 1 atm [b]Includes area for a minor component incompletely separated from 2-furaldehyde

in a 1 5-cm diameter tube-furnace were $\sim$8%, and samples of 10–50 g in a 4 5-cm tube-furnace gave much lower yields, $\sim$2%. The inverse relationship between the yield and sample size is apparently due to the poor heat-transfer in the substrate, resulting in more pyrolysis at lower temperatures, where the charring reaction dominates

These data indicate that high yields of levoglucosenone (**1**) could be obtained through the application of fluidized-bed and other engineering technology for handling the problems of heat transfer. For the laboratory-scale preparation of **1**, however, the simplicity and low cost of batch operation compensates for lower yields The foregoing experiments with pure cellulose indicated the optimum pyrolytic conditions, but, for both industrial and laboratory preparation, waste paper is the preferred substrate, because it is readily available and easily processed

Paper products in general contain some hemicelluloses, lignin, and sizing and other additives, in addition to cellulose, which forms the bulk of the fibrous material G l c analysis of the pyrolyzates obtained from Kraft paper, newsprint, and pure cellulose (see Table II) showed only minor differences in the relative proportions of **1** and the minor products, **2** and 5-(hydroxymethyl)-2-furaldehyde (**4**), in the tar There is, however, an increased proportion of 2-furaldehyde in the tar from the paper substrates, which apparently originates from the hemicellulose component of the paper. The pyrolyzate from white paper and newsprint contained a wax-like or oily substance that could have originated from the sizing materials

Despite the complexity of Kraft paper as a pyrolytic substrate, this material treated with 1 7–5 6% of phosphoric acid gave 5–6% yields of **1**. Based on these data, the following method, which constitutes an improvement over the previously described preparation[4], was developed for laboratory production of **1** from waste paper (including newsprint, or Kraft or white paper)

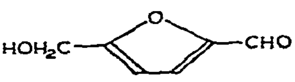
A large quantity of the substrate was readily prepared by soaking shredded waste-paper in aqueous phosphoric acid solution and air-drying The desired concentration of acid in the substrate (determined by pH titration) was obtained by adjusting the concentration of the aqueous acid Soaking of newsprint in 1% phosphoric acid gave a substrate containing 3 2% of phosphoric acid, this was pyrolyzed in 20-g batches. Extraction of a chloroform solution of the accumulated pyrolyzate with aqueous sodium hydrogencarbonate removed acidic and water-soluble impurities which were found to cause degradation of **1** in an attempted, direct distillation of the tar The largely hydrocarbon component, which is presumably derived from the sizing in the paper, was found to co-distil with **1** Therefore, the extracted pyrolyzate was dissolved in methanol–water, and the impurity was removed by precipitation (product from white paper) or by extraction with light petroleum ether (product from newsprint) Fractional, vacuum distillation of the rest gave complete separation of **1** from 2-furaldehyde, thereby avoiding the use of dimedone to remove aldehydic impurities by precipitation[4]

The levoglucosenone fraction, obtained in ~2% yield from waste paper, was ~90–95% pure, and contained 2-furyl hydroxymethyl ketone (**5**) as the major impurity This product was suitable for most synthetic preparations, although further purification was achieved by column chromatography, which provided **5** as a crystalline compound in 0 02% yield Compound **5** has previously been found in pyrolyzates from untreated cellulose[12], and is known as a product of the acid-catalyzed degradation of hexoses in aqueous solution[13]

Acid- and base-catalyzed reactions of levoglucosenone (**1**) — There are three reactive functional groups in **1** the carbon–carbon double bond, the ketone group, and the glycosidic anhydro linkage Each of these groups can react selectively, depending on the conditions employed

When **1** was heated in aqueous mineral acid, 5-(hydroxymethyl)-2-furaldehyde (**4**) was produced The anticipated hydrolysis of the 1,6-anhydro linkage in **1** to give 3,4-dideoxy-D-*glycero*-hex-3-enopyranos-2-ulose (**6**) accounts for the appearance of **4**, as **6** has been shown[14] to be an intermediate in the acid-catalyzed dehydration of hexoses to **4** The reaction gave an apparent "intermediate" compound that was detected by t l c as a green spot, and heating of **1** in aqueous acetic acid gave the same compound as the sole product, in equilibrium with **1** This compound was isolated in 77% yield, and was shown to be 1,6-anhydro-3-deoxy-β-D-*erythro*-hexopyranos-2-ulose (**7**), produced by addition of water to the double bond, instead of hydrolysis of the anhydro linkage

Compound **7** was readily separated from unreacted **1** by extraction of the latter into chloroform The high solubility of **7** in water is due to hydration of the ketone group to form the *gem*-diol **12**, as demonstrated by n m r spectroscopy On gradual addition of D_2O to a solution of **7** in $(CD_3)_2CO$, the resonances for **7** were gradually replaced by those of **12** (see Table III) In D_2O solution, **12** and **7** formed an ~5 1 equilibrium mixture, as estimated from the ratio of their H-1 singlets



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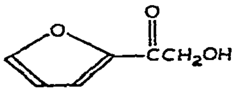

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TABLE III

^{1}H-N M R PARAMETERS (δ AT 60 MHz) FOR ADDITION PRODUCTS OF LEVOGLUCOSENONE (1)

Compound	*Solvent*	*H-1*	*H-3a*	*H-3e*	*H-4*	*H-5*	*H-6*$_{exo}$	*H-6*$_{endo}$	*Other*	$J_{3a,3e}$	$J_{3a,4}$	$J_{3e,4}$
7	$CDCl_3$	5 15s[a]	2 93dd	2 43dm	~4 2m	4 72m	--- 4 0m ---		4 2(b),OH	17	5	small
9	$CDCl_3$	5 18s[b]	2 86dd	2 53dm	3 80m	4 87m	--- 4 0m ---		3 48s,OMe	17 5	5	2
10	$CDCl_3$	5 17s	3 03dd	2 48dm	3 73m	4 68m	--- 4 0m --		7 3–7 7m,Ph	17	7	small
11	$(CD_3)_2SO$	5 20s	3 32dd	2,43dm	3 72dm	4 83m[c]	3 93dd[c]	4 23dd[c]		17	7	small
12	D_2O	5 17s	--- 2 05m ---		3 7–4 2m	4 67m	- - 3 7–4 2m ---					
13	D_2O	5 10s	--- 2 05m ---		3 56m	4 80m	- - 3 9m ---		3,44s,OMe			
14	$CDCl_3$	5 39d[d]	1,77dd	2 30dq	~3 4[e]	4 71m	--- 3 8m ---		3,48, 3 36, 3,31, 3 s, OMe	15	5	3,5

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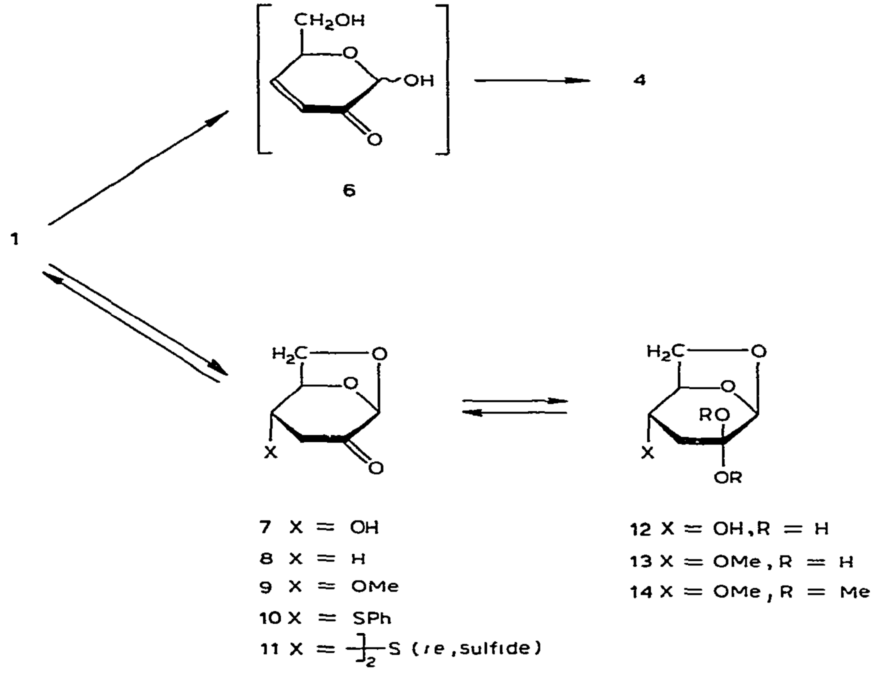
[a] δ 5 30s in D_2O [b] δ 5 25s in D_2O. [c] $J_{5,6endo}$ ~1 5, $J_{5,6exo}$ ~5 5, and $J_{6endo,6exo}$ ~8 5 Hz [d] $J_{1,3e}$ ~1 5 Hz [e] Obscured by methoxyl resonances.

