A Novel Hydroxylactone from the Lewis Acid Catalysed Pyrolysis of Cellulose

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The novel δ-lactone (**1**) of (3*R*,5*S*)-3-hydroxy-5-hydroxymethyltetrahydrofuran-3-carboxylic acid (**2**) has been isolated from tar produced by pyrolysis of cellulose doped with zinc chloride. Using Curie-point pyrolysis-g.l.c. analysis, the lactone was shown to be a significant product of the pyrolysis of cellulose in the presence of a wide variety of other Lewis acids, but not in the presence of protic acids or copper(II) chloride. The lactone (**1**) was readily hydrolysed to the acid (**2**) and yielded the methyl ester (**3**) on methanolysis.

The pyrolysis of cellulose has been extensively studied because the tar produced is a potential chemical feedstock,[1] and a source of optically pure starting materials for synthesis.[2,3] At temperatures above 300 °C cellulose undergoes depolymerisation by intramolecular transglycosylation to yield levoglucosan (1,6-anhydro-β-D-glucopyranose) and minor amounts of other anhydroglucoses.[4] The presence of acids in admixture with the cellulose profoundly influences the course of pyrolysis. In the presence of protic acids, pyrolytic dehydration, rearrangement and charring reactions are substantially accelerated. Thus the pyrolysis of cellulose doped with orthophosphoric acid gives levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) as the predominant volatile carbohydrate product in yields of 2—12%.[3,5] Pyrolysis in the presence of Lewis acids also results in considerable dehydration and charring, but levoglucosenone is produced in reduced yield (*ca.* 0.3%) and is no longer the major product.[6]

Studies in this laboratory have shown that cellulose is converted into a liquid product, composed largely of oxygenated aromatics, by thermolysis in aqueous phenol in the presence of various catalysts.[7] Such liquefactions occur in the same temperature range that cellulose undergoes pyrolytic depolymerisation. A comparative study on the effects of a range of inorganic additives on the pyrolytic depolymerisation of cellulose was undertaken, in expectation that the results would help elucidate the mechanism by which cellulose is liquefied.

For this comparative study, samples were subjected to analysis by Curie-point pyrolysis-gas-liquid chromatography (c.p.p.–g.l.c.).[8] In this method the sample is heated very rapidly to the desired temperature (358 °C) and, because the sample is suspended inside the head of the g.l.c. column, the volatile products are swept directly from the heated wire onto the column packing by a stream of inert gas, thus minimising the extent to which the primary pyrolysis products undergo secondary reactions.

Results and Discussion

An example of the f.i.d. trace obtained from c.p.p.–g.l.c. of a Lewis acid-doped cellulose is shown in the Figure. The pyrolysate contains 2-furaldehyde, levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose, 5-hydroxymethyl-2-furaldehyde, levoglucosan, and also an unknown compound (**1**). The composition of pyrolysates from cellulose doped with $CrCl_3$, $FeCl_3$, $AlCl_3$, $ZnCl_2$, $NiCl_2$, $CoCl_2$, $MnCl_2$, and $SnCl_2$ were qualitatively similar. All contained a substantial proportion of unknown (**1**), but this unknown was not a significant component when protic acids (H_3PO_4, NaH_2PO_4, and $NaHSO_4$) or $CuCl_2$ were used as additives.

