cm^{-1}: 1773, τ 9.14 (C_{10}-Me), 8.74 (C_4-Me), by the treatment (reflux, *p*-TsOH in benzene). Unlike the other 6β lactones (XIII) and (XIV), the lactone (XX) was so stable that it could be recrystallized and could not be epimerized under the aforementioned thermal condition.

Consequently, synthesis of the 6α-hydroxy-hexahydro series (*trans* B/C-ring fusion) was performed by the other way. Catalytic hydrogenation (Pd–C, MeOH) of 6α-hydroxy-tetrahydro-ester (X) afforded oily product, which was chromatographed (Al_2O_3) to convert to a lactone (XXI) (*trans* B/C-ring fusion), $C_{17}H_{26}O_2$, mp 86—87°, ν_{max}^{KBr} cm^{-1}: 1758, τ 9.06 (C_{10}-Me), 8.73 (C_4-Me). The lactone (XXI) is distinguishable from the 6β lactone (XX) and the other isomeric lactones (XIV and VII) (*cis* B/C-ring fusion). Alkaline hydrolysis (KOH–EtOH–H_2O) of the lactone (XXI) gave the corresponding 6α-hydroxy acid (XXII), $C_{17}H_{28}O_3$, mp 227.5—228.5°, which was readily returned (reflux, 10% HCl aq. MeOH) to the original lactone (XXI) and was methylated (CH_2N_2) to the corresponding ester (XXIII), $C_{18}H_{30}O_3$, mp 142.5—144.5°. Further evidence on C_6-configuration of both the lactones (XX and XXI) was adduced by their reduction ($LiAlH_4$) to give the respective diol (XXIV), $C_{17}H_{30}O_2$, mp 141.5—143° and (XXV), $C_{17}H_{30}O_2$, mp 157.5—158.5°, which were also synthesized from the ester (XXVIII) and (XXIII) having reliable C_6-configuration, respectively.

In conclusion, it is clarified that the lactonization mode is very variable depending on the structure of B/C-ring fusion. A quantitative study on the epimerization is necessary and now is in progress.

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Structural Feature of *Pneumococcus* Type XIX Specific Polysaccharide[1)]

Some preliminary analytical data of *Pneumococcus* Type XIX specific polysaccharide have been given by Brown,[2)] Levine, *et al.*[3)] and Baddiley, *et al.*,[4)] little known about its components or that of some serological cross-reactivities of a type XIX antiserum.[5)]

The present communication is concerned with structural feature of a fragment which is considered to be a major unit in the polysaccharide.

Crude type specific material was fractionated by Cetavlon treatment,[6)] DEAE-cellulose column chromatography using borate,[7)] followed by gel-filtration (Sephadex G-100). During these treatments, particularly DEAE-cellulose treatment with sodium borate caused a remarkable fragmentation and serological activity of the material to the antiserum decreased.

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5) M. Heidelberger, "Fortschritte der Organischer Naturstoffe," Vol. 18, Springer-Verlag in Vienna, 1960, p. 503.
6) J.E. Scott, *Chem. Ind.* (London), **1955**, 1568.
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After gel-filtration, a serologically active fraction was re-fractionated by Cetavlon followed by ethanol precipitation.

A main constituent thus obtained, $[\alpha]_D$ +60° (c=0.3, H_2O), electrophoretically pure, gave L-rhamnose, D-glucose and phosphate in an approximate ratio 4:2:2 by acid hydrolysis. Quantitative estimation of the component sugars of the material by means of the colorimetric method using cysteine-sulfuric acid[8] also showed a ratio of rhamnose: glucose of 2:1. A titration curve was similar with that of a dibasic acid derivative. On the other hand, treatment with Dowex 50 (H) resin of the material in the cold produced a fragmentation and changed to serologically inactive (unable to give a precipitation band with the antiserum by the procedure of Ouchterlony[9]).

Periodate oxidation of the material led to the consumption of approximately 5.2 moles of periodate per phosphorylated hexasaccharide unit, and the productions of 2.1 moles of formic acid, 1.68 mole of acetaldehyde per unit and no formaldehyde. Reduction by sodium borohydride of the oxidation product followed by hydrolysis with acidic ion-exchange resin in the cold gave glycerol, 1,2-propandiol and unidentified phosphate, and on further hydrolysis (with 2N hydrochloric acid, at 100°), L-rhamnose, D-glucose, erythritol and a small amount of D-glucose 6-phosphate in addition. The molar ratio of liberated rhamnose: glucose was 1.5:1 approximately.

From these results it appears that: 1) reducing end group of the material is rhamnose because of the productions of acetaldehyde and formic acid, 2) some of the rhamnose residues are presented as 1→2 linkage which should be produced of 1,2-propandiol, 3) other part of rhamnose residues did not contain hydroxyl groups on adjusent carbon atoms, 4) some of the glucose residues have hydroxyl groups on adjusent carbon atoms C-2 and C-3 which is erythritol-produciable linkage, 5) some of the glucose residues have no adjusent hydroxyl groups, 6) a part of the glucose residues are substituted at C-6 by phosphate.

Phosphate ester in the material was presented as a mixture of mono- and diester type linkages. An aklaline titration curve of the material showed the presence of typical dibasic acid. Treatment of the material with alkaline phosphatase liberated slowly, about half of the phosphate content, though using of acid phosphatase liberated less phosphate. The enzyme-treated material after removal of inorganic phosphate then titrated as a monobasic acid showing the presence of diester type phosphate.

Treatment of the starting material with 1N sodium hydroxide (7 days, under nitrogen, at room temperature), sodium borohydride (16 hr, at room temp.) and followed by Dowex 50 (H) resin gave a dialyzable oligosaccharide as a main product, which contained L-rhamnose, D-glucose, L-rhamnitol and phosphate in the same ratio. The oligosaccharide was paper chromatographycally and electrophoretically pure and showed $[\alpha]_D$ +70° (c=0.2, H_2O). Its titration curve showed the presence of dibasic acid. Periodate oxidation study of the oligosaccharide showed that consumption of 2.28 moles of periodate, productions of 0.95 mole of formic acid and 1.23 mole of acetaldehyde per phosphorylated trisaccharide unit.

The derived oligosaccharide I, therefore, appears to be one of the repeating unit which may be joined through phosphoric acid residues to other sugar units II, III and IV thus yielding a polymer.

The most probable structures of these sugar units in the polysaccharide will be as follows:

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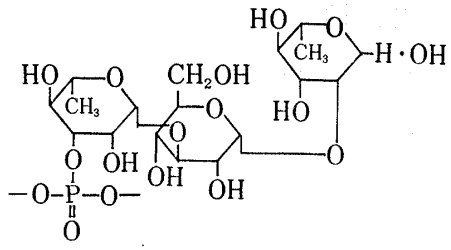

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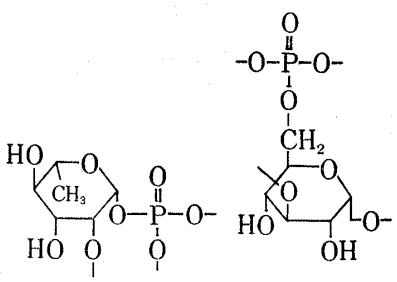
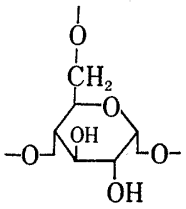


II III



IV

The recognition of amino sugar and totol structure of the type specific polysaccharide will be reported in the near future.

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