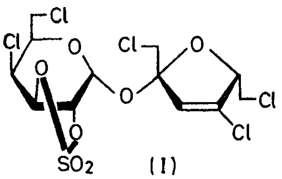
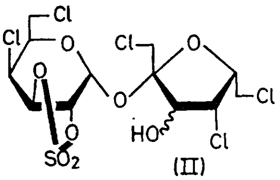
Reaction of Sucrose with Sulphuryl Chloride

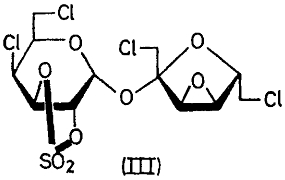
By J. M. Ballard, L. Hough,* and A. C. Richardson
(Department of Chemistry, Queen Elizabeth College, London W8 7AH)

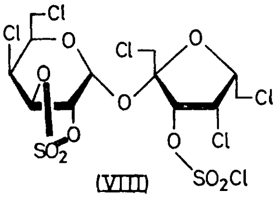
Summary The reaction of sucrose with sulphuryl chloride affords, *inter alia*, two pentachloro- and one tetrachloro-derivative, the structures of which have been elucidated by physical methods.

In seeking new sucrose derivatives for chemical exploitation,[1] the reaction of the disaccharide with sulphuryl chloride offered promise since a previous study had suggested[2] that a mixture of di- and tri-chloro-derivatives was formed, the structures of which were not ascertained. We have re-investigated this reaction with a view to isolating pure products for subsequent conversion, by nucleophilic displacement reactions of the chloro-substituents,[3] into a variety of sucrose analogues.

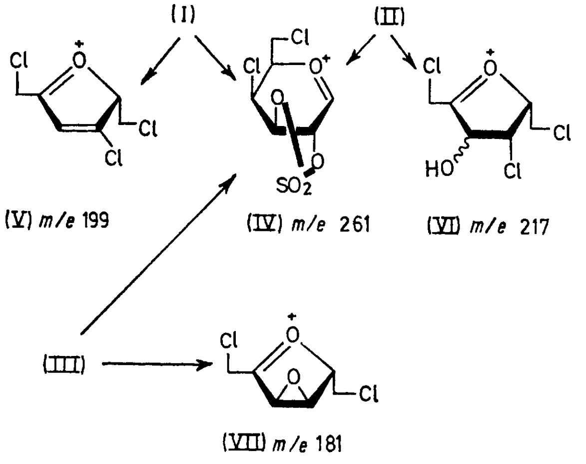

(I)


(II)


(III)


(VIII)

Treatment of sucrose with sulphuryl chloride (8·8 mol) in pyridine at 50° afforded a complex mixture of products from which three major components (A), (B), and (C) were isolated (3, 0·2, and 2%, respectively) as crystalline solids by dry column chromatography. The first eluted component, (A) [m.p. 111—112°, $[\alpha]_D$ +79° ($CHCl_3$)], was identified as 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 1′,4′,6′-trichloro-1′,3′,4′,6′-tetradeoxy-β-D-*glycero*-hex-3′-enofuranuloside 2,3-sulphate (**1**) on the basis of its ^1H n.m.r. and m.s. data. The n.m.r. assignments were confirmed by extensive decoupling experiments and the *galacto* configuration of the pyranosyl ring was clearly indicated by the appearance of 2-H and 3-H as a pair of strongly coupled double doublets (*J ca.* 10 and 3 Hz).[4] The 4-H resonance appeared as a very broad singlet devoid of fine structure, which, upon irradiation of the slightly broadened 1-H doublet, resolved into a double doublet (*J* 3·1 and 1·8 Hz), which was typical of 4-H of a galactopyranoside.[5] The small coupling (0·5—1·0 Hz) between 1-H and 4-H is unusual and has not previously been encountered in galactopyranosides, although coupling between *eq*-1-H and *eq*-4-F has been observed in 4-deoxy-4-fluoro-hexose derivatives.[6] The vinylic proton 3′-H appeared as a doublet at τ 3·78, irradiation of which collapsed a double triplet at τ 5·06 (5′-H) to a triplet. The m.s. data indicated fragments at *m/e* 261 and 199 corresponding to the two glycosyloxy-carbonium ions derived from (I) [(IV) and (V), respectively].