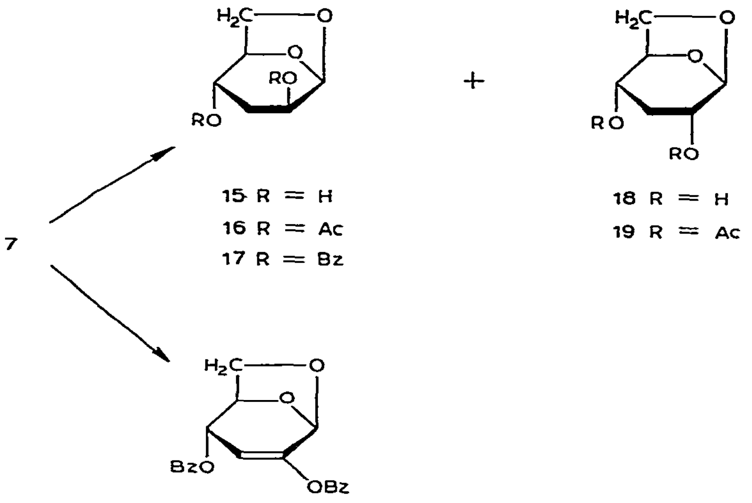


Hydration of 7 is also reflected in the marked difference between the specific rotation of a carefully dried sample in chloroform (—255°) and in aqueous solution (—143°) Compound **8**, the 4-deoxy analog of **7**, also forms a hydrate[15], and it has a much larger, negative specific rotation in aprotic solvents than in water Hydrogen bonding between the 2-hydroxyl groups and the two ring-oxygen atoms has been postulated as the reason for the facile hydration of the 1,6-anhydro-hexos-2-ulose structure

The structure of **7**, in particular the stereochemistry at C-4, was confirmed by reduction with sodium borohydride, which yielded 1,6-anhydro-3-deoxy-β-D-*arabino*-hexopyranose (**15**) as the major product, characterized as its known diacetate (**16**) and dibenzoate (**17**) A small proportion of the D-*ribo* isomer **18** was also produced in the reduction Chromatographic fractionation of the crude, acetylated, reduction product yielded the crystalline, isomeric D-*arabino* and D-*ribo* diacetates **16** and **19**, in 71 and 15% yield, respectively

Attempts to benzoylate the 4-hydroxyl group of **7** with benzoyl chloride in pyridine resulted in sequential enolization and benzoylation of the 2-ketone group, yielding 1,6-anhydro-2,4-di-*O*-benzoyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (**20**) This compound was characterized by elemental analysis, and its n m r spectrum, which revealed resonances for two benzoate groups, and an olefinic proton (H-3) having long-range coupling to H-1 and H-5.

Acid-catalyzed addition of methanol to the 3,4 double bond in **1** by use of methanolic hydrogen chloride initially produced the 4-*O*-methyl-2-ulose **9**, which was rapidly converted into its dimethyl acetal (**14**) in almost quantitative yield The



15 R = H
16 R = Ac
17 R = Bz

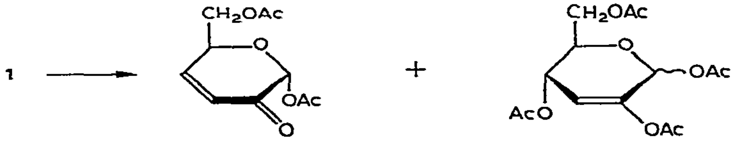
18 R = H
19 R = Ac

20

mass-spectral fragmentation-pattern of **14** appeared to be very similar to those reported for other permethylated, anhydro sugars[16]. There was no molecular ion, but fragment ions formed from it by the loss of CH_3 , CH_3O , CH_3OH, and HCOO were present

Hydrolysis of **14** under acidic conditions regenerated **9**, which was isolated in 56% yield by chromatographic fractionation, along with unchanged **14** (20%), and **1** (3%) The 4-*O*-methyl-2-ulose **9** displayed properties similar to those of its 4-hydroxy analog **7** It had a much higher specific rotation in chloroform (—214°, carefully dried sample) than in water (—130°), and n m r spectroscopy (see Table III) showed that, in D_2O solution, it formed an ~5 1 equilibrium mixture of hydrate **13** and **9**.

The 1,6-anhydro ring of **1** was cleaved under acetolyzing conditions using boron trifluoride diethyl etherate as the catalyst, this reaction gave the diacetate **21** as the major product Anomeric tetraacetates **22** and **23** were formed in lesser proportions by further acetylation of the enone function Fractionation of the reaction mixture by liquid chromatography gave small quantities of **21** and a mixture of **22** and **23** Presence of the enone function in **21** was confirmed by characteristic u v (λ_{max} 223 nm, ε_{mM} ~10 00) and i r (1707 and 1635 cm^{-1}) spectral data The small value of $J_{4\ 5}$ (~1 5 Hz) in the n m r spectrum of **21** indicated the α stereochemistry at C-1, because studies with related hex-3-enopyranos-2-uloses[17], have shown that



21 22 (α) + 23 (β)

$J_{4,5}$ is characteristically smaller for α anomers (~2 Hz) than for β anomers (~3 0–3 5 Hz), as they adopt different conformations The β anomer of **21** could not be detected by n m r spectroscopy, although at least a small proportion of it would be expected in the reaction product

Addition reactions of the 3,4 double bond in **1** were also catalyzed by base In the presence of a small proportion of triethylamine, **7** and **9** were the sole products from the reaction of **1** in water, and anhydrous methanol, respectively Interestingly, base-catalyzed addition of methanol proceeded faster in aqueous than in dry methanol, without competitive addition of water, demonstrating the greater methoxide nucleophilicity of this system

Sulfur nucleophiles also add to **1** under basic conditions Benzenethiol in chloroform containing triethylamine reacted rapidly with **1**, to yield the crystalline 4-*S*-phenyl compound **10**, isolated in 85% yield In an attempt to prepare the parent 4-thio sugar, hydrogen sulfide was passed into a solution of **1** and triethylamine in chloroform The main product was, however, the symmetrical sulfide **11** (containing two sugar units), which crystallized directly from the reaction mixture in 42% yield Evidently, the 4-thio sugar initially produced adds rapidly to another unit of **1** to yield **11**

As expected for nucleophilic addition to the carbonyl group of an α,β-unsaturated ketone, regiospecific attack occurs at the β-carbon atom In addition, the 1,6-anhydro bridge must provide sufficient steric hindrance that reagents tend to approach from "below" the plane of the pyranose ring, to produce 3-deoxy-4-*C*-substituted compounds having the D-*erythro* configuration Adducts having the alternative, D-*threo* configuration were not detected

Reduction of levoglucosenone (**1**) — It has already been shown that the double bond and ketone group of levoglucosenone can be reduced selectively[4 18 19] Reduction of the ketone group with sodium borohydride ($NaBH_4$) or lithium aluminum hydride ($LiAlH_4$) gives the allylic alcohol **24** as the major product In a previous study made in this laboratory, this compound was obtained as a syrup by reduction of **1** with $LiAlH_4$ and was assigned the D-*erythro* configuration, based on the absence of spin–spin coupling between H-1 and H-2 in the n m r spectrum In this study, the major product from the reduction of **1**, both with $LiAlH_4$ and with $NaBH_4$, was isolated as a crystalline compound that gave the coupling constants $J_{1,2} \simeq J_{1,3} = \sim J_{2,3} = \sim 2$ Hz reported[18 20] for the D-*threo* isomer **24** This product gave a 3,5-dinitrobenzoyl derivative (**25**) that was the same as that previously obtained in this laboratory, and its structure was confirmed by sequential hydrolysis and reduction, with $NaBH_4$, providing the known[21] crystalline compound (*Z*)-3,4-dideoxy-D-*threo*-hex-3-enitol (**31**) The D-*erythro* compound **27** was synthesized from its isomer **24** as discussed later

