0.76; mp 193–194°; $[\alpha]^{25}D$ −47° (c 1.2, water) (reported mp 190–191°, $[\alpha]^{25}D$ −45.2°,[16] and mp 190°, $[\alpha]D$ −45.2[17]).

2-Acetamido-1,6-anhydro-2-deoxy-4-*O*-*tert*-butyl-β-D-glucopyranose (VIII).—Deacetylation of VI (150 mg) as above, followed by crystallization from ethyl acetate–ether–hexane afforded 102 mg (78%) of VIII: mp 139–140°; $[\alpha]D$ −25.3°; tlc [ethyl acetate–methanol (9:1)] R_{VI} 0.88; nmr τ 7.98 (three *N*-acetyl protons) and 8.74 (nine *tert*-butyl protons).

Anal. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.70; H, 8.24; N, 5.25.

2-Acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranose (X).—Tetra-*O*-acetyl-α-D-galactosyl bromide (1.03 g, 2.5 mmol) was dissolved in dry ethylene chloride (40 ml), the aglycon VII (0.37 g, 1.51 mmol) and mercuric cyanide (0.63 g, 2.5 mmol) were added, and the mixture was stirred at 40°, with protection from light, until no more aglycon was detectable on tlc (3 days). The cooled solution was poured into a mixture of ice–water and chloroform, and the organic layer was shaken thoroughly with 5% sodium hydrogen carbonate and washed with water. The residue obtained after evaporation of the solvent was dissolved in methylene chloride (5 ml) and chromatographed on a column (40 mm i.d.) of silica gel (E. Merck, 60, 70–230 mesh, 70 g). The compound eluted by a mixture of methylene chloride–ethyl acetate (3:7) weighed 0.72 g (83%) and was crystallized twice from 2-propanol: mp 187–188°; $[\alpha]^{25}D$ −79.4° (*c* 2, chloroform) tlc (ethyl acetate) R_{VII} 1.9. The ir spectrum (KBr) showed bands at 11.2 (β-glycoside) and 11.45 μ (galactopyranose ring).

Anal. Calcd for $C_{24}H_{33}NO_{15}$: C, 50.08; H, 5.78. Found: C, 50.02; H, 5.88.

2-Acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (XI).—Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (2.5 mmol) in ethylene chloride (40 ml) was treated with aglycon VII (1.51 mmol) and mercuric cyanide (2.5 mmol) as described for X. Elution from the silica gel column with methylene chloride–ethyl acetate (2:8) gave 0.76 g (87%) of the chromatographically pure compound. After crystallization from ethyl acetate–ether (1:4) and recrystallization from 2-propanol–isopropyl ether (1:2) it had mp 118–119°; $[\alpha]^{25}D$ −77.5° (*c* 2, chloroform); tlc (ethyl acetate) R_{VII} 1.84, R_X 0.97; ir (KBr) 11.2 μ (β-glycoside).

Anal. Calcd for $C_{24}H_{33}NO_{15}$: C, 50.08; H, 5.78. Found: C, 50.30; H, 5.69.

2-Acetamido-2-deoxy-1,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranose (XII).—Opening of the 1,6-anhydro ring in X (115 mg) was effected by treating with acetic anhydride (7 ml), glacial acetic acid (3 ml), and concentrated sulfuric acid (0.05 ml) at 15° for 24 hr. Anhydrous sodium acetate (0.3 g) was added, and the suspension was taken to dryness by coevaporation *in vacuo* with toluene. The residue was extracted with chloroform, and the extract was washed with water, dried over sodium sulfate, and evaporated at reduced pressure. The residue was chromatographed on a silica gel column (10 g, 15 mm i.d.). The fraction eluted by ethyl acetate–methylene chloride (8:2) was crystallized from alcohol–ether and recrystallized from 2-propanol–isopropyl ether: yield 66 mg (45%); mp 223–225°; $[\alpha]^{25}D$ +57.9°; tlc [benzene–methanol (9:1)] R_X 0.9 (reported mp 224–225°, $[\alpha]^{18}D$ +57.7°[7]).

2-Acetamido-2-deoxy-1,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranose (XIII).—Acetolysis of XI (230 mg) as described for X yielded after column chromatography 124 mg (46%) of XIII. Crystallization from alcohol–ether (1:1) and recrystallization from ethyl acetate–isopropyl ether (9:1) gave the pure octaacetyl derivative: mp 229–230°; $[\alpha]^{26}D$ + 46.4°; tlc [benzene–methanol (9:1)] R_{XII} 0.93, R_{XI} 0.99.

Anal. Calcd for $C_{28}H_{39}NO_{18}$: C, 49.63; H, 5.80. Found: C, 49.68; H, 6.00.

