Electrolyte	Fraction (g)	Distillation pressure mm	B.p.	n_D^{25}	Yield of dimethoxydihydrofuran
NH_4NO_3	1 (13.4)	14	49– 51°	1.4327	15.6 g (fractions 1 and 2)
–	2 (2.2)	–	51– 60°	1.4326	= 40 %.
–	3 (1.8)	–	68–130°	partly crystalline	
$NaNO_3$	1 (11.8)	14	52– 53°	1.4326	15.4 g (fractions 1 and 2)
–	2 (3.6)	–	53– 58°	1.4330	= 40 %.
–	3 (1.5)	–	60–125°	1.4407	
NaOOCH	1 (14.7)	11	50–56°	1.4329	14.7 g (fraction 1)
–	2 (1.0)	–	59–110°	1.4393	= 38 %.
BF_3	1 (19.6)	12	48– 52°	1.4321	21.7 g (fractions 1 and 2)
–	2 (2.1)	13	52– 60°	1.4320	= 56 %.
–	3 (5.2)	–	61–138°	1.4383	
H_2SO_4	1 (8.6)	13	48– 52°	1.4318	16.0 g (fractions 1 and 2)
–	2 (7.4)	–	52– 55°	1.4319	= 41 %.
–	3 (5.6)	14	54– 86°	1.4282	
–	4 (3.3)	–	88–156°	1.4382	

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On the Existence of *a*-Glycol Groups in Lignin

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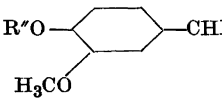
Lignin appears to contain three types of sulphonatable groups [1], designated X, Z and B, and model experiments (treatment with sulphite solutions [2] and sulphide solutions [3]) have shown that the Z-groups may be *p*-alkoxybenzyl alcohol groups. Two phenylglycerol derivatives containing *p*-alkoxybenzyl alcohol groups, *viz.* veratrylglycerol (I) and its *β*-guaiacyl ether (II), have recently been studied by Adler *et al.* [4,5] Like other *p*-alkoxybenzyl alcohols these substances are converted by sulphite solutions into sulphonic acids (III resp. IV). The rate of the sulphonation of veratrylglycerol is of about the same order of magnitude as the rate at which the Z-groups in lignin are sulphonated. It was therefore of inter-

est to investigate whether groups of structure V might be present in lignosulphonic acids.



I	R=H	R′=OH	R″=CH_3
II	R= o-(H_3CO)C_6H_4	R′=OH	R″=CH_3
III	R=H	R′=SO_3H	R″=CH_3
IV	R= o-(H_3CO)C_6H_4	R′=SO_3H	R″=CH_3
V	R=H	R′=SO_3H	R″=alkyl
VI	R=H	R′=OH	R″=alkyl

The structure V contains a terminal α-glycol group, and thus on periodate oxidation it should yield formaldehyde. Our experiments have shown, however, that no formaldehyde is formed when spruce lignosulphonic acid is treated with periodate at pH 3.5. This shows that the lignosulphonic acid does not contain any large number of groups such as V.

The di-*p*-toluenesulphonates of terminal α-glycol groupings, when heated with sodium iodide in acetone, react as follows (*cf.* experiments with erythritol [6], 1,2,3,4-dibenzylidene-D-sorbitol [7], glycol [8], and glyceraldehyde acetal [9])

$$-CH(OSO_2C_7H_7)-CH_2(OSO_2C_7H_7) + 2\,NaI \rightarrow -CH=CH_2 + I_2 + 2\,C_7H_7SO_3Na.$$

It has been found that the di-toluenesulphonate of safrol glycol [= 3-(3′,4′-methylenedioxyphenyl)-propane-1,2-diol] reacts in the same way.

Tosylated spruce lignosulphonic acids yield only small amounts of iodine – about one mol. of iodine for every 20 methoxyl groups, and this also indicates that lignosulphonic acids do not contain any considerable amount of terminal α-glycol groups.

Spruce lignin contains about one Z-group per 6 methoxyl groups [1], and thus the main part of the Z-groups may not be phenylpropane monomers containing a non-etherified glycerol side-chain (VI). Naturally these experiments do not exclude the possibility that the Z-groups are *p*-alkoxybenzyl alcohols with a structure other than VI.

EXPERIMENTAL. *Periodate oxidation of lignosulphonic acid.* Sodium periodate solution (25 ml, 0.2 N) was added to a solution of 2.5 g of a calcium lignosulphonate (Ca 11.7, S 5.4 and OCH_3 10.7 %) in 100 ml of an acetate buffer of pH 3.5, and the mixture was set aside at room temperature for 30 minutes. Lead nitrate solution (12.5 g/100 ml, 20 ml) was added to precipitate the iodate and periodate ions [10], and the solution was evaporated to dryness under reduced pressure in a stream of coal gas. The distillate was treated with dimedone in the usual way; no precipitate was obtained.