Reduction of **1** with $NaBH_4$ also produced small proportions of the D-*erythro* allylic alcohol **27**, the saturated D-*threo* alcohol **29**, and an unidentified component (possibly the D-*erythro* isomer of **29**) Reduction of conjugated ketones frequently leads to saturated alcohol products[22 23], evidently through 1,4- followed by 1,2-

TABLE IV

PRODUCT FROM REDUCTION OF LEVOGLUCOSENONE (**1**)

Reducing agent	*Solvent*	*Relative, g.l.c. peak-areas (%)*[a]			
		24	**27**	**29**	*Unidentified*
$NaBH_4$	H_2O	95	2	3	trace
	1:1 EtOH–H_2O	84	4	11	1
	EtOH	67	4	26	3
$LiAlH_4$[b]	Et_2O	87	4	1	trace

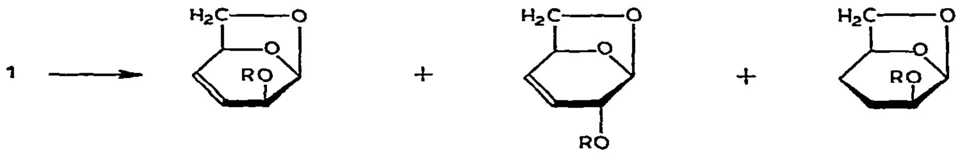
[a]Retention times 17.8 (**24**), 20.7 (**27**), 20.3 (**29**), and 19.0 min (unidentified, possibly the C-2 epimer of **29**). [b]Product mixture contains an additional component, at 13.1 min (8%).

reduction of the enone function, this mechanism also accounts for the production of **29**. The results summarized in Table IV show the influence of solvent on the course of these reactions. In water, 1,2-reduction predominated, and **24** was formed in 95% yield. In aqueous ethanol, 1,4-reduction became more competitive, and, in absolute ethanol, a 2.5:1 ratio of **24** to **29** was obtained. Such a solvent effect does not appear to have been observed before. Thus, for production of **24** from **1**, reduction with $NaBH_4$ in water is preferred, whereas reduction in ethanol gives the highest yield of **29** as the secondary product. Reduction with $LiAlH_4$ provides, in addition to small proportions of **27** and **29**, another compound, in ~8% yield, that, as reported previously[4], does not form a trimethylsilyl derivative, indicating the absence of a hydroxyl group.

The use of pyridine or bis(2-methoxyethyl) ether as the solvent in the reduction of enones with $NaBH_4$ has been reported[23] to favor 1,4-reduction. Therefore, attempts were made to employ these conditions for the production of **29** from **1**. Although low yields of **24** and **29** were obtained, the majority of **1** was converted into an unidentified mixture of water-soluble products; this approach was therefore abandoned in favor of chromatographic fractionation of the product formed by reduction of **1** with $NaBH_4$ in aqueous ethanol, which yielded a syrupy mixture (~15:1) of **29** and the unidentified component (see Table IV). This mixture provided a crystalline 3,5-dinitrobenzoate (**30**), identical with a compound prepared previously[4] from **1** through hydrogenation over Pd–$BaSO_4$ followed by reduction with $LiAlH_4$ (**1**→**8**→**29**), or *vice versa* (**1**→**24**→**29**). The latter reaction determined that the stereochemistry of **29** is D-*threo*, as in the allylic alcohol **24**, not D-*erythro*.

Reduction of the ketone groups of **1**, **7**, and **8** is subject to a stereochemical control similar to that observed for addition to the double bond in **1**. The 1,6-anhydro bridge hinders the approach of reagents from "above" the plane of the pyranose ring; consequently, D-*erythro* compounds are formed in addition reactions, and D-*threo* compounds are favored in the reduction.

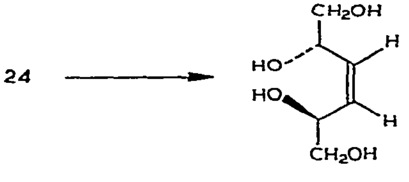
Reactions of the allylic alcohol derivative (**24**). — A synthesis of the D-*erythro* allylic alcohol **27** was undertaken so that its presence in the reduction products of **1**



24 R = H
25 R = 3,5-dinitrobenzoyl
26 R = Ts

27 R = H
28 R = Bz

29 R = H
30 R = 3,5-dinitrobenzoyl



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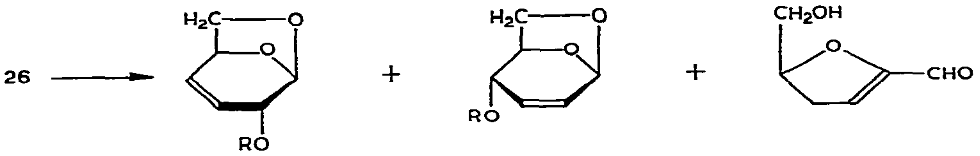
could be confirmed. The simplest route appeared to be inversion of the stereochemistry at C-2 of **24**, involving tosylation (to give **26**), displacement of the tosyloxy group by using sodium benzoate in *N*,*N*-dimethylformamide (to give **28**), and debenzoylation of **28** to afford **27**. This approach gave a reaction mixture which, on separation by column chromatography, gave the expected product **27** in 24% yield, along with the known compound 1,6-anhydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranose (**32**, 22% yield) and a low-melting, crystalline aldehyde considered to be (5*S*)-4,5-dihydro-5-(hydroxymethyl)-2-furaldehyde (**34**, 10% yield). The structure of **34** was assigned on the basis of its n.m.r. spectrum, which included a singlet for an aldehydic proton (δ 9.13), and a triplet for a vinylic proton (δ 5.87) coupled to an adjacent methylene group, and its u.v. (λ_{max} 257 nm, ε_{mM} 8.40) and i.r. (ν_{max} 1690 and 1640 cm^{-1}) data, which indicated an α,β-unsaturated aldehyde.

Production of **32** instead of its C-4 epimer indicated that **26** reacts partly by dissociation to an allylic carbonium ion, which is attacked, at either C-2 or C-4, by benzoate anion, from the side unhindered by the anhydro bridge.

To determine the origin of **34**, the displacement reaction was repeated, and the products were subjected to chromatographic fractionation prior to debenzoylation. In addition to the expected benzoate **33**, (1*R*)-2-(benzoyloxy)-3,8-dioxabicyclo-[3.2.1]oct-6-ene (**35**) was isolated as a crystalline material, and characterized by elemental analysis and n.m.r. spectroscopy. Compound **35** is evidently a ring-contraction product, formed as shown by the proposed mechanism. Similar ring-contractions have been observed in the deamination of 2-amino-2-deoxy-pyranosides where the ring-oxygen atom and the leaving groups are antiperiplanar[24], as is the case in **26**. The small values $J_{1,2} \sim 1$, $J_{4,5} \sim 2$, and $J_{4,5} < 1$ Hz in the n.m.r. spectrum of **35** are consistent with adoption of a chair conformation by the dioxane ring, but do not allow definite assignment of the stereochemistry at C-2.

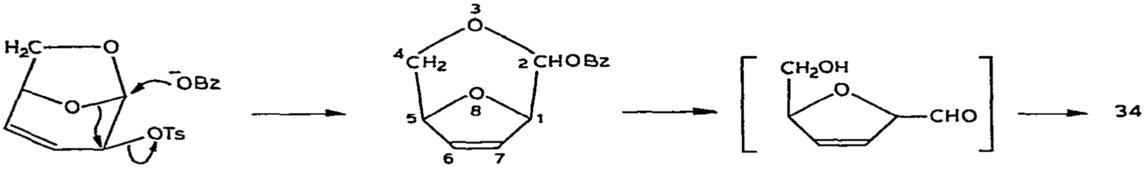
Conversion of **35** into **34** in methanol containing a catalytic amount of sodium methoxide indicated the mechanism for production of the unusual compound **34**



27 R = H
28 R = Bz

32 R = H
33 R = Bz

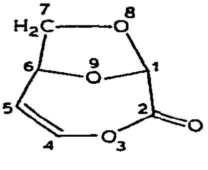
34



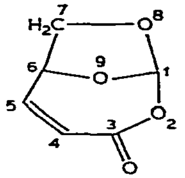
26

35

36



37a



37 b

This mechanism involves conventional debenzoylation to produce the corresponding bicyclic hemiacetal, which is converted into the unconjugated aldehyde **36**, this is isomerized under the basic conditions to the conjugated aldehyde **34**