2-Acetamido-2-deoxy-4-*O*-(β-D-glucopyranosyl)-D-glucopyranose (XIV).—Catalytic deacetylation of the preceding compound (XIII, 100 mg) gave the free disaccharide XIV, which was crystallized from methanol–ether (8:2) and recrystallized from 2-propanol: yield 39 mg (69%); mp 168–170°; $[\alpha]^{24}D$ +12.9 ± 1° (*c* 1, water); tlc [benzene–methanol (1:2)] $R_{lactose}$ 0.8; ir (KBr) 6.0, 6.45 (amide group), and 11.2 μ (β linkage).

Anal. Calcd for $C_{14}H_{25}NO_{11}\cdot 2H_2O$: C, 40.09; H, 6.97. Found: C, 40.10; H, 7.03.

Registry No.—II, 36949-97-0; III, 36949-98-1; IV, 36949-99-2; V, 37042-48-1; VI, 37042-49-2; VII, 37042-50-5; VIII, 37042-51-6; IX, 37042-52-7; X, 36954-61-7; XI, 36954-62-8; XII, 36954-63-9; XIII, 36954-64-0; XIV, 36954-65-1.

Levoglucosenone (1,6-Anhydro-3,4-dideoxy-Δ³-β-D-Pyranosen-2-one). A Major Product of the Acid-Catalyzed Pyrolysis of Cellulose and Related Carbohydrates

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Levoglucosenone (1,6-anhydro-3,4-dideoxy-Δ³-β-D-pyranosen-2-one) was isolated as the major component of the tar fraction from the acid-catalyzed pyrolysis of cellulose, D-glucose, or levoglucosan (1,6-anhydro-β-D-glucopyranose). Its structure was determined and a mechanism describing its formation from levoglucosan is proposed.

Until the early 1950's studies of the pyrolysis of cellulose and cellulosic fuels, neat and treated with various fire retardants, were largely confined to determination of such gross fractions as gas, tar, and char and to simple observation of how the combustibility of the sample varied with the relative proportions of these fractions. Such studies clearly established that high "tar" yields favor high flammability.[1,2]

As early as 1918, Pictet and Sarasin[3] isolated as a major constituent of the tar fraction a substance they named "levoglucosan." This constituent was subsequently identified by Josephson[4] as 1,6-anhydro-β-D-glucopyranose (I).

Unfortunately, many of the more recent studies of the combustion behavior of cellulose have tended to equate levoglucosan and tar. Since high levoglucosan yield—and, consequently, high tar yield—favors high flammability, it was assumed that reducing the levoglucosan yield—and, therefore, presumably the tar yield—would lower flammability. In particular, since both acidic and basic retardants were found to lower drastically the levoglucosan yield on pyrolysis of treated cellulose, such materials have frequently been

(1) S. Coppick in "Flameproofing Textile Fabrics," R. W. Little, Ed., ACS Monograph 104, 1947, p 41.

(2) K. Tamaru, *Bull. Chem. Soc. Jap.*, **24**, 164 (1951).

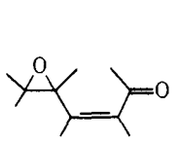
(3) A. Pictet and J. Sarasin, *Helv. Chim. Acta*, **1**, 87 (1918).

(4) K. Josephson, *Chem. Ber.*, **62B**, 313 (1929).

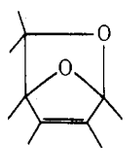
considered more or less interchangeable in their potentials as fire retardants.

Recently Tsuchiya and Sumi[5] demonstrated that with acidic retardants a new unidentified compound replaced levoglucosan as the major constituent of a still significant tar fraction. Subsequently they and their colleagues[6] demonstrated that the decrease in levoglucosan yield was not necessarily related to the effectiveness of flame retardants, with results implying that the overall tar yield is a more important criterion for flammability than is the yield of levoglucosan. Further, they purified a sample of the new compound and, using infrared (ir), nuclear magnetic resonance (nmr), and mass spectral analyses, identified it as *cis*-4,5-epoxy-2-pentenal (II).

Working independently during the same period, Wodley[7] pyrolyzed both cellulose and levoglucosan with acidic retardants and reported a major unknown tar constituent with the empirical formula $C_5H_6O_2$. On the basis of ir, nmr, and mass spectrometric results essentially the same as those reported for II, Lipska and McCasland[8] assigned to this compound the structure 1,5-anhydro-2,3-dideoxy-β-D-pent-2-enofuranose (III).