Almost identical product mixtures were obtained by tube-furnace pyrolysis–g.l.c.–m.s. (see Experimental section), and
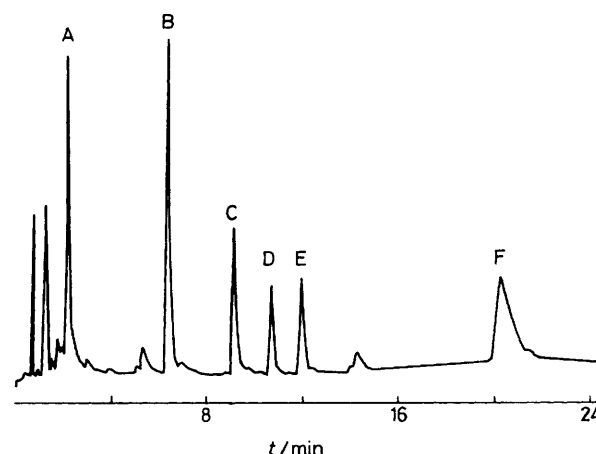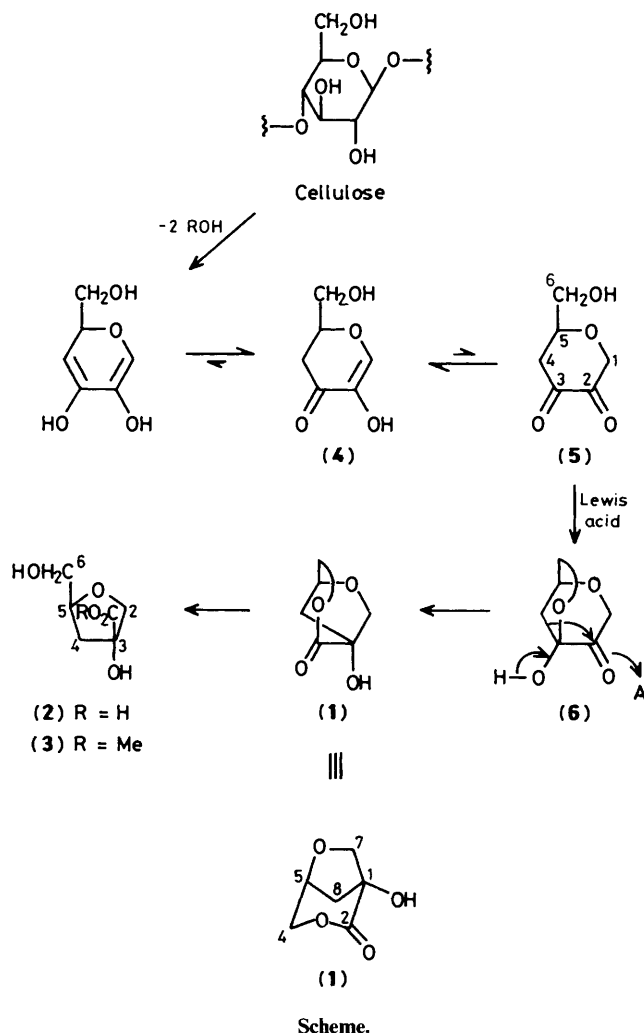

Figure. C.p.p.–g.l.c. trace from cellulose containing 5% zinc chloride; A, 2-furaldehyde; B, levoglucosenone; C, lactone (**1**); D, 1,4:3,6-dianhydro-α-D-glucopyranose; E, 5-hydroxymethyl-2-furaldehyde; F, levoglucosan

thus a mass spectrum of unknown (**1**) could be obtained. Chemical ionization m.s. showed its molecular weight to be 144, suggesting a formula of $C_6H_8O_4$. No molecular ion was observed on e.i.–m.s., so an accurate mass determination could not be undertaken.

Initial attempts to isolate unknown (**1**) following conventional tube-furnace pyrolysis were frustrated by a sharp decline in the yield of this compound when the scale of pyrolysis was increased beyond 0.5 g of substrate, and by its facile decomposition. It could not be recovered after chromatography of the tar on silica gel, and its concentration in crude pyrolysates decreased markedly on storage for a few days. We therefore resorted to preparative g.l.c. which yielded sufficient pure (**1**) for [1]H n.m.r. and i.r. spectra to be obtained. The presence of a δ-lactone moiety in unknown (**1**) was suggested by a carbonyl absorption at 1 750 cm^{-1} in the i.r. spectrum[9] and by its ready hydrolysis in solution (*e.g.* from moisture in [$^2H_6$]acetone while awaiting [13]C n.m.r. spectroscopy) to a product (**2**) that was immobile in t.l.c. and had a [13]C n.m.r. resonance at 175.5 p.p.m., consistent with the presence of a carboxylic acid group.

The lactone (**1**) reacted readily with methanolic hydrogen chloride to give the more stable methyl ester (**3**) that could be isolated chromatographically. The ester (**3**) had a molecular weight of 176 (c.i.–m.s.) and a molecular formula of $C_7H_{12}O_5$ (accurate mass on M^+ ion) indicating that each molecule of the lactone (**1**) had reacted on methanolysis with one molecule of methanol. The presence of an ester carbonyl was confirmed by i.r. (1 730 cm^{-1}) and [13]C n.m.r. (174.4 p.p.m.) data.

Scheme.