Oxidation of levoglucosenone (**1**). — Treatment of **1** ($C_6H_6O_3$) with *m*-chloroperoxybenzoic acid in dichloromethane yielded the syrupy oxidation product **37** ($C_6H_6O_4$) in 37% yield Such reaction conditions can, in principle, result either in Baeyer–Villiger oxidation, where an oxygen atom is inserted on either side of the ketone group, or in epoxidation of the double bond[25]. The presence of vinylic protons (δ 6 34 and 7 15) in the n m r. spectrum of **37** shows that epoxidation had not occurred The alternative structures for **37** are thus the enol-lactone **37a** and the α,β-unsaturated lactone **37b** Most frequently, such oxidation reactions have led to enol-lactones as the primary products[25]

At this stage, it is not possible to differentiate between the two alternatives on the basis of n m r -, i r -, and u v.-spectral data, because of the unusual conformations available for this unsaturated, trioxabicyclo[4 2 1]nonane system The H-1 singlet (δ 8 17) in the n m r spectrum of **37** is surprisingly deshielded relative to the C-2 protons in the model compounds 2-(methoxycarbonyl)-1,3-dioxolane (δ 5 22)[26] and 2-acetoxy-1,3-dioxolane (δ 6 80)[27] The u v - and i r -spectral maxima of the conjugated lactone **37b** might be predicted to occur at wavelengths longer than those of **37a** However, inspection of molecular models showed that the enone function in **37b** cannot attain planarity, and, hence, conjugation would be restricted

The aforementioned, bicyclic, seven-membered-ring lactone, and the other anhydro, deoxy, keto, thio, unsaturated, and furan compounds discussed in this article, indicate the wide range of interesting, and potentially useful chemical compounds that could be produced through catalytic pyrolysis of paper products which constitute the major component of industrial and municipal solid waste in this country

EXPERIMENTAL

General methods — The following solvents were used for chromatography *A*, 3 2 dichloroethane–ethyl acetate, *B*, 8 2 1 dichloroethane–ethyl acetate–methanol, *C*, *D*, *E*, and *F*, 1 4, 1 3, 1 2, and 1 1 ethyl acetate–light petroleum ether, *G* and *H*, 1 1 and 1 2 tetrahydrofuran–light petroleum ether, *I*, 1 3 tetrahydrofuran–2,2,4-trimethylpentane, and *J*, 5 4 1 acetone–ethyl acetate–water Acetonitrile (1–2%) was added to solvents used for column chromatography T l c was performed on Baker-flex silica gel IB2-F, carbohydrates were detected by using a 3 5 95 anisaldehyde–sulfuric acid–ethanol spray-reagent and heating at 120° N m r spectra were recorded with a Varian EM 360 60-MHz instrument with tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the internal standard, and were interpreted with the aid of spin–spin decoupling experiments Pyrolysis and g l c analysis of the tarry products was conducted as previously described[5] Other g l c analyses were performed on a nickel column [2 m × 2 2 mm (i d)] packed with 5% of Carbowax 20M (TPA) on 80–100 mesh Gas-Chrom Q Unless otherwise noted, optical rotations were measured in chloroform and within the concentration range of 0 4–1 8 g/100 ml of solution

Acid–substrate mixtures — For analytical studies of pyrolysis, cellulosic substrates containing known proportions of phosphoric acid were prepared as a slurry in methanol, and the solvent was evaporated *in vacuo* at 50° Paper samples were first ground to <20 mesh in a Wiley mill For preparative pyrolysis, paper was shredded into 0 5-cm strips, and soaked in an aqueous solution of phosphoric acid The paper was then squeezed to remove the excess of the solution, and spread out to air-dry

The concentration of phosphoric acid remaining in the paper could be determined by pH titration A convenient procedure involved grinding of acid-treated paper in a Wiley mill, suspending 1 5 to 3 g of the ground sample in 0 5M sodium chloride (50 ml), and titrating with 0 05M sodium hydroxide Because a portion of the base was neutralized by acidic residues in the polymer (*e g* , glucuronic acid groups), it was necessary to correct the titration figures with blank values determined for a Wiley-milled sample of the untreated paper The method was checked by using known mixtures of paper and phosphoric acid, and the second end-point was found to give reliable values for concentration of acid (limits of error, ±5%), whereas the first end-point was often somewhat high The use of aqueous phosphoric acid solutions having concentrations of 1.0, 0 27, and 0 13% was thus shown to provide newsprint samples containing 3 2, 1 0, and 0 5% of acid, respectively

Laboratory-scale preparation of levoglucosenone (**1**) — Shredded newsprint containing ~3 2% of phosphoric acid was pyrolyzed in 20-g batches in aluminum boats (4 × 13 cm) inside a Pyrex-glass tube (4.5 cm, i.d) preheated to 360–385° by a tube furnace (30 cm long) and swept by a nitrogen flow of 800 ml min^{-1} Each pyrolysis was complete within ~20 min The tarry products were collected in a water-cooled condenser, and were allowed to accumulate during 15–20 runs The crude pyrolyzate was then partitioned between chloroform and aqueous sodium hydrogencarbonate solution, with considerable evolution of carbon dioxide The organic phase was evaporated, and the residue partitioned between light petroleum ether and 4 1 methanol–water The aqueous alcoholic phase yielded a dark syrup (35–45% of **1**, by weight) which was distilled at 0 7 torr Early fractions, b p 30–50°, contained largely 2-furaldehyde and a variety of minor products, and a light-yellow syrup having b p 68–72° contained **1** (~2% yield, >90% purity based on g l c analysis) The residue contained mostly polymeric material, together with 1,4 3,6-dianhydro-α-D-glucose (**2**) and 5-(hydroxymethyl)-2-furaldehyde (**4**) Redistillation of **1** gave a product containing ~5–10% of impurity as judged by n m r and g l c evidence, and having $[\alpha]_D$ —490°, and $\lambda_{max}^{95\% EtOH}$ 218 nm (ε_{mM} 7 90) Levoglucosenone (**1**), $[\alpha]_D$ —530°, containing negligible impurities (n m r , t l c , and g l c evidence), was obtained by the chromatographic fractionation described next, and was used as the starting material for the synthetic experiments Samples of **1** prepared previously by pyrolytic methods[4 28] had $[\alpha]_D$ —460 and —458°, and $\lambda_{max}^{95\% EtOH}$ 218 nm (ε_{mM} 7.60), whereas **1** obtained by chemical synthesis[18] had $[\alpha]_D$ —518° The solvent fractionations and vacuum distillation used in the foregoing procedure were shown (by t l c and g l c analysis) to result in little loss of **1**

The light petroleum ether extract of the methanol–water solution of the pyrolyzate from newsprint yielded a dark oil which was shown by n m r. ($CDCl_3$) to contain mainly saturated hydrocarbon residues showing resonances centered at δ 0 90 and 1 27 When white paper was used as the substrate for acid-catalyzed pyrolysis, the hydrocarbon by-product precipitated from the methanol–water solution of the pyrolyzate as a waxy solid having a single n m r absorption, at δ 1 30

2-Furyl hydroxymethyl ketone (**5**) — T l c (solvent *A*) of crude distillate prepared as just described indicated the presence of a misleadingly intense, u v - detectable, component (R_F 0 45, red-brown, then blue) in addition to **1** (R_F 0 52, greenish-black) Chromatographic fractionation of distilled levoglucosenone (25 g) on a column of silica gel eluted with solvent *E* yielded this minor component (**5**) as a syrup that crystallized spontaneously Recrystallization from ether–light petroleum ether at —20° provided needles (0 25 g, 1%), m p 80–81° [lit[13] m p 80–81°]. The n m r , u v . and mass spectral characteristics of this product were identical to those previously reported[13 29] for **5**

Anal Calc for $C_6H_6O_3$ C, 57 1, H, 4 8 Found C, 56 9, H, 4 7

G l c analyses of **5** on Carbowax 20M (TPA), Silar 5CP, and ECNSS-M packings in nickel tubing all resulted in poor peak-shapes, indicating the relative instability of **5** under g l c conditions Moreover, the presence of **5** in the crude levoglucosenone could not be detected, even under conditions where the retention times of **5** and **1** were different