II



III

The two proposed structures have a number of common features and most likely represent the same compound. Since we believed the determination of the correct structure of this compound to be important to the understanding of the thermal behavior of cellulose, *i.e.*, of the reaction mechanisms which should be the basis of fire-retardant technology, we undertook a further study to elucidate this structure. This paper reports the results of that investigation.

Experimental Section

Preparation of 1,6-Anhydro-3,4-dideoxy-Δ³-β-D-pyranosen-2-one. A.—One gram of acidic additive ($NH_4H_2PO_4$, NaH_2PO_4, or $NaHSO_4$) was thoroughly mixed with 10 g of powdered cellulose (Cellex MX, Bio-Rad Laboratories, Richmond, Calif.). The sample was then introduced into a Pyrex tube, 1.5 × 10 in., which was connected to a Dry Ice–acetone trap and vacuum pump. The tube was evacuated and introduced into a preheated furnace positioned about 10° from the horizontal in order to allow liquid products to flow readily out of the hot zone and thus minimize secondary reactions. After 45 min at 300° the system was brought to room temperature and air was introduced. The nonaqueous fraction (about 500 mg total) of the mixture of liquid products was extracted essentially quantitatively into about 50 ml of methylene chloride, washed with water, and dried over anhydrous sodium sulfate. The volume of the above solution was reduced tenfold by evaporation of the methylene chloride at room temperature and reduced pressure. The major product was purified by preparative gas chromatography (gc) using a 10% Carbowax 20M on Chromosorb W copper column (0.25 in. × 3 ft) at 175° with helium carrier. Injector and detector temperatures were maintained at 235°. The pure compound was collected in an ice-cooled Pyrex tube covered with aluminum foil.

B.—A 50–100 mg sample of cellulose, D-glucose (Calbiochem, La Jolla, Calif.) or levoglucosan (prepared and purified by the procedure of Ward[9]) was placed in a small Pyrex tube (0.25 × 3 in.) and covered with a layer of clean glass wool 0.125 in. thick. On top of this layer was placed a second one, 0.5 in. thick, containing 100 mg of the additive. The tube was introduced into the system detailed above; pyrolysis conditions and work-up procedure were the same as previously described.

Analyses.—Both the preparative column and a 5% SE-30 on Chromosorb W glass column at 100° were used for analytical gc. Carbon and hydrogen analyses by the ultramicro method[10] and molecular weight by osmometry with chloroform as solvent were determined at the Microchemical Analytical Laboratory, University of California, Berkeley. Additional molecular weight data were obtained using the Rast freezing point lowering of camphor method.[11] Mass and infrared spectra were obtained on the neat material. For ultraviolet spectra, solvents were *n*-hexane spectrograde (Matheson Coleman and Bell) and ethanol (95%), distilled immediately before analysis. Proton nmr (pmr) and carbon-13 nmr (^{13}C nmr) spectra were obtained in $CDCl_3$ for the unknown. The ^{13}C nmr spectrum of levoglucosan was determined in water. Refractive index, optical activity, and optical rotatory dispersion (ORD) were also measured.

Instrumentation.—Two gc instruments were used: a Packard Model 7831 with a flame ionization detector and a splitter of ratio 50:1 when used preparatively and an Aerograph Model 1520 with thermal conductivity detector. The pmr spectra were obtained on a Varian HA-60 nmr spectrometer equipped with a variable-temperature probe and on a Varian HA-100 equipped with a proton decoupler. A 14-kG instrument (home built, Department of Chemistry, University of California, Berkeley) was used for the ^{13}C nmr spectrum of the unknown, and a Varian HA-100 nmr spectrometer for the spectrum of levoglucosan. Other instruments used were a Microlab Model 301 osmometer, a Consolidated Electrodynamics Corp. Model 21103B mass spectrometer, Perkin-Elmer Model 337 and Unicam Model SP-800 spectrophotometers, a Bausch and Lomb 33-45-58 refractometer, a Zeiss LEP-A2 polarimeter, and a Cary Model 60 recording spectropolarimeter.

Results

The gas chromatogram of the methylene chloride extract showed the presence of a major product constituting about 90% of the solute. This product, after collection from either preparative gas chromatograph, was shown to be pure both by reinjection into the same column and by using the other column and separation conditions.

As collected, the compound was a faintly greenish-yellow liquid ($n^{25}D$ 1.5084) which darkened during several days' storage, even under refrigeration. Elemental analysis of both a freshly prepared sample and one stored for 10 days showed essentially identical results: C, 57.04; H, 4.85.