$C(4)H_2-C(5)H-C(8)H_2$ and the 'isolated' methylene $C(7)H_2$ (now identified by the 3,6-dioxabicyclo[3.2.1]octane numbering system). The interproton couplings, however, are altered from those in ester (3) as a result of the configuration induced by the bridging lactone ring. An absence of coupling between 5-H and 8a-H, requiring a dihedral angle of *ca.* 90°, and W-coupling of 1.5 Hz between 4e-H and 8e-H were consistent with geometries found on examination of a molecular model of lactone (1). The C-7 protons of lactone (1) are in a stereochemical environment similar to that of the C-6 protons of 1,6-anhydrohexopyranoses and likewise exhibit reduced geminal coupling (*i.e.*, $J_{7,7'}$ 8.9 Hz, *cf.* $J_{6,6'}$ in the 1,6-anhydrides of 7—8.5 Hz[12]).

The lactone (1) is an anhydride of an isosaccharinolactone. Isosaccharinic acids are the products of benzylic acid-type rearrangements of α-dicarbonyl compounds derived from hexoses and are normally formed through degradation of sugars in hot alkali.* We propose that lactone (1) is formed by a similar rearrangement as shown in the Scheme. Two eliminations from a D-glucopyranosyl residue in the cellulose chain lead to 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (4), a known pyrolysis product.[4] The enolone (4) is the mono-enol tautomer of the 2,3-diketone (5), which may be envisaged as forming a hemiketal (6) and undergoing a benzylic acid-type rearrangement to yield the lactone (1). The product formed by this mechanism retains a chiral centre at C-5 [carbohydrate numbering, shown in structure (5)]. Retention of stereochemistry at this centre has been observed in the formation of other pyrolysis products [*e.g.* levoglucosenone[3] and enolone (4)[4]]. A new chiral centre is formed at the branching point, the stereochemistry of which is defined by the hemiketal bridge. Thus we are able to assign an absolute stereochemistry to lactone (1) and ester (3) and would predict that both compounds would be optically active. In fact ester (3) was observed to have an optical rotation of +10°. Formation of hemiketal (6) bridging C-3 and C-6 (carbohydrate numbering) is consistent with the enhanced production of 3,6-anhydroglucose from cellulose by pyrolysis in the presence of the Lewis acid zinc chloride,[6] but an alternative pathway involving formation and rearrangement of a 2,6-hemiketal would lead to the same product.

The structure of lactone (1) is unusual amongst pyrolysis products in that it contains a branched chain and therefore cannot be formed through the dehydration and transglycosylation reactions that predominate in the pyrolysis of cellulose. Its formation indicates that other types of reactions may, under favourable conditions, play a significant role in the pyrolytic process.

The [13]C n.m.r. spectrum of the ester (3) contained resonances assigned, with the aid of a GASPE experiment,[10] to two oxygenated methylene carbon atoms (78.8 and 64.3 p.p.m.), one non-oxygenated methylene carbon (42.1 p.p.m.), one oxygenated methine carbon (81.0 p.p.m.), and one quaternary carbon (82.0 p.p.m.). The [1]H n.m.r. spectrum revealed the presence of two hydroxy groups. The only structure consistent with these data and with the [1]H n.m.r. coupling pattern is the substituted tetrahydrofuran (3). The $C(6)H_2-C(5)H-C(4)H_2$ spin system was revealed by geminal coupling between the C-6 protons (δ 3.88 and 3.62 p.p.m.; $J_{6,6'}$ 12.0 Hz) and between the C-4 protons (δ 2.35 and 2.04 p.p.m.; $J_{4,4'}$ 12.9 Hz), and by vicinal coupling of each of these four protons to the sole methine proton (δ 4.34 p.p.m.; $J_{4,5}$ 10.2, $J_{4',5}$ 5.7, $J_{5,6}$ 2.5, and $J_{5,6'}$ 4.8 Hz). The remaining 'isolated' methylene protons, on C-2 (δ 4.23 and 3.85 p.p.m.) showed geminal coupling ($J_{2,2'}$ 9.4 Hz) and a small long-range coupling ($J_{2',4'}$ 0.9 Hz). Additional support for the proposed structure comes from the remarkably deshielded ^{13}C resonance of methylene C-2, at 78.8 p.p.m., that may be compared with the resonance position for C-4 in apiofuranose (3-*C*-hydroxymethyltetrofuranose) derivatives. This latter carbon is similarly part of a tetrahydrofuran ring and adjacent to a tertiary alcohol centre, and resonates at *ca.* 74 p.p.m.[11] Since the ester (3) has been formed by cleavage of a δ-lactone, the carboxyl substituent at C-3 and the hydroxymethyl group at C-5 must be on the same side of the tetrahydrofuran ring.