Hydrolysis of levoglucosenone (**1**) — A solution of **1** (0 51 g) in 0 5M hydrochloric acid (50 ml) was heated in a boiling-water bath, and the reaction was monitored by t l c (solvent *B*) During the first few minutes, **1** (R_F 0 70) was partly converted into a less mobile component (R_F 0 40, green) with the same mobility as **7** (see later) These two components were then gradually replaced by a third component (R_F 0 50, blue) The reaction was complete within 2 5 h, the solution was then dark yellow, and a tarry material had precipitated The solution was made neutral with a basic resin, and evaporated to dryness, and the residue was purified by chromatography on a column of silica gel eluted with solvent *D* 5-(Hydroxymethyl)-2-furaldehyde (**4**) was thus obtained as a light-yellow syrup (0 08 g, 16%) that had the same t l c and n m r - and i r -spectral characteristics as an authentic sample

*1,6-Anhydro-3-deoxy-β-*D-erythro-*hexopyranos-2-ulose* (**7**) — (*a*) *Acid-catalyzed hydration of levoglucosenone* (**1**) A mixture of **1** (0 70 g) and 2 0M aqueous acetic acid (3 ml) was heated in a boiling-water bath for 4 h, with swirling, the mixture became homogeneous within a few minutes The solution was kept overnight at room temperature, and the acetic acid was then removed by azeotropic distillation with four portions of water under diminished pressure, and, finally, evaporation at 50°/1 torr The yellow, syrupy product was then partitioned between water and dichloromethane The organic phase yielded a light-yellow syrup (0 08 g) containing mostly unreacted levoglucosenone (**1**), and the aqueous phase gave compound **7** as a light-yellow syrup (0 61 g, 77%), single component in t l c (green, R_F 0 40, solvent *B*) Purification by chromatography on silica gel eluted with solvents varied from *D* to *E* gave a colorless syrup (0 48 g) which, after careful drying at 50°/1 torr, had $[\alpha]_D$ —255° (chloroform), $[\alpha]_D$ —143° (water) {lit [30] $[\alpha]_D$ —217° (chloroform)}, ν_{max}^{film} 3430 (OH), 2975, 2900, 1735 (C=O), 1485, 1405, 1245, 1115, 1055, 1010, 965, 910, 870, and 780 cm^{-1}, *m/e* 145 (0 8%, M + 1), 144 (1 8, M^+), 126 (5, M — H_2O), 116 (26, M — CO), 101 (8), 99 (9), 98 (25), 97 (8), 96 (6), 95 (7), 85 (9), 73 (8), 72 (8), 71 (15), 70 (38), 69 (16), 58 (9), 57 (52), 56 (19), 55 (19), 53 (8), and 43 (100%) The n m r spectrum of **7** in $CDCl_3$ was in agreement with that previously reported[30]

Anal Calc for $C_6H_8O_4$ C, 50 0, H, 5 6 Found C, 50 2, H, 5 7

(*b*) *Base-catalyzed hydration of levoglucosenone* (**1**) Triethylamine (0 1 ml) was added to a solution of **1** (0 10 g) in water (10 ml), and the solution was kept for 1 h at room temperature, t l c then indicated complete conversion of **1** into a less-mobile, carbohydrate product Evaporation of the solvent *in vacuo* yielded **7** as a yellow syrup (0 10 g, 93%) that had the same i r spectrum and t l c characteristics as the product from (*a*)

Reduction of **7** — Compound **7** (0 35 g) was reduced with sodium borohydride in water as previously described[10], to yield a yellow syrup (0 33 g) shown by t l c (solvent *A*) to contain a major (R_F 0 04, **15**) and a minor (R_F 0 09, **18**) component

The major component was characterized as its acetyl and benzoyl derivatives. Half of the syrup was acetylated with acetic anhydride–pyridine in the usual way[10]. 2,4-Di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-*arabino*-hexopyranose (**16**) crystallized from diethyl ether at −20°, and was recrystallized from 95% ethanol as white needles, m.p. 100–101°, $[\alpha]_D$ −136° {lit.[31,32] m.p. 99.5–101° and 99–101°, $[\alpha]_D$ −139° and −140°; lit.[33] m.p. 100°, $[\alpha]_D$ +(?)139°}, n.m.r. data ($CDCl_3$): δ 1.9–2.2 (m, 8, 2 OAc and H-3,3′), 3.9 (m, 2, H-6,6′), 4.65 (m, 1, H-5), 4.8–5.15 (m, 2, H-2,4), and 5.50 (s, broad, 1, H-1).

Anal. Calc. for $C_{10}H_{14}O_6$: C, 52.2, H, 6.1. Found: C, 52.1, H, 6.1.

The other half of the reduction product was benzoylated with benzoyl chloride–pyridine in the usual way[10]. 1,6-Anhydro-2,4-di-*O*-benzoyl-3-deoxy-β-D-*arabino*-hexopyranose (**17**) crystallized upon evaporation of the solvent, and was recrystallized from 95% ethanol as white needles, m.p. 120.5–121°, $[\alpha]$ −204° {lit.[31] m.p. 120–121.5°, $[\alpha]_D$ −204°}; n.m.r. data ($CDCl_3$): δ 2.2–2.5 (m, 2, H-3,3′), 3.8–4.2 (m, 2, H-6,6′), 4.8 (m, 1, H-5), 5.2–5.6 (m, 2, H-2,4), 5.72 (s, broad, 1, H-1), 7.5–7.7 (m, 6, *m*- and *p*-benzoate), and 8.1–8.35 (m, 4, *o*-benzoate).

Anal. Calc. for $C_{20}H_{18}O_6$: C, 67.8, H, 5.1. Found: C, 67.9, H, 5.2.

To determine the stereospecificity of the reduction reaction, compound **7** (0.10 g) was reduced and the product acetylated as already described, to yield a colorless oil (0.15 g) shown by t.l.c. (solvent *A*) to contain a major (R_F 0.50) and a minor (R_F 0.44) component. The two components were separated on a column of silica gel, eluted with solvent *C*; both crystallized upon removal of the solvent. The major component (0.11 g, 71%) was shown to be **16** by mixed melting point; the minor component (0.22 g, 14%) was recrystallized from diethyl ether–light petroleum ether, and found to be 2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-*ribo*-hexopyranose (**19**), m.p. 118–119°, $[\alpha]_D$ −74° {lit.[31,32] m.p. 114–116°, $[\alpha]_D$ −74°}.

*1,6-Anhydro-2,4-di-O-benzoyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose* (**20**). — Compound **7** (0.102 g) was dissolved in pyridine (1 ml), and benzoyl chloride (1 ml) was added. After 4 h at room temperature, the mixture was processed in the usual way[10], to yield a yellow syrup which was shown by t.l.c. (solvent *E*) to contain largely a single carbohydrate component. Chromatographic fractionation on a column of silica gel eluted with solvent *E* yielded **20** as a colorless syrup (65 mg, 26%), $[\alpha]_D$ ~ +50° (*c* 0.2), n.m.r. data ($CDCl_3$): δ 8.0–8.3 (m, 4, *o*-benzoate), 7.3–7.7 (m, 6, *m*- and *p*-benzoate), 5.93 (dt, 1, H-3, $J_{1,3}$ ~1.5, $J_{3,4}$ ~5, $J_{3,5}$ ~1.5 Hz), 5.70 (d, 1, H-1), 5.32 (dd, 1, H-4, $J_{4,5}$ ~1 Hz), 4.93 (dm, 1, H-5), 4.07 (dd, 1, H-6_{exo}, $J_{5,6exo}$ ~6, $J_{6endo,6exo}$ ~8 Hz), and 3.73 (dd, 1, H-6_{endo}, $J_{5,6endo}$ ~2 Hz).

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.2, H, 4.6. Found: C, 68.1; H, 4.7.