The initial molecular weight obtained by the Rast method, 165, appeared unreasonably high. Quantitative determination by gc of the compound in the camphor mixture showed that its amount was reduced to about 75% of the original on melting the mixture (1 min at 180°, in order to obtain maximum homogeneity) and that heating the mixture further in the melting point determination reduced the amount to 50%. This, and the fact that no smaller products were detected by gc, indicated that the material was polymerizing on heating. Repetition of the melting point determination on the same sample gave a molecular weight of about 250.

(5) Y. Tsuchiya and K. Sumi, *J. Appl. Polym. Sci.*, **14**, 2003 (1970).
(6) D. P. C. Fung, Y. Tsuchiya, and K. Sumi, *Wood Sci.*, **5**, 38 (1972).
(7) F. A. Wodley, *J. Appl. Polym. Sci.*, **15**, 835 (1971).
(8) A. E. Lipska and G. E. McCasland, *ibid.*, **15**, 419 (1971).
(9) R. B. Ward in "Methods in Carbohydrate Chemistry," Vol. II, R. L. Whistler and M. L. Wolfrom, Ed., Academic Press, New York, N. Y., 1963, p 394.
(10) C. W. Koch and E. E. Jones, *Mikrochim. Acta*, **4**, 734 (1963).
(11) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longman Group Limited, London, 1970, p 1037.

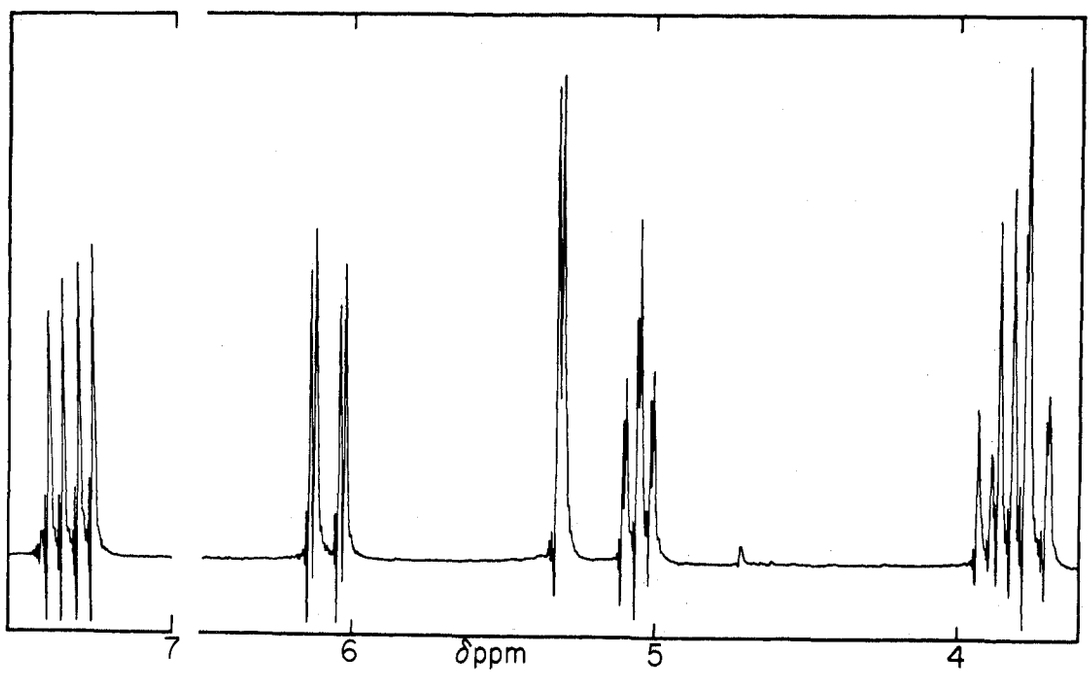


Figure 1.—100-MHz pmr spectrum of levoglucosenone in $CDCl_3$: δ in parts per million from internal TMS.

By osmometry, a freshly prepared sample and one which was kept refrigerated in the dark for 2 days (in which no detectable color change was observed) each gave a molecular weight of 131. A sample which was kept under similar conditions but for 10 days, and during this period was exposed to light several times at room temperature, showed a distinct color darkening and gave a molecular weight of 139.

Mass spectroscopic analysis showed the major fragment at *m/e* 39. The main peaks (>25% of the base mass) were *m/e* (rel intensity) 98 (52), 96 (43), 68 (61), 53 (58), 42 (43), 41 (39), 39 (100), 29 (75), 27 (42), 26 (28).

The infrared spectrum of the neat compound exhibited absorptions at the following frequencies: 2990, 2900, 1720, 1700, 1610, 1380, and 1100 cm^{-1}.