The [1]H n.m.r. spectrum of lactone (1) revealed the spin system

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* An anhydroisosaccharinic acid with the structure of the acid (2) but of undefined stereochemistry has been characterised as a product from hydrolysis of cellulose under acidic and basic conditions. See G. Peterson and O. Samuelson, *Acta. Chem. Scand., Ser. B*, 1976, **30**, 27, and references therein.

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packed with 5% Pluronic F-68 on Gas-Chrom Q (100—120 mesh) using the same temperature program as above. A Pye GCV fitted with an outlet splitter was used for preparative g.l.c. A 1.5 m × 4 mm i.d. column of 7% Pluronic F-68 on Gas-Chrom Q (100—120 mesh) was programmed from 160 to 210 °C at 5 °C min⁻¹. ¹H N.m.r. spectra were obtained on a Varian XL200 at 200 MHz. ¹³C N.m.r. spectra were obtained at 20 MHz on a Varian FT-80A and at 22.5 MHz on a Bruker AC-200. For i.r. spectroscopy a Perkin-Elmer 580 was used. T.l.c. analyses were done on aluminium-foil-backed silica gel plates (Merck Cat. No. 5554).

Pyrolysis.—Cellulose powder (Whatman CF-11; 9.5 g) was suspended in ethanol (*ca.* 20 ml) containing metal chloride (0.5 g). The bulk of the solvent was removed on a rotary evaporator and then the cellulose was held at 60 °C overnight.

For preparative experiments, the cellulose was pyrolysed under flowing nitrogen in a preheated tube furnace. The details of this method have been described previously.[13]

Curie-point pyrolysis requires that the sample be held in contact with the pyrolysis wire. This was best achieved by hammering one end of the wire flat, flaming it, and then folding the flattened end over a small quantity of cellulose substrate and crimping tightly. Wires with Curie points of 480 and 358 °C were used interchangeably. Pyrolysis was carried out directly above the column packing under flowing nitrogen with a pyrolysis time of 4 s.

For pyrolysis g.l.c.–m.s. a sample of treated cellulose (*ca.* 0.1 mg) was weighed into a platinum dish. This was purged with nitrogen and then inserted into the furnace which was preheated to 320 °C. The pyrolysate was swept through a short, heated tube onto the column. The 70 eV total-ion-current trace from the mass-spectrometer was very similar to the f.i.d. trace obtained on Curie point pyrolysis-g.l.c. Thus the unknown (1) could be positively identified and its mass-spectrum obtained.

(3R,5S)-3-*Hydroxy-5-hydroxymethyltetrahydrofuran-3-carboxylic acid* (2) *and its* δ-*Lactone*, (1R)-1-*Hydroxy-3,6-dioxabicyclo*[3.2.1]*octan-2-one* (1).—Cellulose impregnated with 5% (w/w) ZnCl₂ was pyrolysed in 0.5 g batches at 350 °C. After each pyrolysis the tar was washed from the furnace liner with acetone. The acetone solutions were combined and evaporated to near dryness. Preparative g.l.c. separation of aliquots of this solution provided a pure sample of the title lactone (1) (1 mg), obtained as a syrup, having the same retention and mass spectrum as the unknown found through pyrolysis g.l.c.–m.s. (1); δ(CDCl₃) 4.54 (1 H, ddd, $J_{5,8e}$ 5.9, $J_{4e,5}$ 1.4, $J_{4a,5}$ 1.6, $J_{5,8a} \sim 0$ Hz, 5-H), 4.45 (1 H, ddd, $J_{4a,4e}$ 11.9, $J_{4e,8e}$ 1.5 Hz, 4e-H), 4.30 (1 H, dd, 4a-H), 4.08 (1 H, d, $J_{7,7'}$ 8.4 Hz, 7-H), 3.75 (1 H, d, 7'-H), 3.50 (1 H, OH, br s), 2.54 (1 H, ddd, $J_{8a,8e}$ 11.6 Hz, 8e-H), and 2.19 (1 H, d, 8a-H); R_F 0.25 (hexane–ethyl acetate, 1:1); v_{max}(film) 1 750 cm⁻¹ (C=O); *m/z* (e.i.) 116 (6%), 144 (4), 98 (1), 96 (6), 86 (11), 85 (32), 77 (23), 70 (49), 69 (72), 58 (32), 57 (53), 43 (100), and 41 (74); and *m/z* (c.i.) 145 (100%, *M* + 1).

