LETTERS TO THE EDITORS

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Significance of Oligosaccharide Intermediates in Dextran Synthesis

The recent isolation[1] of O-α-D-glucopyranosyl-(1→6)-O-α-D-glucopyranosyl-(1→2) β-D-fructofuranoside (I) from a complex mixture of oligosaccharides produced by the action of a cell-free extract of *Aspergillus niger* '152' on a sucrose–maltose mixture prompted us to examine its role in dextran synthesis, since the first step in the synthesis of dextran could be :

$$\underset{\text{(Sucrose)}}{\text{Glu-(1}\rightarrow\text{2)-Fru}} + \underset{\text{(Sucrose)}}{\text{Glu-(1}\rightarrow\text{2)-Fru}} \longrightarrow \underset{\text{(I)}}{\text{Glu-(1}\rightarrow\text{6)-Glu-(1}\rightarrow\text{2)-Fru}} + \underset{\text{(Fructose)}}{\text{Fru}}$$

It was observed that dextransucrase[2] prepared from *Betacoccus arabinosaceous* (Birmingham strain) had no action on (I) alone ; but if the enzyme (0·5 c.c.) was incubated with a mixture of (I) (5 mgm.) and sucrose (10 mgm.) at 25° and *p*H 5, both these components rapidly disappeared. Paper chromatographic analysis showed the appearance of fructose and a series of oligosaccharides, which had R_F values less than the trisaccharide (I) in a solvent containing butanol, ethanol, water and ammonia (40 : 12 : 20 : 1) and which gave positive reactions with naphtharesorcinol[3].

Using fructose production (after 22 hr. at *p*H 5) as a criterion, the conversion of sucrose (300 mgm.) by dextransucrase was much greater in the presence of trisaccharide (I) (50 mgm. ; fructose production increased 95 per cent) than with sucrose alone. In the presence of added maltose (50 mgm. ; 100 mgm.) the increases in fructose production were 146 and 248 per cent respectively.

The digest containing the products from the trisaccharide (I) – sucrose mixture was adjusted to *p*H 7, heated at 60° for 15 min., cooled and freeze-dried. The mixture was dissolved in water (10 per cent w/v), streaked across sheets of Whatman No. 1 paper and irrigated with the above solvent for four days. After being dried, the strips containing the suspected tetra-, penta- and hexa-saccharide were eluted severally with water and each extract freeze-dried. The tetrasaccharide (29 mgm.) had $R_{Glucose}$ 0·21 (cf. trisaccharide (I), 0·40) in the above solvent mixture and showed an almost constant rotation after hydrolysis with 0·1 *N* hydrochloric acid at 100° for 4 min. The partial hydrolysate contained components which had the same mobilities as *iso*-maltotriose and fructose. The pentasaccharide and hexasaccharide had $R_{Glucose}$ 0·12 and 0·07, respectively, and on partial hydrolysis as above gave rise to components which had the same mobilities as *iso*maltotetraose and *iso*maltopentaose, respectively, together with fructose in each case.

In the region 1,027–715 cm.$^{-1}$, trisaccharide (I) showed infra-red absorption peaks at 978(s), 919(s), 870(m), 852(m), 835(m), 803(vw), 769(m) cm.$^{-1}$. The infra-red spectra of the tetra- and penta-saccharide showed the expected similarity to that of trisaccharide (I) with decreased absorption at 870 and 852 cm.$^{-1}$ as the proportion of the fructose moiety became less. It is therefore concluded that dextransucrase acting on sucrose can use trisaccharide (I) as a receptor, but not as a substrate, to synthesize a homologous series of oligosaccharides by the addition of α-1 : 6-linked glucose residues to the glucose end of trisaccharide (I), thus :

$$\underset{\text{(Sucrose)}}{\text{Glu-(1}\rightarrow\text{2)-Fru}} + \underset{\text{(I)}}{\text{Glu-(1}\rightarrow\text{6)-Glu-(1}\rightarrow\text{2)-Fru}} \longrightarrow \underset{\text{(Tetrasaccharide)}}{\text{Glu-(1}\rightarrow\text{6)-Glu-(1}\rightarrow\text{6)-Glu-(1}\rightarrow\text{2)-Fru}} + \text{Fructose}$$

Several points of interest emerge from the above observations. Since trisaccharide (I) is not a substrate for dextransucrase, in contrast to sucrose, it is probable that higher homologues of (I) also cannot function as substrates. If this is so, then unbranched dextrans must be built up by successive transfers of single glucose units, and transfers of preformed chains are not involved. Moreover, any fructose-terminated oligosaccharide formed from an acceptor molecule such as sucrose or trisaccharide (I) would eventually lead to a dextran molecule carrying a terminal fructose residue[4] (cf. inulin and lævan). The fact that oligosaccharides do not accumulate when dextransucrase acts on sucrose alone may be due either to the operation of a single-chain mechanism[5] or to a multi-chain mechanism in which a slow initial synthesis of trisaccharide (I) is followed by a rapid polymerization to dextran. Since oligosaccharides are now shown to be formed from sucrose and trisaccharide (I), when present together in comparable amounts, it is likely that the multi-chain mechanism is operative. The results obtained with mixtures of sucrose and other acceptors (for example, methyl-α-D-glucoside) point to the same conclusion[2].

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Optical Activity of Homologous Series

The optical activity of asymmetric molecules has frequently been used as a criterion of purity and also a means of identification of naturally occurring chemical compounds. In this laboratory we are particularly interested in the *anteiso* series of fatty acids found in natural fats[1,2]. These optically active fatty acids were recently synthesized in a high state of purity by Milburn and Truter[3] and the optical rotations of this homologous series are therefore available to test Tschugaeff's rule[4]. According to this the specific rotations of members of a homologous series are inversely proportional to the molecular weights within certain limits, and the molecular