Ultraviolet spectra showed an absorption of λ_{max} 211 mμ (log $\epsilon^{1\%}_{1\,cm}$ 2.82) in *n*-hexane and λ_{max} 218 mμ (log $\epsilon^{1\%}_{1\,cm}$ 2.78) in 95% ethanol. In both solvents there was a second, much smaller, absorption, λ_{max} 275 mμ (log $\epsilon^{1\%}_{1\,cm}$ 1.5). The maximum at the shorter wavelength in both solvents obeyed the Beer–Lambert law for concentrations smaller than 10^{-4} *M*. It was difficult to determine accurately this behavior for the weaker absorption at the longer wavelength.

The 100-MHz pmr spectrum of a deuteriochloroform solution at room temperature is shown in Figure 1. Integration of the proton signals showed the presence of six nonequivalent protons. The pmr spectrum displayed no temperature dependence over the range of 25–65°. In addition, no change in the spectrum was observed when it was determined in the presence of deuterium oxide, even after 30 min at 30°.

A pmr spectrum in deuteriochloroform of the methylene chloride extract which, based on gc, consisted of the major product to an extent of about 90%, revealed the presence of the same peaks as in the purified compound.

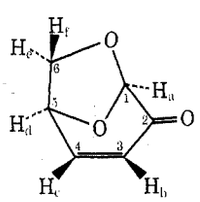
The 14-kG proton-noise decoupled cmr spectrum of the pure compound in deuteriochloroform is shown in Figure 2a. The spectrum shows six different carbons each of which appears as a sharp singlet.

The compound was highly optically active, with a specific rotation of $[\alpha]^{25}D$ −460° (*c* 1.0, $CHCl_3$). No change in activity was observed as a function of time.

The ORD determination showed that the shorter wavelength uv band is optically active and exhibits a positive Cotton effect curve (Figure 3).

Discussion

On the basis of these results the correct structure of the compound is 1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one (levoglucosenone) (IV).



IV

We wish to show how this structure follows from the results and to suggest a mechanism which describes the formation of IV from I.

The formation of IV is qualitatively independent of the acid used as an additive. In our experiments the same compound was isolated whether $NH_4H_2PO_4$, NaH_2PO_4, or $NaHSO_4$ was added. This fact eliminated the possibility that the compound contained elements other than carbon, hydrogen, and oxygen, and hence on the basis of the elemental analysis, the compound has the empirical formula $(C_2H_2O)_n$ (calcd C, 57.14; H, 4.76).

The increased molecular weight on standing (with no change in elemental analysis) implies that even the lowest value observed, 131, was high as a result of some polymerization. With $n = 3$ in the empirical formula, *viz.*, the molecular formula $C_6H_6O_3$, the molecular