Corresponding oxidations at pH 6 and 7 (phosphate buffer solutions) gave small amounts of formaldehyde (0.01 mol. per OCH_3).

Tosylation of lignosulphonic acid. A mixture of 1 g of a low-sulphonated lignin [11] (S 3.95, OCH_3 13.6 %), 5 g of tosyl chloride, and 20 ml of pyridine was set aside for 92 hours, and the insoluble product (1.12 g: S 9.08, OCH_3 9.00 and Cl 1.68 %) was collected.

A mixture of this material (0.4 g), sodium iodide (1.5 g), and acetone (10 ml) was heated in a sealed tube at 100° for 17 hours. Water was added and the liberated iodine was titrated with thiosulphate. 1.30 Ml of 0.1011 N-thiosulphate was required, corresponding to 0.05 mol. of I_2 per OCH_3 group.

Safrole glycol ditoluenesulphonate. A mixture of safrole glycol (3 g), tosyl chloride (5.85 g), and pyridine (15 ml) was set aside at room temperature for 24 hours, then evaporated to dryness in a vacuum desiccator. Sodium bicarbonate solution was added to the residue and the mixture was extracted with chloroform. The chloroform solution was dried, filtered through a column of alumina and evaporated, yielding 2.85 g of a substance melting at 128° (yield: 39 %). The melting point was raised to 135° by recrystallization from benzene.

$C_{24}H_{24}O_8S_2$	Found	C 57.2	H 4.80	OCH_3	12.7
	Calc.	» 57.2	» 4.77	»	12.7

When this substance was heated with NaI and acetone in a sealed tube at 100° for 12 hours, toluenesulphonic acid (isolated as the benzylthiuronium salt) was obtained in a yield of *ca.* 95 % and I_2 (determined by titration with thiosulphate) in a yield of *ca.* 90 %.

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A Preliminary X-Ray Investigation of Dipicrylamine and some of Its Salts

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The potassium salt of dipicrylamine, or 2,4,6 - 2′,4′,6′-hexanitrodiphenylamine, is almost insoluble in water, and it has been proposed to make use of this to manufacture potassium from sea-water [1]. The salt exists in at least two polymorphic forms, one red and one violet. These are distinguished by their different reactivity towards nitric acid, which is used to regenerate the amine from the salt [2]. It was therefore thought to be of interest to investigate the crystal structure of the two polymorphic forms. Besides, the dipicrylamine molecule presents in itself interesting stereochemical problems.

We have studied a number of dipicrylaminates by X-ray methods in order to find a compound suitable for complete structure determination. Single crystals of the substances were prepared by dissolving the calcium salt in water and precipitating the alkaline salts by adding the corresponding cations. The red form of the potassium salt was obtained by evaporating an aqueous solution of the salt at room temperature, the violet form by evaporation at 70° C [2]. X-ray oscillation and Weissenberg diagrams were taken, using CuKα and FeKα radiation (wave lengths 1.542 Å and 1.937 Å resp.), and the densities measured by the flotation method. The results are believed to be correct to about 1 %.

In the following the results of the measurements are given, the dipicrylamine anion being called *D* for short.

HD (dipicrylamine). The yellow, well-developed crystals have the shape of short prisms elongated parallel to *a*. Forms $\{010\}$, $\{210\}$, and $\{011\}$ were observed. The crystals are ortorhombic, with cell dimensions $a = 18.94$ Å, $b = 11.72$ Å, and $c = 7.37$ Å. Reflexions $h00$, $0k0$ and $00l$ are absent for h, k and l odd respectively and as no other systematic absences occur, the space group is $P2_12_12_1$. The density was found to be 1.77 g/cm [3] and there are four (calc. 3.97) molecules in the unit cell.

After this investigation was completed, McCrone [3] has published crystal data on HD. His findings are in agreement with the measurements reported above ($a = 11.75$Å, $b = 19.10$ Å, $c = 7.43$ Å; density 1.750 g/cm [3]; space group not given).

NaD. Red orthorhombic plates $\{001\}$, with $a = 17.61$ Å, $b = 11.77$ Å, and $c = 7.86$ Å. Density 1.89 g/cm^3 four (calc. 4.02) mols. in the unit cell. Space group $P2_12_12_1$.

KD, red form. Thick, rhombic plates, bounded by $\{11l\}$ and $\{001\}$, the latter form predominant. The *b* axis bisects the oblique angle. The crystals are monoclinic, with $a = 15.77$ Å, $b = 13.00$ Å, $c = 11.02$ Å, and $\beta = 130°$. Density 1.84