(7.8 g) were added and the solution was boiled for 15 minutes on the steam bath. When cold the solution was washed with water, dried over calcium chloride and concentrated under reduced pressure. The residue was recrystallized from ethanol. Yield 6.2 g. M.p. 141—143°. After further recrystallizations from ethanol the m.p. was raised to 144—144°.5. $[\alpha]_D^{20}$–11°.

Tetraacetyl-β-tertiary butylglucoside and titanium tetrachloride. Tetraacetyl-β-tertiary butylglucoside (2 g) was dissolved in absolute chloroform (20 ml) and titanium tetrachloride (1.3 g) in absolute chloroform (12 ml) was added. The clear, yellow solution soon grew turbid and both white and yellow particles appeared in the resulting precipitate. The solution was heated for 40 minutes on the steam bath. When cold it was shaken with ice water, the chloroform phase washed with water and dried over calcium chloride. The brown solution was filtered through a column of aluminium oxide (Brockmann). After filtration it was yellow. The chloroform was evaporated under reduced pressure and the residue dissolved in ethanol and diluted with water. Pale yellow crystals (0.4 g) precipitated. M.p. 72—73°. $[\alpha]_D^{20}$ + 165°. By recrystallization from ether-petrol ether the m.p. was raised to 74—75° and the specific rotation to + 166°. As the substance prooved to contain chlorine and the data are consistent with those of acetochloroglucose, it must evidently be that substance.

Tetraacetyl-α-tertiary butylglucoside. Tetraacetyl-β-tertiary butylglucoside (3 g) was dissolved in absolute benzene (75 ml), saturated with boron trifluoride and allowed to stand at room temperature for 10 minutes. The solution was then neutralized with absolute pyridine (10 ml) and shaken with cold bicarbonate solution. The benzene solution was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residual oil was dissolved in ether (40 ml) and extracted with water (5 × 100 ml). After each extraction the ether volume was made up to 40 ml again. Now petrol ether was added (20 ml) and the extraction with water continued (5 × 100 ml). The ether phase was dried over sodium sulfate and concentrated under reduced pressure. The residual oil was dissolved in ethanol and poured into water. An oil separated which soon solidified to white crystals of m.p. 65—66°. Yield 1.1 g. After recrystallization, first from methanol and then from petrol ether, the substance was obtained in a pure state. M.p. 69—70°. $[\alpha]_D^{20}$ + 113°.

The acetyl content was determined according to Clark.

$C_{10}H_{16}O_6(OCCH_3)_4$ (404.2)
Calc. Acetyl 42.6 Found Acetyl 42.5

A grant from *Statens Naturvetenskapliga Forskningsråd* is gratefully acknowledged.

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Received November 5, 1948.

Aromatic Keto- and Hydroxy-polyethers as Lignin Models. I

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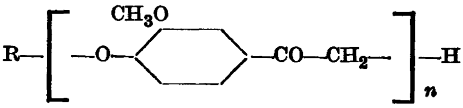
According to modern views regarding the structure of lignin, this material is built up from simple building stones containing an aromatic nucleus with a three carbon atom side chain. This idea is supported by a multitude of experimental results *e. g.* the fact that lignin and several lignin derivatives give a comparatively high yield of vanillin on oxidation with aromatic nitro compounds (Freudenberg[1]).

Biogenetic considerations and the results of dehydrogenation experiments with *iso*-eugenol[2] and ferulic acid[3] appear to show that the β-carbon atom of the side chain may be involved in the connection of the phenyl propane building stones of many binuclear or polynuclear natural products of phenyl propane type.

Lignin contains reactive groups responsible for its sulphonation by sulphite cooking acid. Holmberg found that α-phenetyl-alcohol reacted with bisulphite with the formation of α-phenethylsulphonic acid[4]. Thus the hydroxyl group was substituted by a sulphonic acid group. In his extensive analytical studies on lignin and the products obtained by the reaction between lignin and various SH-containing reagents he arrived of the conclusion that a substitution of a hydroxyl group in lignin was a more probable course of reaction than for example a fission of an oxide ring[5].

Lindgren[6] recently found that suitably substituted benzyl alcohols or phenethyl alcohols constitute excellent lignin models, reacting by substitution of hydroxyl groups by sulphonic acid groups.

In unpublished experiments it has been directly shown that during the sulphonation of lignin, hydroxyl groups disappear when sulphonic acid groups are introduced. Consequently we were interested in synthesising compounds containing several building stones similar to those assumed to occur in lignin and connected in various ways, which would furnish vanillin on oxidation and sulphonic acids when heated with sulphite cooking acid. The two following series of ethers were first synthesised:



R=H

$n=2$, m.p. 140—142°. $n=3$, m.p. 181—183°. $n=4$, m.p. 201—202°.

R=CH_3

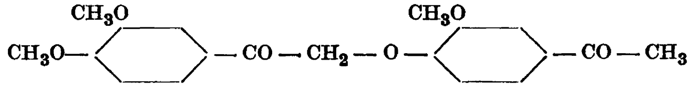
$n=2$, m.p. 138—139°. $n=3$, m.p. 145—146°. $n=4$, m.p. 146—147°.

The syntheses were accomplished in the following way:

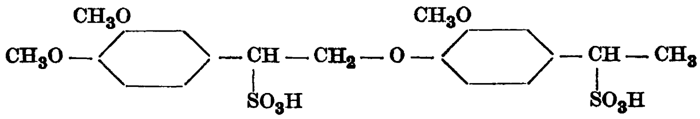
$$R'COCH_2 — \boxed{Br + Na} — OR' \rightarrow R'COCH_2 — O — R'$$

These ketonic compounds did not react with sulphite cooking acid but, of course, yielded vanillin on oxidation with nitrobenzene and alkali. If the keto groups were reduced to hydroxyl groups, compounds capable of sulphonation should be obtained.

In our first experiments we have subjected the following compound to reduction with aluminium isopropoxide in boiling isopropyl alcohol[7].



An alcohol was obtained in excellent yield. This readily reacted with sulphite cooking acid to yield the corresponding sulphonic acid: (isolated as the barium salt)



$C_{19}H_{22}O_{10}S_2Ba$

Calc.	Ba	22.5	OCH_3	15.2
Found	»	22.6	»	15.1

A more complete communication on the reactions of the abovementioned and related compounds will follow shortly.

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Received November 6, 1948.