

with dihydroxyphenyl derivatives. The reaction with adrenaline is illustrated in Fig. 2. At pH 8 Tabun is hydrolysed yielding hydrocyanic acid and dimethylamido phosphoric acid⁴. The more adrenaline present the less acid is produced and we explain this by postulating a phosphorylation of adrenaline during the hydrolysis.

The inhibitory effects of the reaction products on cholinesterase have been tested. A concentration of DFP which is more than 1000 times higher than that required to give 50 % inhibition does not give any inhibition at all when the DFP has been incubated with adrenaline for 10 hours or more; the concentration of adrenaline was 20 times the concentration of DFP. Similar results were obtained with Tabun.

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Diheterolevulosan III and IV

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The recent publication by Sattler *et al.*¹ prompts us to report the isolation of two new compounds which are probably isomerides of the previously known

diheterolevulosans I and II. The substances were isolated from the unfermentable residue from hydrochloric acid treated fructose² by fractionating the mixture on a column of animal carbon, using the gradient elution technique³ combined with fractional crystallisation. Both substances are non-reducing and difficult to hydrolyse, and on paper chromatograms they travel at about the same speed as diheterolevulosan II. The analytical data for one of the substances is consistent with its formulation as a diheterolevulosan (C₁₂H₂₀O₁₀). It has not been possible to analyse the second compound as yet owing to certain technical difficulties in the micro analytical department, but the periodic acid oxidation and the general properties of the substance indicate a diheterolevulosan type of structure.

Diheterolevulosan III, m.p. 279–281° ** (dec.), $[\alpha]_D^{20}$ –309° (water, *c* = 2), (Analysis: Found C, 44.5; H, 6.12. Calc. for C₁₂H₂₀O₁₀ C, 44.44; H, 6.18 %), consumes 4 moles of periodic acid and forms 2 moles of formic acid, and is thus probably an anomer of diheterolevulosan I. Acetate: M.p. 268–269° (sublimes), $[\alpha]_D^{20}$ –199° (chloroform, *c* = 2). Analysis: C, 50.2; H, 5.67. Calc. for C₂₄H₃₂O₁₆ C, 50.0; H, 5.55 %.

“Diheterolevulosan IV”, m.p. 240–242° (dec.), $[\alpha]_D^{20}$ –183° (water, *c* = 2), consumes 3 moles of periodic acid and forms 1 mole of formic acid. Acetate: M.p. 130–131°, $[\alpha]_D^{20}$ –159° (chloroform, *c* = 2).

A more detailed report will be published shortly in this journal.

Added in proof (29.7.52): Since this note was submitted for publication Wolfrom, Hilton and Binkley (*J. Am. Chem. Soc.* **74** (1952) 2867) have described a new di-D-fructose dianhydride “diheterolevulosan III” which appears to be identical with our “diheterolevulosan IV”. To avoid confusion we propose that our names “diheterolevulosan III” and “diheterolevulosan IV” should be interchanged.

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** All melting points uncorrected.

Diheterolevulosan III: Found C, 44.4; H, 6.14. Calc. for $C_{13}H_{20}O_{10}$ C, 44.4; H, 6.18%. Acetate: Found C, 50.1; H, 5.63. Calc. for $C_{24}H_{32}O_{16}$ C, 50.0; H, 5.55%.

Hydrolysis of the methyl ether of diheterolevulosan IV (m.p. 122–122.5°, $[\alpha]_D^{20} - 243^\circ$ (chloroform, $c = 2$) gave D-fructose 3,4,5-trimethylether (70% yield) identified by conversion to D-arabonamide 2,3,4-trimethylether (80% yield). This proves that diheterolevulosan IV is a di-D-fructopyranose 1,2', 2,1'-dianhydride.

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Note on the Electrolytic Methoxylation of Furan

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The electrolytic methoxylation of furan to 2,5-dimethoxy-2,5-dihydrofuran has previously been carried out by electrolyzing a methanolic solution of furan and ammonium bromide¹. It has now been found,

that dimethoxydihydrofuran is also formed, when the ammonium bromide is replaced by ammonium nitrate, sodium nitrate, sodium formate, boron fluoride etherate or sulfuric acid. The yield of dimethoxydihydrofuran (38–56 per cent) is somewhat lower than when ammonium bromide is used (86 per cent). These experiments indicate, that not only halogens, but also other oxidizing agents can oxidize furan in methanolic solution to dimethoxydihydrofuran.

EXPERIMENTAL

Solutions of ammonium nitrate (5.0 g), sodium nitrate (5.0 g), sodium formate (5.0 g), boron fluoride etherate (5.0 ml) and concentrated sulfuric acid (1.00 ml), in a mixture of methanol (250 ml) and furan (20.4 g = 0.30 mole) were electrolyzed as described previously¹. 16.1 ampere hours (0.60 faraday) was passed through the cell. After electrolysis, the acid electrolytes were neutralized with a solution of sodium methoxide. The results of the electrolyses are summarized below.

The methanol was in each case distilled off through a Vigreux column and the residues filtered or centrifuged to remove the inorganic salts (washing with ether). The resulting brown liquids were then distilled.

Electrolyte	Time of electrolysis (hours)	Current (ampere)	Potential across the cell (volt)	Temperature in the cell (°C)	Colour of the electrolyte after electrolysis	g of sodium used for neutralization
NH_4NO_3	6.7	2.9–2.0	5.8–6.8	–10°	yellowish-brown	1.46
$NaNO_3$	6.8	2.6–0.9	6.2–7.4	–10° to –14°	reddish-brown	0
$NaOOCH$	8.3	3.1–0.6	7.0–8.8	–9° to –18°	yellowish-brown	0
BF_3	6.0	2.8–1.9	6.1–6.6	–10° to –13°	slightly yellow	2.30
H_2SO_4	8.3	2.3–1.8	6.0–7.0	–11° to –12°	yellowish-brown	0.95