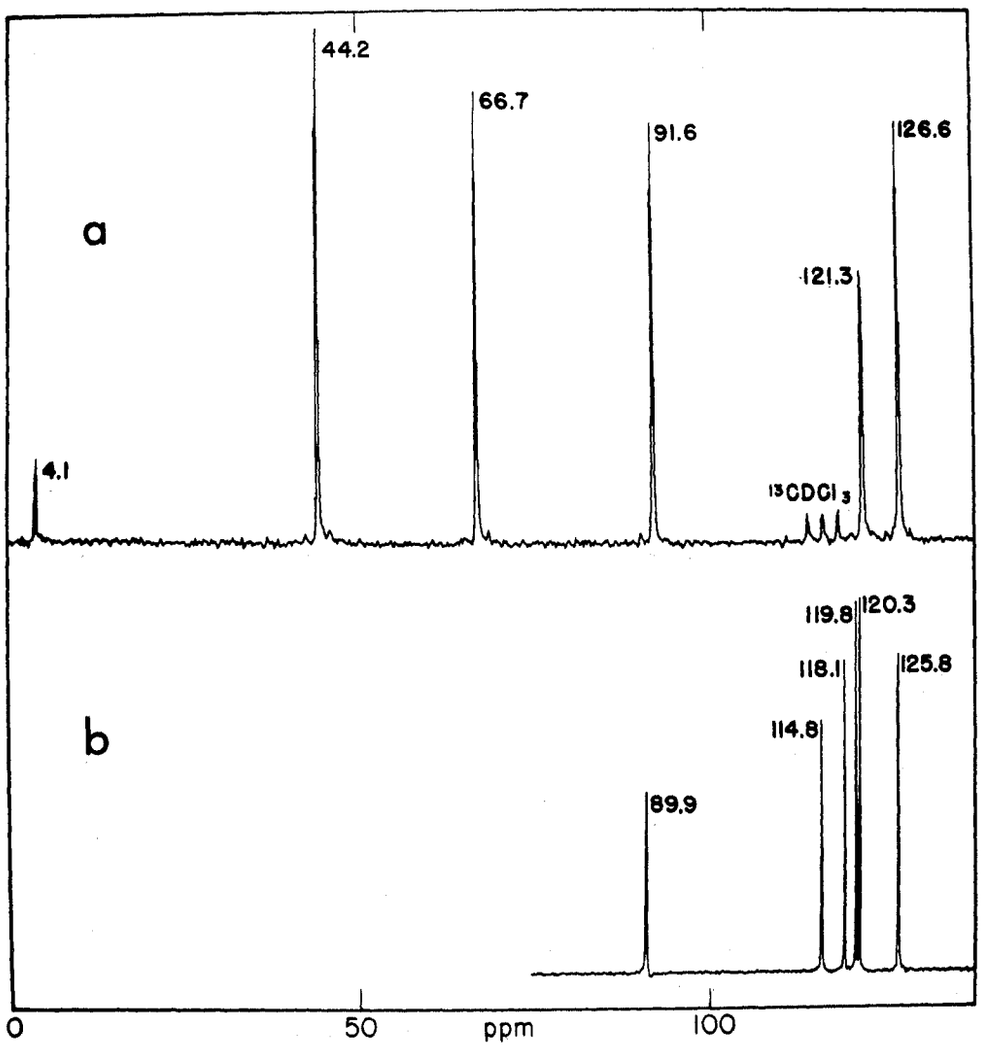


Figure 2.—Proton-noise decoupled ^{13}C nmr spectra (chemical shifts calculated from external CS_2): (a) levoglucosenone; (b) levoglucosan.

weight is 126. Then, the presence of 8, 19, and 47% by weight of an assumed dimer would cause an increase in the average molecular weight to 131, 139, and 165, respectively. This last value, resulting from heating during the Rast procedure, is in good agreement with quantitative gc determination.

Of the major peaks in the mass spectrum, the highest value of m/e is 98, with isotope peaks at P + 1 and P + 2 corresponding to the formula $C_5H_6O_2$. However, the spectrum does show small (~0.1%) peaks at higher m/e, including 126, not clearly attributable to impurities. In any case, mass spectra do not necessarily show significant parent peaks, and without additional data the value 98 only serves to set a lower limit on the molecular weight.

The infrared spectrum shows the presence of a CH_2 group (2900, 2990 cm^{-1}), C=C (1380, 1610), COC (1100), and most significantly a carbonyl group, probably conjugated to a double bond (1700, 1720). This carbonyl absorption is in conflict with the reported ir interpretation for III.

Strong support for the presence of a conjugated system emerges from the ultraviolet spectrum. The wavelengths of the two maxima and the values of the molar absorptivity are characteristic of α,β-unsaturated carbonyl compounds. The bathochromic shift observed for the higher maximum when going from a

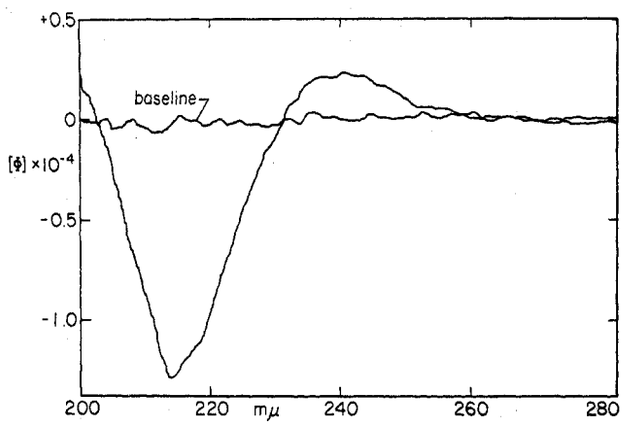


Figure 3.—ORD spectrum of levoglucosenone in n-hexane (concentration 2×10^{-3} g/100 ml).

nonpolar (n-hexane) to a polar one (95% ethanol) is normal behavior for the $\pi \rightarrow \pi^*$ transition in α,β-unsaturated carbonyl compounds. Such compounds are also known to dimerize under the influence of heat or light.[12]

The pmr spectrum (Figure 1) together with the above data permitted us to write a structure for the molecular

(12) D. J. Trecker in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 72.

formula $C_6H_6O_3$. The assignments of H_a through H_d are straightforward; those of H_e and H_f are based on their coupling constants with H_d and the dihedral angles (about 30° and 80°, respectively) as shown in a Dreiding model. The observed coupling constants agree well with values calculated for similar angles.[13] The entire spectrum interpretation is shown in Table I.