The ^1H n.m.r. spectrum of component (B) (m.p. 107—111°) showed that it contained an identical galactopyranosyl residue as (A) because of the pair of identical double doublets at τ 4·67 and 4·89 due to 3-H and 2-H, respectively, and the 1-H doublet at τ 4·22; the remaining resonances were complex and overlapped. However, addition of trichloroacetyl isocyanate to the n.m.r. solution resulted in the appearance of a singlet at τ 1·35 (1H) due to NH of the carbamate ($Cl_3C{\cdot}CONHCO_2R$) formed, thereby indicating the presence of a single hydroxy-group. Furthermore, a methine proton resonance, a doublet at τ 4·29 (*J ca.* 6 Hz), was deshielded by *ca.* 1 p.p.m. The only methine proton to occur as such a doublet in sucrose is 3′-H so that by implication the original hydroxy-group was at C-3′. The deshielding of 3′-H in this way resulted in 4-H being 'uncovered' at τ 5·15 as a broad singlet, similar to that observed previously for (A). The mass spectrum of (B) indicated major fragments at *m/e* 261 and 217 due to the two oxycarbonium ions [(IV) and (VI)]. Isotope peaks associated with the latter indicated that it contained three chlorine atoms and consequently structure (II) was indicated for (B). The configuration at C-3′ cannot be assigned on the basis of the data available.

The ^1H n.m.r. spectrum of (C) [m.p. 146—148°, $[\alpha]_D$ +67° ($CHCl_3$)] similarly indicated the presence of the galactopyranosyl 2,3-sulphate unit. The 3′,4′-H resonances arising from the furanosyl ring were present as an approximate AB quartet (*J* 2·5 Hz), the higher field doublet being further slightly split (*J* < 1 Hz). Such a pattern was reminiscent of an epoxide derivative since it is well established that coupling between hydrogens which form part of an oxiran ring fused to a six-membered ring are not coupled to *trans* hydrogens which are not part of the oxiran ring. Data for oxirans fused to five membered rings are sparse, but Wright, Taylor, and Fox[8] report zero couplings for $J_{1,2}$ and $J_{3,4}$ in methyl 2,3-anhydro-5-*O*-

benzyl-α-D-ribofuranoside. The 5′-H resonance in (C) was observed as a triplet with further small couplings. These results suggested that (C) was 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 3′,4′-anhydro-1′,6′-dichloro-1′,6′-dideoxy-β-D-*ribo*furanuloside 2,3-sulphate (III). This structure was substantiated by the presence of major ionic fragments at *m/e* 261 and 181 in the mass spectrum corresponding to the two oxycarbonium ions, (IV) and (VII), respectively.

The conversion of the glucopyranosyl ring into a 4,6-dichloro-galactopyranosyl 2,3-sulphate residue was not unexpected from previous results obtained with methyl α-D-glucopyranoside.[9] The action of sulphuryl chloride on the fructofuranosyl moiety is less easy to predict but the expected order of displacement would be 6′ > 1′, 4′ > 3′.[10] Hence the presence of chlorine substituents at C-6′, C-1′ was not unexpected. The 3′-ene (I) must have arisen *via* the 1′,4′,6′-trichloro-3′-chlorosulphate (VIII) by an *E*2 elimination and (II) could have arisen from (VIII) by either dechloro-sulphation during work-up or by ring-opening of the epoxide (III) by chloride. The epoxide (III) may have arisen from either the 4′-hydroxy-3′-chloro-sulphate or the 3′,4′-bis(chlorosulphate). The formation of epoxides from vicinal bis(chlorosulphate)s is not without precedent in pyranosides[11] but (III) represents the first example of an epoxide being formed from a furanoside. Satisfactory analytical data and i.r. spectra were obtained for (I), (II), and (III).

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