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Note

Identification of 3-hydroxy-6-methyl-2*H*-pyran-2-one from pyrolysis of phosphoric acid-treated cellulosic materials

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Pyrolysis of cellulosic materials proceeds through a complex series of chemical reactions, which provide a variety of compounds. In recent studies[1-3], 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (**1**, levoglucosenone) has been detected as a main product from the pyrolysis of cellulosic materials impregnated with an acid catalyst.

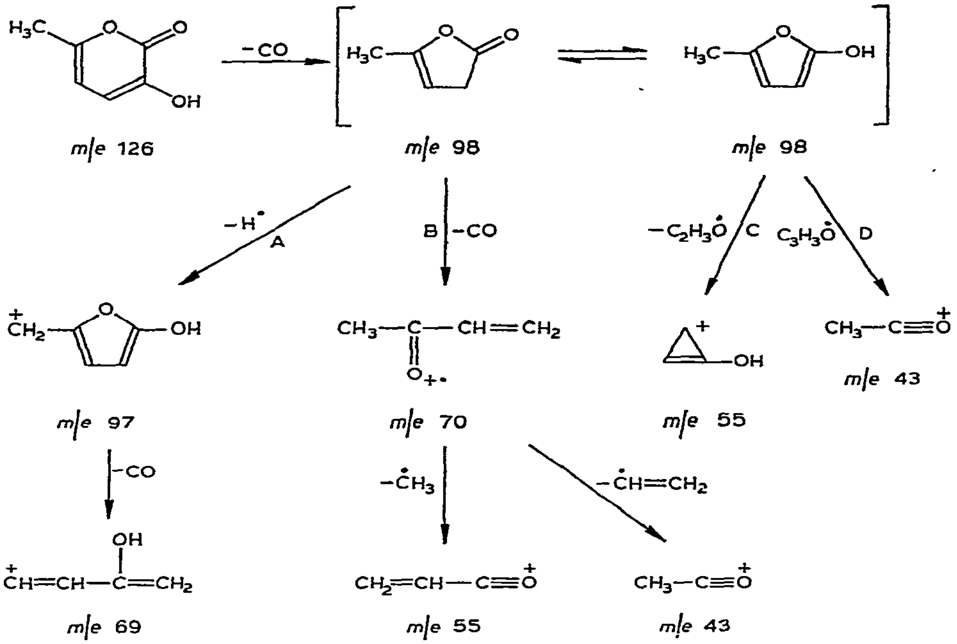
3-Hydroxy-6-methyl-2*H*-pyran-2-one (**2**), first prepared[4] by distillation of rhamnono-δ-lactone, reacts characteristically with $FeCl_3$, reduces Fehling's reagent, and turns violet by the action of light. Bromo and benzoyl derivatives of **2** have been prepared[4].

We now report on the isolation of **2** after acid-catalysed pyrolysis of cellulosic materials, and its characterisation.

Shafizadeh and Chin[2] showed that the fraction distilling at 55–60°/1.5 torr contained 96% (by g.l.c.) of **1**. Identification of the residual 4% is difficult, because the components are unstable and have the same molecular weight (126) as **1**.

T.l.c. of the pyrolysate fraction having b.p. 55–60°/1.5 torr revealed **1**, 2-furyl hydroxymethyl ketone, and 5-hydroxymethyl-2-furaldehyde, plus two other fractions, one of which (R_F 0.51, 0.2% of levoglucosenone fraction) was identified as 3-hydroxy-6-methyl-2*H*-pyran-2-one (**2**). The u.v. spectrum of **2** exhibited two absorption maxima (λ_{max} 302 and 240 nm) consistent with those expected for the α-pyrone chromophore, and the i.r. spectrum showed ν_{max} 3348 (OH), and 1692 and 1647 cm^{-1} $[{=}C(OH){-}\overset{|}{C}{=}O]$. The mass spectrum of **2** (Scheme 1) showed peaks at *m/e* 126 (100%) and 127 for M^+ and $(M + 1)^+$, and major fragmentation peaks at *m/e* 98, 70, 55, and 43 (*cf.* ref. 5).

The ^{1}H-n.m.r. spectrum (100 MHz, C_6D_6) of **2** contained signals at δ 6.06 (d, 1 H, $J_{4,5}$ 7.19 Hz, H-4), 4.97 (d, 1 H, $J_{4,5}$ 7.19 Hz, H-5), 1.48 (s, 3 H, Me), and 6.78 (bs, 1 H, OH). The doublet at δ 4.97 was further split by long-range coupling (0.87 Hz). The ^{13}C-n.m.r. spectrum (C_6D_6) of **2** contained signals at 162.11 (C-2),



Scheme 1. Mass-spectral fragmentation of 3-hydroxy-6-methyl-2*H*-pyran-2-one

151.87 (C-3), 115.65 (C-4), 103.47 (C-5), 140.66 (C-6), and 18.35 p.p.m. (Me).

All spectral data were identical with those of the authentic[4] **2**. The benzoyl and bromo derivatives of **2** had physical constants similar to those of the compounds reported by Votoček[4]. The mechanism of formation of **2** is not known; it could originate from the cellulose or from **1** after its formation.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. U.v. spectra were recorded with a Beckman DB-GT spectrophotometer, and i.r. spectra with a Perkin–Elmer 457 spectrophotometer. Mass spectra (70 eV) were obtained on a JMS-100-D spectrometer with direct sample introduction. ^{13}C-N.m.r. and ^{1}H-n.m.r. spectra were recorded with a JEOL-JNM-FX-100 spectrometer. T.l.c. was performed on Kieselgel 60 F_{254} (Merck) with benzene–ethyl acetate (1:1) and detection by u.v. light; R_F values: **1**, 0.60; **2**, 0.51; 2-furyl hydroxymethyl ketone, 0.39; 5-hydroxymethyl-2-furaldehyde, 0.22; and 0.18 (unknown). The products were eluted with chloroform. G.l.c. of the levoglucosenone fraction was performed using a glass column (1800 × 3.1 mm) packed with 10% of Carbowax 20-M on Chromosorb WAW (80–100 mesh), with an injector temperature of 210°, and the column temperature programmed from 140→210° at 4°/min; **2** had *T* 14 min.

The pyrolysis was carried out in a Pyrex flask, preheated to 300°, at 1–3 torr for ~30 min. The trap was kept at —78°.

*3-Hydroxy-6-methyl-2*H*-pyran-2-one* (**2**). — The levoglucosenone fraction[2] was kept at —20° for ~2 weeks. The crystals were collected, quickly dried between filter papers, and recrystallised from benzene, to yield **2**, m.p. 120–121°.

Anal. Calc. for $C_6H_6O_3$: C, 57.25; H, 4.76. Found: C, 57.17; H, 4.79.

*3-Hydroxy-6-bromomethyl-2*H*-pyran-2-one.* — To a mixture of **2** (1.26 g, 10 mmol), dibenzoyl peroxide (48 mg, 0.2 mmol), and dry CCl_4 (20 ml) warmed to boiling point, was added *N*-bromosuccinimide (1.77 g, 10 mmol). After boiling under reflux for 3 h, the mixture was filtered, and concentrated *in vacuo*, and the product was recrystallised from water, to yield the title compound (1.8 g), m.p. 148–149°; lit.[4] m.p. 147°.

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