TABLE I

INTERPRETATION OF THE 100-MHz PMR SPECTRUM OF IV

Proton	δ^a	$J_{H,H}$,[b] Hz
H_a	5.31	a,b = 1.7[c]
H_b	6.09	b,c = 10.1; a,b = 1.7[c]
H_c	7.34	b,c = 10.1; c,d = 4.8
H_d	5.05	c,d = 4.8; d,e = 4.8; d,f = 1.0
H_e	3.87	d,e = 4.8; e,f = 6.6
H_f	3.74	d,f = 1.0; e,f = 6.6

[a] Chemical shifts in parts per million from internal TMS. [b] Absolute values of proton–proton coupling constants in hertz. [c] Long-range coupling constant (through four bonds) as found in similar α,β-unsaturated cyclic carbonyl systems (see, *e.g.*, ref 13, p 312).

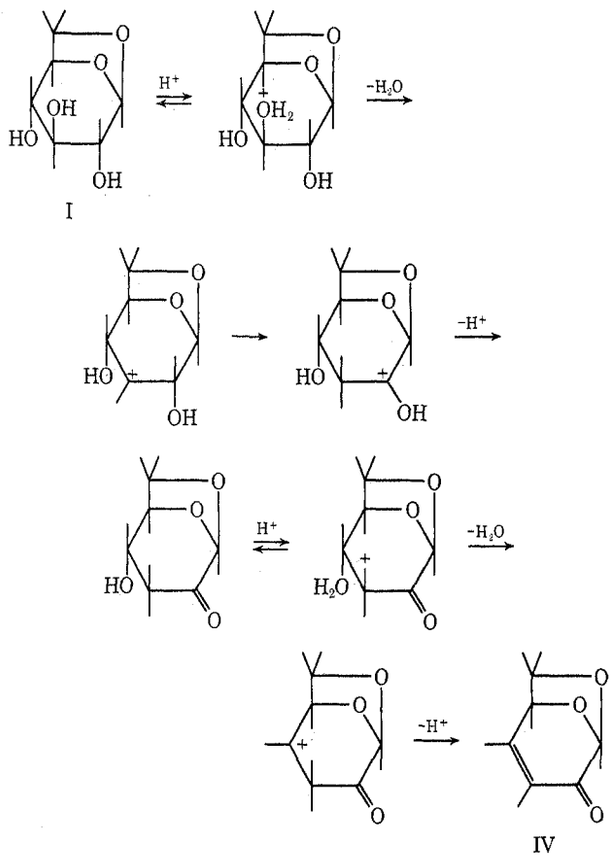
The values given were verified by proton–proton decoupling experiments.

The proton-noise decoupled ^{13}C nmr spectrum (Figure 2a) shows the presence of six different carbons. The signal at δ 4.1 ppm (upfield from CS_2) is in good agreement with the chemical shift of the carbonyl carbon in α,β-unsaturated ketones somewhat shielded by the two oxygens on the α' carbon.[14] Carbons 3 and 4 appear as olefinic carbons conjugated to a carbonyl group at 66.7 and 44.2 ppm, respectively.[15] Carbon 1 appears at 91.6 ppm and is in good agreement both with the acetal carbon of β-pyranosides[16] and with carbon 1 of I (Figure 2b). Carbons 5 and 6 appear at δ 121.3 and 126.6, respectively, in the region of the reported chemical shifts for the corresponding carbons in a pyranose ring.[17] Carbon 6 appears at somewhat lower field than in glucose because of the deshielding effect accompanying the transformation from a hydroxyl to an ether group.[17] In an off-center resonance proton decoupling experiment on I only one signal (at 125.8 ppm) appeared as a triplet; all the others were doublets. This permitted us to assign the triplet to carbon 6 and indicated that the 126.6 peak in IV was likewise carbon 6.

The ^{13}C nmr data for carbons 1, 5, and 6 in IV reflect the similarity between the latter and I. Moreover, the ^{13}C chemical shift of carbon 1 in IV indicated that this carbon still had the same configuration as in I, *i.e.*, the β configuration; α-anomeric carbon appears at higher field, around 100 ppm.[17]

IV was formed as a major product in the acid-catalyzed pyrolysis of cellulose. In addition, when cellulose, D-glucose, and levoglucosan were pyrolyzed in the absence of additives and the products were passed through an acidic filter while still in the vapor phase, IV was found to be the major product. In all these cases little or no I was found. On the other hand, when the filter contained no additives, the major constituent of the tar fraction was I, whether the sample pyrolyzed was cellulose, glucose, or levoglucosan itself. Results to date neither establish nor contradict a route by way of I for the formation of IV from the other carbohydrates. Further work is in progress.

The following mechanism can be drawn for the acid-catalyzed transformation of I to IV.