*1,6-Anhydro-4-O-methyl-β-D-*erythro*-hexopyranos-2-ulose dimethyl acetal* (**14**). — Levoglucosenone (**1**, 0.37 g) was dissolved in methanolic hydrogen chloride (7 ml, 3%). The reaction was monitored by t.l.c. (solvent *A*); **1** (R_F 0.52) was converted, by way of an intermediate component (R_F 0.43), into a single product (R_F 0.20) within 4 h at room temperature. The mixture was made neutral with solid sodium hydrogencarbonate, and partitioned between chloroform and water. The organic phase was washed with water, and evaporated to a yellow syrup (0 46 g, 100%), $[\alpha]_D$ $-78°$, shown by g l c (programmed from 70 to 340° at 6°/min) to be a 49 1 mixture of compound **14** and a minor product (retention times 21 4 and 22 2 min, respectively) Distillation of this syrup at 100°/0 2 torr yielded a colorless syrup, $[\alpha]_D$ $-85°$, which had no i r absorption in the 2000–1550-cm^{-1} region Chromatographic fractionation of this distillate on silica gel removed a small, less-mobile component, and redistillation gave pure **14**, $[\alpha]_D$ $-86°$, *m/e* 189 ($M - CH_3$, 1%), 173 ($M - CH_3O$, 13), 172 ($M - CH_3OH$, 6), 159 ($M - HCOO$, 15), 145 (3), 143 (5), 141 (3), 131 (25), 129 (25), 127 ($M - HCOO - CH_3OH$, 29), 117 (6), 113 (6), 111 (20), 103 (4), 101 (14), 98 (8), 97 (7), 96 (8), 95 (5), 89 (8), 88 ($M - HCOO - CH_2$ $CHCHOCH_3$, 100), 87 (5), 85 (6), 81 (10), 75 (11), 71 (39), 58 (19), and 43 (27%)

Anal Calc for $C_9H_{16}O_5$ C, 52 9, H, 7 9 Found C, 52 7, H, 7 7

*1,6-Anhydro-3-deoxy-4-O-methyl-β-*D-erythro-*hexopyranos-2-ulose* (9) — (*a*) *Hydrolysis of dimethyl acetal* **14** Compound **14** (1 0 g) was dissolved in acetone (10 ml) plus 5M hydrochloric acid (10 ml) After 40 min at room temperature, the mixture was made neutral with solid sodium hydrogencarbonate, and evaporated to dryness, the residue was extracted with chloroform, and the extract was evaporated to a red syrup (0 83 g) T l c (solvent *A*) revealed components at R_F 0 52 (minor), 0 43 (major), and 0 20 (secondary), these were isolated by column chromatography on silica gel, eluted with solvent *E* The major component was the title compound (**9**), isolated as a colorless syrup (0 43 g, 56%), $[\alpha]_D$ $-214°$ (chloroform), $[\alpha]_D$ $-130°$ (water), ν_{max}^{KBr} 1750 cm^{-1} (C=O)

Anal Calc for $C_7H_{10}O_4$ C, 53 2, H, 6 4 Found C, 53 3, H, 6 6

The minor and secondary components were determined by n m r spectroscopy and t l c to be levoglucosenone (**1**, 0 025 g, 3%) and the starting material **14** (0 20 g, 20%), respectively

(*b*) *Base-catalyzed addition of methanol to levoglucosenone* (**1**) Triethylamine (0 1 ml) was added to a solution of **1** (0 16 g) in dry methanol (10 ml) T l c (solvent *A*) revealed that, after 45 min at room temperature, a significant amount of **1** (R_F 0 52) remained, but that, after 3 h, it had been completely converted into **9** (R_F 0 43), this was isolated as a yellow syrup (0 21 g, 100%) by removal of the solvent *in vacuo*, and shown by n m r - and i r -spectral and t l c evidence to be identical to that obtained in part (*a*)

This reaction was repeated, but using 1 1 methanol–water as the solvent Under these conditions, **1** was completely converted into **9** within 15 min Attempted vacuum distillation of **9** yielded a colorless syrup containing largely **9** and a little of **1** (t l c evidence)

Acetolysis of levoglucosenone (**1**) — Boron trifluoride diethyl etherate (95 mg) was added to a solution of **1** (0 25 g) in acetic anhydride (3 ml) The solution immediately became dark and slightly warm, and t l c (solvent *G*) indicated complete conversion of **1** (R_F 0 45) into a major (R_F 0 50, blue-green) and a minor (R_F 0 57, yellow, not u v.-detectable), new component The mixture was partitioned between chloroform and aqueous sodium hydrogencarbonate, and the organic phase was washed with water, and evaporated to a red syrup (0 43 g) Conventional chromatography on a column of silica gel eluted with a variety of solvents failed to fractionate the mixture, and a light-yellow syrup (0 26 g), $[\alpha]_D$ −86°, was obtained This mixture was separated by liquid chromatography [Waters Associates Liquid Chromatograph and Differential Refractive Index detector, μ-Porasil column (3 9 mm i d , × 30 cm), and elution with solvent *I* at 1 0 ml/min] into two components Two fractions, having retention times 8 7 and 10 6 min, respectively, were collected preparatively from ten 7-mg injections The less-mobile product (major component) was 1,6-di-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranos-2-ulose (**21**), $[\alpha]_D$ −85°, λ_{max}^{EtOH} 223 nm (ε_{mM} 10 00), ν_{max}^{film} 1755 (C=O, acetate), 1707 and 1635 (w) cm^{-1} (C=C—C=O), n m r data (CDCl$_3$) δ 7 15 (dd, 1, H-4, $J_{3\,4}$ ~11, $J_{4\,5}$ ~1 5 Hz), 6 34 (dm, 1, H-3, $J_{3,5}$ ~2 Hz), 6 23 (s, 1, H-1), 4 83 (m, 1, H-5), 4 3 (m, 2, H-6,6′), 2.17 and 2 15 (2 s, 3, OAc)

The minor product was shown by n m r spectroscopy to be an ~4 1 mixture of tetra-*O*-acetyl-3-deoxy-α-D-*erythro*-hex-2-enopyranose (**22**) [δ 6 36 (s, 1, H-1), 5 91 (d, 1, H-3, $J_{3\,4}$ ~2 Hz), 5 57 (dm, 1, H-4, $J_{4\,5}$ ~9 Hz), 4 0–4.4 (m, 3, H-5,6,6′), 2 16 and 2 20 (12, OAc), lit [34] 6 35 (s, 1), 5 90 (d, 1, *J* 2 0 Hz), 5 58 (dm, 1, *J* 8 8 Hz)], and its β anomer (**23**) [δ 6 45 (s, H-1), lit [34] δ 6 44 (s)] The n m r spectrum of the original, crude reaction-product was consistent with an ~3.1 mixture of **21** and **22**

*1,6-Anhydro-3,4-dideoxy-4-S-phenyl-4-thio-β-*D-erythro*-hexopyranos-2-ulose* (**10**) — Compound **1** (0 70 g) was dissolved in chloroform (10 ml) containing benzenethiol (0 71 g, 1 2 mol. equiv.), and triethylamine (0 1 ml) was added T l c indicated complete conversion of **1** into a more-mobile product within a few minutes at room temperature After removal of the solvent, the crude reaction-product was purified on a column of silica gel eluted with solvent *C* The phenylthio derivative **10** was obtained as a yellow syrup (1 12 g, 85%) which crystallized spontaneously at −20° Two recrystallizations from diethyl ether–light petroleum ether gave white needles, m.p 48–48 5°, $[\alpha]_D$ −179°

Anal Calc for $C_{12}H_{12}O_3S$ C, 61 0. H, 5 1, S, 13 6 Found. C, 60 9, H, 5 2, S, 13 6

*Bis(1,6-anhydro-3,4-dideoxy-β-*D-erythro*-hexopyranos-2-ulos-4-yl) sulfide* (**11**) — Compound **1** (0 49 g) was dissolved in chloroform (20 ml) containing triethylamine (0.1 ml), and nitrogen was bubbled through the solution for 15 min Hydrogen sulfide was then bubbled into the solution for 10 min, during which time, a white solid was precipitated The mixture was allowed to stand for 1 h, and was then filtered, and the precipitate was washed with light petroleum ether This procedure yielded pure sulfide **11** (0 23 g, 42%), m p 181–181 5°, $[\alpha]_D$ −239° (acetonitrile), ν_{max}^{KBr} 1740 cm^{-1} (C=O) The n m r-spectral interpretation (see Table III) was made with the aid of a spectrum recorded in pyridine-d_5

Anal Calc for $C_{12}H_{14}O_6S$ C, 50 3, H, 4 9, S, 11 2 Found C, 50 6, H, 5 1; S, 11 1

Reduction of levoglucosenone (**1**) — (*a*) *With sodium borohydride in water.* To a solution of **1** (1.69 g) in water (25 ml) was added a solution of sodium borohydride (0.85 g, 1.6 mol. equiv.) in water (10 ml). After 5 min, acetone (2 ml) was added to decompose the excess of the reagent. Although t.l.c. (solvent *A*) indicated complete conversion of **1** into two less-mobile components, R_F 0.32 (brown) and 0.21 (pink), the high intensity of the second spot was misleading, as g.l.c. analysis revealed mainly one product [see (*e*)]. The solution was 5 times extracted with chloroform, and the extracts were evaporated to a syrup that spontaneously crystallized (1.54 g). Recrystallization from ether–light petroleum ether gave needles, m.p. 68.5–69°, which were still contaminated by traces of the minor product (t.l.c. evidence). This product was purified by chromatography on a column of silica gel eluted with solvent *E*, to yield 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**24**), m.p. 70–70.5°, $[\alpha]_D$ −30° {lit.[18] m.p. 65–66.5°, $[\alpha]_D$ −35.3°, lit.[19] m.p. 67–69°, $[\alpha]_D$ −34°}. The n.m.r. spectrum of this product was identical to those reported by other workers[18,20] for **24**.