The lactone (1) hydrolysed spontaneously in moist acetone solution over several days. The resulting acid (2) was immobile on t.l.c. and could not be eluted from either packed or capillary g.l.c. columns. ¹³C N.m.r. (22.5 MHz, [²H₆]acetone) 175.5 (CO₂H), 82.0 (C-3), 81.0 (C-5), 78.8 (C-2), 64.3 (C-6), and 42.1 (C-4); and v_{max}(film) 1 730 cm⁻¹.

Methyl (3R)-trans-3-*Hydroxy-5-hydroxymethyltetrahydrofuran-3-carboxylate* (3).—Cellulose impregnated with 5%

(w/w) ZnCl₂ (5 g) was pyrolysed in 10 batches at 350 °C. After each pyrolysis the tar was washed from the furnace liner with acetone. The acetone solutions were combined and evaporated to near dryness. The residue was suspended in water (0.5 ml) and half applied to each of two C₁₈ reversed-phase silica cartridges (Sep-Pak, Waters) which had been washed with methanol then water. Each cartridge was eluted with water (2 ml). The combined eluates were evaporated to dryness and redissolved in anhydrous methanol (1 ml). This solution contained lactone (1) and 1,4:3,6-dianhydro-α-D-glucopyranose in roughly equal amounts (g.l.c.) and also a considerable amount of levoglucosan (t.l.c.; MeOH–CHCl₃, 1:9). Dry methanolic hydrogen chloride (1.0M; 30 µl) was added to the solution. After 2 h, g.l.c. analysis showed that the lactone (1) had been completely converted into the methyl ester (3). The solution was brought to pH 6 by addition of methanolic sodium hydroxide (0.75M) and applied to a column of silica gel which was eluted with ethyl acetate. The ester (3) streaked on silica gel chromatography and could not be completely resolved from the anhydroglucoses, but a fraction adjudged pure by g.l.c. and t.l.c. was obtained and yielded the syrupy ester (3) (5.5 mg, 0.1%); ¹H n.m.r. (CDCl₃) 4.34 (1 H, dddd, $J_{4,5}$ 10.2, $J_{4,5'}$ 5.7, $J_{5,6'}$ 4.8, $J_{5,6}$ 2.8 Hz, 5-H), 4.23 (1 H, d, $J_{2,2'}$ 9.4 Hz, 2-H), 3.88 (1 H, dd, $J_{6,6'}$ 12.0 Hz, 6-H), 3.85 (1 H, dd, $J_{2',4'}$ 0.9 Hz, 2'-H), 3.85 (3 H, OCH₃, s), 3.62 (1 H, dd, 6'-H), 3.60 (1 H, br s, 3-OH), 2.35 (1 H, dd, $J_{4,4'}$ 12.9 Hz, 4-H), 2.04 (1 H, ddd, 4'-H), and 1.73 (1 H, br s, 6-OH); ¹³C n.m.r. (20 MHz, CDCl₃) 174.4 (*CO₂Me*), 81.3 (C-3), 80.0 (C-5), 77.9 (C-2), 63.4 (C-6), 53.1 (OCH₃), and 40.8 (C-4); v_{max}(film) 1 740 cm⁻¹ (C=O); *m/z* (e.i.) 176 (0.3%, *M⁺*), 158 (2, *M⁺* − H₂O), 146 (3), 145 (15, *M⁺* − MeO), 128 (16), 127 (100), 85 (12), 83 (20), 59 (35), 55 (16), 43 (14); *M⁺*, 176.071 (C₇H₁₂O₅ requires 176.068), and *M⁺* − H₂O 158.057 (C₇H₁₀O₄ requires 158.058); *m/z* (c.i.) 177 (100%, *M* + 1); and $[\alpha]_D^{20}$ +10° (*c* 0.2, CHCl₃).

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