According to the proposed mechanism, asymmetric carbons C_1 and C_5 are not involved in the transformation process; thus if one starts with levoglucosan ($[\alpha]^{25}D$ −55° (*c* 0.5, H_2O)) the product levoglucosenone must also be optically active.[18] The results of the optical activity measurement were consistent with the mechanism on this point.

The third step in the proposed mechanism shows a 1,2-hydride shift from carbon 2 to the carbenium[19] center at carbon 3. This is justified by the formation of a more stable hydroxycarbenium ion from the secondary ion initially formed at carbon 3.

An alternate 1,2-hydride shift forming a hydroxycarbenium ion is possible from carbon 4, but in the former case (from carbon 2) the ion has additional stability owing to the proximity of oxygen. Carbenium ions may be stabilized by oxygen on adjacent carbon by overlap of the filled 2p orbital of the oxygen with the empty 2p orbital of the sp^2-hybridized carbon; models show that the carbon-6 oxygen is spatially in a favorable position to so stabilize the carbon-2 carbenium center. Possibly the alternate route also occurs to some degree; this would result in the formation of 1,6-

(13) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 281.

(14) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

(15) D. H. Marr and J. B. Stothers, *ibid.*, **43**, 596 (1965).

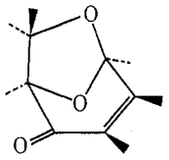
(16) D. E. Dorman and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4463 (1971).

(17) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(18) According to the proposed mechanism, 1,6-anhydrohexoses of the D family would yield levoglucosenone, while L-anhydrohexoses would result in the formation of its mirror image.

(19) For definition see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

anhydro-2,3-dideoxy-Δ^2-β-D-pyranosen-4-one (isolevoglucosenone), a structural isomer of IV. A search for this compound in the pyrolysate is in progress.



V

According to the above mechanism, the transformation of I to IV does not involve a configuration change at asymmetric carbon 5. Models show that the enone of the D series is of a right-handed chirality. If IV is of this configuration, its skewed transoid α,β-unsaturated carbonyl system, which is inherently dissymmetric, should be manifested in a positive Cotton effect in the ORD spectrum.[20] The results showed this to be the case.

In addition to the elucidation of the structure of IV, two further questions require discussion. (1) Is IV a direct product of the pyrolysis process or a secondary compound formed during purification? (2) Is IV the same product isolated by the two other groups?

With respect to question 1, it is exceedingly unlikely that the mild conditions used during the work-up process before injection into the gc would alter a compound formed during the severe pyrolysis process. Isolation of the same compound using two different column packings and operating conditions strongly indicate that the product was not formed in the gc. Furthermore, a pmr spectrum obtained on the methylene chloride extract indicated that the identified end product is the major component of the tar mixture.

With respect to question 2, the principal preparation procedure of all three groups was quite similar. Although no direct comparison of the products was possible, our pmr spectrum and the comparable (*i.e.*, major) peaks of the mass spectrum corresponded closely to those observed for II[21] and III.[22] Furthermore, although we did not see the ir spectrum for III, that of II was fundamentally equivalent to that for IV. Finally, a sample of our material injected into the gc used by Lipska showed a retention time consistent with that found for III. Thus it is unlikely that more than one compound is involved.

Registry No.—I, 498-07-7; II, 25073-23-8; III, 37112-30-4; IV, 37112-31-5.

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Terpenoids. LXVIII.[1] 23ξ-Acetoxy-17-deoxy-7,8-dihydroholothurinogenin, a New Triterpenoid Sapogenin from a Sea Cucumber[2]

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A new triterpenoid sapogenin was isolated and found to be 3β,20ξ-dihydroxy-23ξ-acetoxylanost-9(11)-ene-18-carboxylic acid lactone (18 → 20) (**5**). The functionality at C-23 is unprecedented in sapogenins from the sea cucumber.

Sapogenins from sea cucumbers have been very actively investigated in recent years. Structure proof of many of these compounds has been carried out.[1,5-12] All of these sapogenins have been found to be triterpenoids with a lanostane skeleton. These have included 22,25-oxidoholothurinogenin (**1a**) and its deoxy analog **1b** from *Actinopyga agassizi*[6] obtained by rigorous acid cleavage of saponins obtained from the Cuvier glands. Milder hydrolytic conditions[7] led to the isolation of 12β-methoxy-7,8-dihydroholothurinogenins of which **2** is an example. Enzymatic hydrolysis has led to a 12α-hydroxy analog. Using vigorous acid hydrolysis of the saponins from other sea cucumbers our group and others have found lanostane derivatives

(1) For part LXVII see P. Roller, B. Tursch, and C. Djerassi, *J. Org. Chem.*, **35**, 2585 (1970).

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