Anal. Calc. for $C_6H_8O_3$: C, 56.3; H, 6.3. Found: C, 56.4; H, 6.5.

A further sample (0.29 g) was derivatized by using 3,5-dinitrobenzoyl chloride (0.43 g, 1.2 mol. equiv.) in pyridine (4 ml) overnight at room temperature. The mixture was partitioned between chloroform and 5M hydrochloric acid, and the organic phase washed successively with aqueous acid, aqueous sodium hydrogencarbonate, and water, and evaporated to dryness. On crystallization from ethanol–2-butanone, the residue yielded 1,6-anhydro-3,4-dideoxy-2-*O*-(3,5-dinitrobenzoyl)-β-D-*threo*-hex-3-enopyranose (**25**) as pale-yellow needles (0.45 g, 79%), m.p. 158–159°; n.m.r. data ($CDCl_3$): δ 9.25 (m, 3, aromatic), 6.42 (m, 1, H-4), 5.65–5.95 (m, 3, H-1,2,3), 4.80 (t, 1, H-5, $J_{4,5} = {\sim}J_{5,6exo} = {\sim}4$ Hz), 4.08 (d, 1, H-6$_{endo}$, $J_{5,6endo}$ small, $J_{6endo,6exo}$ ~6.5 Hz), and 3.85 (dd, 1, H-6$_{exo}$). This derivative was identical (t.l.c. and mixed m.p. evidence) to the material isolated previously[4] following reduction of **1** with lithium aluminum hydride, but incorrectly assigned as the *erythro* isomer of **24** (lit.[4] m.p. 158–160°).

Attempts to process reduction mixtures in the usual way[10] (in which the crude mixture is made neutral with an acidic resin, and evaporated to a residue which is several times dissolved in methanol and distilled to remove boric acid as its methyl ester) were repeatedly unsuccessful. The resulting residues were insoluble in ether, but soluble in methanol or dimethyl sulfoxide. The n.m.r. spectrum of such a residue in Me_2SO-d_6 revealed, in addition to the resonances expected for **24**, certain as-yet-unexplained peaks. However, synthetic mixtures of **24** and boric acid in Me_2SO-d_6 showed no anomalous resonances, indicating the absence of complex-formation under these conditions.

(*b*) *With sodium borohydride in aqueous ethanol.* A solution of crude levoglucosenone (**1**, estimated to be 80% pure by g.l.c., 20 g) in ethanol (50 ml) and water (20 ml) was stirred and cooled in an ice-bath, and a solution of sodium borohydride (1.9 g, 0.4 mol. equiv.) in water (25 ml) was added dropwise, while the reaction temperature was kept below 15°. After evaporation of the ethanol from the mixture, the solution was processed as in (*a*), to yield a syrup that was fractionated by column chromatography on silica gel eluted with solvent *E* The allylic alcohol **24** was eluted first, and it crystallized on evaporation of the solvent (8 8 g, 95% pure by g l c , 51%)

The next fraction yielded a syrup (0.51 g, 3%) that contained 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hexopyranose (**29**) and a component assumed to be the C-2 epimer of **29**, in the ratio of 15 1 as shown by g l c [as in (*e*)] A portion of this syrup (0 18 g) was dissolved in pyridine (3 ml), 3,5-dinitrobenzoyl chloride (0 35 g, 1 1 mol equiv) was added, and the solution was kept overnight at room temperature The solvent was then evaporated *in vacuo*, and a solution of the residue in acetone was poured into ice–water The brownish solid precipitated was purified by elution through a short column of silica gel, and recrystallized twice from 95% ethanol, to yield 1,6-anhydro-3,4-dideoxy-2-*O*-(3,5-dinitrobenzoyl)-β-D-*threo*-hexopyranose (**30**) as pale-yellow needles, m p 165 5–167 5°, $[\alpha]_D$ −94° This derivative was identical (t l c and mixed m p evidence) to the material obtained previously[4] following reduction with lithium aluminum hydride and catalytic hydrogenation, of **1**, but incorrectly assigned as the *erythro* isomer of **30** {lit [4] m p 165–167°, $[\alpha]_D$ −90 2° (*c* 5 32)}

(*c*) *With sodium borohydride in other solvents*. Reduction of **1** in anhydrous pyridine as the solvent led to a red-brown reaction solution which was added to an excess of 10% aqueous potassium iodate solution, to decompose the pyridineborine formed during the reaction The resulting solution was exhaustively extracted with chloroform Analysis by t l c and g l c showed that the organic phase contained **24** and **29**, but fractionation by column chromatography on silica gel provided these in yields of only 1 and 7%, respectively The aqueous phase was shown (t l c) to retain a variety of unidentified, carbohydrate components No improvement in the yields of **24** and **29** was observed when this procedure was varied by (*a*) addition of water to the pyridine (either initially, or during the reaction), (*b*) direct, chromatographic fractionation of the product to avoid using the iodate reagent, or (*c*) replacing pyridine with bis(2-methoxyl)ether as the solvent

(*d*) *With lithium aluminum hydride* Reduction of **1** was conducted in ether as described previously[4], to provide a yellow syrup that yielded allylic alcohol **24** in 52% yield on crystallization from ether–light petroleum ether This product had the same t l c. and g l c. characteristics as the product from method (*a*)

(*e*) *Product analysis by g l c* Samples of **1** were reduced with sodium borohydride, and the products were isolated as in method (*b*) as yellow syrups which were analyzed by g l c (8°/min from 70 to 230°) The crude product from method (*d*) was similarly analyzed Care was taken to minimize losses of the readily volatilized **24** during evaporation of reaction mixtures Components were identified from their retention times and by co-chromatography with authentic samples The results are summarized in Table IV

(Z)-*3,4-Dideoxy*-D-threo-*hex-3-enitol* (**31**) — A solution of allylic alcohol **24** (0 21 g) in 0 5M hydrochloric acid (2 ml) was heated for 40 min in a boiling-water bath, t l c (solvent *J*) then indicated conversion of all but a trace of **24** (R_F 0 62) into a new component (R_F 0 39) The solution was made neutral with an acidic resin, and filtered, and the filtrate was treated with sodium borohydride (0 10 g) in the usual way[10]. A solution of the resulting syrup in water was extracted with chloroform (to remove unreacted **24**), and the aqueous phase was evaporated, to yield **31** as a colorless syrup (0 15 g, 65%) that crystallized from 95% ethanol–ethyl acetate at —20° Recrystallized from 2-propanol, it had m p 76 5–77 5°, $[\alpha]_D$ +12° (water) {lit [21] m p 72–74°, $[\alpha]_D$ +13 3° (*c* 0 18, water)}, n m r data (C_5D_5N) δ 6 15 (sextet, 2, H-3,4), 5 20 (oct, 2, H-2,5), and 4 10 (apparent d, 4, H-1,6, width ~6 Hz)

*1,6-Anhydro-3,4-dideoxy-2-O-tosyl-β-*D-threo-*hex-3-enopyranose* (**26**) — Allylic alcohol **24** (3 2 g) was added to a solution of *p*-toluenesulfonyl chloride (5 7 g, 1 2 mol equiv) in dry pyridine (10 ml) After 3 h at room temperature, the reaction was complete (t l c) A few drops of water were added, and the solution was partitioned between chloroform and 0 05M sulfuric acid The organic phase was washed successively with aqueous acid, aqueous sodium hydrogencarbonate solution, and water, and evaporated to a thin, yellow syrup which crystallized from ether to yield **26** (5 8 g, 83%) Recrystallized twice from ether at —20°, it had m p 81 5–83°, $[\alpha]_D$ —28° {lit [19] m p 74–75°, $[\alpha]_D$ —41°}, n m r data ($CDCl_3$) δ 7 95 and 7 46 (2 d, 2, aromatic, *J* 8 2 Hz), 6 26 (o, 1, H-4, $J_{3\ 4}$ ~10 7, $J_{4\ 5}$ ~4, $J_{2\ 4}$ ~1 3 Hz), 5 53 (dt, 1, H-3, $J_{1,3}$ = ~$J_{2\ 3}$ = ~2 Hz), 5 47 (1, H-2, merged with H-3), 5 25 (m, 1, H-1), 4 70 (t, 1, H-5, $J_{5\ 6exo}$ ~4 Hz), 3 98 (d, 1, H-6_{endo}, $J_{5,6endo}$ small, $J_{6endo\ 6exo}$ ~7 Hz), and 3 77 (dd, 1, H-6_{exo})

Anal Calc for $C_{13}H_{14}O_5S$ C, 55 3, H, 5 0, S, 11 4 Found C, 55 4, H, 5 1, S, 11 3

*Reaction of 1,6-anhydro-3,4-dideoxy-2-O-tosyl-β-*D-threo-*hex-3-enopyranose* (**26**) *with sodium benzoate* — Tosylate **26** (3 0 g) and sodium benzoate (1 68 g, 1 1 mol equiv) were stirred and heated in dry *N*,*N*-dimethylformamide (50 ml) under gentle reflux for 2 h, during which time, the mixture became homogeneous and dark-brown T l c (solvent *G*) indicated complete conversion of **26** into two, more-mobile, u v.-detectable components, accompanied by traces of two less-mobile components (presumably hydrolysis products) The solvent was removed at 50°/1 torr, the residue was partitioned between chloroform and water, and the organic phase was evaporated to dryness Column-chromatographic fractionation of this product on a column of silica gel eluted with solvent *C* yielded a mixture of benzoylated derivatives (n m r evidence) as a light-yellow syrup (1 87 g, 76%) This syrup was debenzoylated with a catalytic amount of sodium methoxide in methanol, and the solution was made neutral with an acidic resin Fractionation of the product on a column of silica gel eluted with solvents varied from *C* to *F* yielded the following products in order of elution (*i*) 1,6-Anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**27**, 0 33 g, 24%), recrystallized twice from ether, it had m p 58 5–60 5°, $[\alpha]_D$ —238° {lit [35] m p. 67–68° (DL isomers), lit [18] m p 54–55°, $[\alpha]_D$ —236°} The n m r spectrum was identical to those reported previously[18,35] for **27** (*ii*) 1,6-Anhydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranose (**32**, 0 31 g, 22%), crystallized from ether, and then recrystallized from ether–light petroleum ether, it had m p 50–52°, $[\alpha]_D$ +200° {lit.[18] m p. 58–59°, $[\alpha]_D$ +214°} The n m r spectrum was identical to that reported previously[18] for **32** (*iii*) (5*S*)-4,5-Dihydro-5-(hydroxymethyl)-2-furaldehyde (**34**, 0.135 g, 10%), it crystallized from ether–acetone–light petroleum as needles, m.p. ~39°, $[\alpha]_D$ +35° (ethanol), ν_{max}^{melt} 3460 br (hydroxyl), 1690 and 1640 cm^{-1} (C=C—C=O), $\lambda_{max}^{95\%EtOH}$ 257 nm (ε_{mM} 8.40), n.m.r. data ($CDCl_3$) δ 9.13 (s, 1, C*H*O), 5.87 (t, 1, H-3, $J_{3,4}$ = ~$J_{3,5}$ = ~4 Hz), 3.8–4.4 (m, 3, H-5 and C*H*$_2$OH), 3.45 (br s, 1, OH), and 2.50 (m, 2, H-4,4').

The reaction was repeated with **26** (1.60 g) and sodium benzoate (0.9 g, 1.1 mol. equiv.) in dry *N*,*N*-dimethylformamide (25 ml). When the crude mixture of benzoylation products was chromatographed on a column of silica gel eluted with solvent *H*, it was partially separated into two components (t.l.c., solvent *G*), R_F 0.63 (blue) and 0.57 (brown). The more-mobile component was shown by n.m.r. to be 1,6-anhydro-2,3-dideoxy-4-*O*-benzoyl-β-D-*erythro*-hex-3-enopyranose (**33**), crystallized from ether–light petroleum ether, it had m.p. 90–92°, $[\alpha]_D$ +210°, n.m.r. data ($CDCl_3$) δ 9.0–8.4 (m, 2, *o*-benzoate), 7.4–7.8 (m, 3, *m*- and *p*-benzoate), 6.33 (dd, 1, H-2, $J_{1,2}$ ~3.3, $J_{2,3}$ ~10 Hz), 5.96 (complicated dd, 1, H-3, $J_{3,4}$ ~4 Hz), 5.69 (d, 1, H-1), 5.09 (complicated d, 1, H-4, $J_{4,5}$ ~0.8 Hz), 4.91 (dm, 1, H-5, $J_{5,6exo}$ ~6.5 Hz), 4.05 (dd, 1, H-6$_{exo}$, $J_{6exo,6endo}$ ~8 Hz), and 3.64 (dd, 1, H-6$_{endo}$, $J_{5,6endo}$ ~2.2 Hz).

Anal. Calc. for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2. Found: C, 67.3; H, 5.2.

The less-mobile component was shown by n.m.r. to be a mixture, from which (1*R*)-2-(benzoyloxy)-3,8-dioxabicyclo[3.2.1]oct-6-ene (**35**) crystallized from ether–light petroleum ether at −20°. Recrystallized from the same solvent, it had m.p. 97–98°, $[\alpha]_D$ +61°, n.m.r. data ($CDCl_3$). δ 8.0–8.4 (m, 2, *o*-benzoate), 7.3–7.8 (m, 3, *m*- and *p*-benzoate), 5.66 (m, 1, H-6,7), 5.98 (narrow d, 1, H-2, $J_{1,2}$ ~1 Hz), 4.65 (m, 2, H-1,5), 4.41 (dd, 1, H-4, $J_{4,5}$ ~2, $J_{4,4'}$ ~8.5 Hz), and 3.46 (d, 1, H-4', $J_{4',5}$ <1 Hz).

Anal. Calc. for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2. Found: C, 67.5; H, 5.4.

Debenzoylation of **35** with a catalytic amount of sodium methoxide in methanol yielded **34**, as judged by n.m.r. and t.l.c. evidence.

Oxidation of levoglucosenone (**1**). — To a solution of compound **1** (0.53 g) in dichloromethane (5 ml) was added a solution of *m*-chloroperoxybenzoic acid (1.02 g, 85% pure, 1.2 mol. equiv.) in dichloromethane (15 ml). The mixture was kept for three days at room temperature, and then concentrated to a small volume under vacuum, whereupon most of the *m*-chlorobenzoic acid precipitated. The solution remaining was chromatographed on a column of silica gel eluted with solvents varied from *D* to *E*. Fractions shown by t.l.c. to contain largely one compound (R_F 0.48, solvent *A*, light-green) were combined, and evaporated, to yield **37** as a yellow syrup (0.22 g, 37% yield). Vacuum distillation gave a thin, colorless syrup, $n_D^{23°}$ 1.476, $[\alpha]_D$ −139°, $\lambda_{max}^{95\%EtOH}$ 212 nm (ε_{mM} 4.90), ν_{max}^{film} 3095, 2945, 1750 and 1710 (strong, broad, and merged), 1595, 1450, 1370, 1340 (shoulder), 1320, 1260, 1155 (strong and broad), 1105, 1090 (shoulder), 1050, 955, 915, 895, 865, and 815 (strong) cm^{-1}, n.m.r. data ($CDCl_3$) δ 8.17 (s, 1, H-1), 7.60 (dd, 1, H-5, $J_{4,5}$ ~6, $J_{5,6}$ ~1.8 Hz), 6.32 (dd, 1, H-4, $J_{4,6}$ ~2.0 Hz), 5.33 (m, width 13 Hz, 1, H-6), and

4 52 (apparent d, 2, H-7,7′, separation 4 5 Hz), m/e 98 (0 7%), 97 (5), 96 (100), 69 (5), 68 (91), 55 (5), 54 (60), 53 (13), 51 (14), 50 (20), 49 (9), 42 (92), and 40 (39), and metastable at $\sim$48 4 (calc 48 2, m/e 96→68)

Anal Calc for $C_6H_6O_4$ C, 50 7, H, 4 3 Found C, 51 0, H, 4 3

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