

## Note Concerning the Sulphonation Rates of Vanillyl and Syringyl Alcohol

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It has been observed earlier<sup>1</sup> that during sulphite cooking in acidic conditions the lignin dissolved from birchwood is sulphonated to a higher degree than that from pinewood. However, during a less extensive dissolution of lignin by neutral sulphite solutions, the opposite is true. One important reason for this may be the differences in chemical structure between the two kinds of lignin and a notable difference is that lignin from coniferous wood consists mainly of guaiacyl propane units, whereas considerable amounts of syringyl propane units are present in lignin from deciduous wood (see, *e.g.*, Refs. 2 and 3). It is thus of interest to know whether compounds of these two types react at different rates with sulphite solutions. For that reason, a comparison has been made between the sulphonation rates of the following two model compounds: 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol) and 4-hydroxy-3,5-dimethoxybenzyl alcohol (syringyl alcohol), which represent the above-mentioned structural elements.

The sulphonation of vanillyl alcohol has been studied by Lindgren<sup>4</sup> who examined the reaction product together with sulphonation products formed from some other lignin models. Migita *et al.*<sup>5</sup> as well as Ivnäs and Lindberg<sup>6</sup> studied the sulphonation of vanillyl alcohol kinetically. The sulphonation of syringyl alcohol, however, seems not to have been investigated.

In the present work vanillyl alcohol and syringyl alcohol were allowed to react in sodium sulphite-bisulphite solutions of three different pH values. In all experiments the molar ratio between the alcohol and sulphur dioxide was 1:1 and the pH was kept constant by adding buffer solution to the reaction mixtures. The consumption of sulphur dioxide (sulphite + bisulphite) was followed iodometrically and the alcohol was assumed to be converted equivalently, since Lind-

gren found<sup>4</sup> that one mole vanillyl alcohol reacts almost quantitatively with sulphite to form one mole guaiacylmethane sulphonic acid. The conversion of these two alcohols into the corresponding sulphonates is recorded in Figs. 1 and 2. It is seen that in the actual pH range (4.4–8.3) the sulphonation of both compounds proceeds faster at higher pH values. Ivnäs and Lindberg,<sup>6</sup> who studied the sulphonation of vanillyl alcohol at pH 3.4–6.9, found a rate minimum at a pH value of about 5. Our experiments, which were performed at nearly the same temperature (80°), gave rather similar results for vanillyl alcohol. As shown by the figures, the sulphonation rate of syringyl alcohol is more dependent on the pH value than is that of vanillyl alcohol. Syringyl alcohol reacts faster than vanillyl alcohol at high pH values, whereas the reverse is true at low pH values. However, the differences in the reaction rates are relatively small, and these cannot explain the different behaviour of pine and birch lignin during sulphite cooking of wood, which instead must be sought elsewhere, *e.g.* in the differences in amounts and distribution of free phenolic groups.

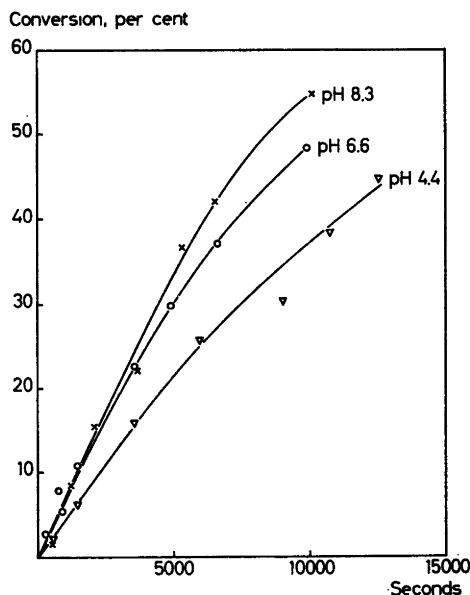


Fig. 1. Conversion of vanillyl alcohol into the sulphonate at 80°. The dependence of the reaction rate on the pH-value.

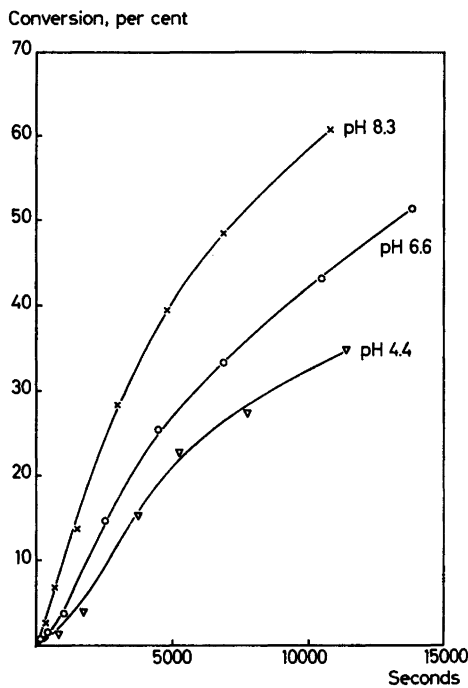


Fig. 2. Conversion of syringyl alcohol into the sulphonate at 80°. The dependence of the reaction rate on the pH-value.

The over-all reaction between vanillyl alcohol and sulphite was found by Migita *et al.*<sup>5</sup> to follow approximately first order kinetics with respect to the alcohol in the pH interval 2–9. Ivnäs and Lindberg<sup>6</sup> also observed first order kinetics at pH 4–5, but at both lower and higher pH values the reaction approached second order kinetics, *i.e.* first order with respect to each reactant. These observations have been interpreted in terms of a mechanism involving formation of a quinone methide as an intermediate.<sup>5,6</sup> According to the present data the reaction follows first order kinetics at pH 4.4 and second order at pH 8.3. The reaction thus obviously involves several steps and the values given in Table 1 are therefore “apparent” rate constants for the over-all reaction.

*Experimental.* Vanillyl alcohol, m.p. 111.5–114°, and syringyl alcohol, m.p. 132.5–133.5°,

Table 1. Rate constants calculated after first ( $k_I$ ) and second ( $k_{II}$ ) order kinetics for sulphonation of vanillyl and syringyl alcohol at 80°.

pH	Vanillyl alcohol		Syringyl alcohol	
	$10^5 \times k_I$ s <sup>-1</sup>	$10^2 \times k_{II}$ l·mole <sup>-1</sup> ·s <sup>-1</sup>	$10^5 \times k_I$ s <sup>-1</sup>	$10^2 \times k_{II}$ l·mole <sup>-1</sup> ·s <sup>-1</sup>
4.4	4.8		4.3	
6.6	7.0			0.75
8.3		1.07		1.22

were prepared according to Refs. 7 and 8, respectively.

The buffer solutions consisted of 1 M sodium acetate (pH 4.3), 0.2 M sodium phosphate (pH 6.5) and 0.3 M sodium borate (pH 8.4). Sodium chloride was added to each buffer solution to give an ionic strength of 2.0. Each reaction mixture was prepared by mixing 40 ml buffer solution, 20 ml 0.0500 M vanillyl (or syringyl) alcohol and 20 ml 0.0500 M sodium hydrogen sulphite solution in a test tube which was placed in a water thermostat at 80.0 ± 0.1°. The mixture was kept under a nitrogen atmosphere. At suitable intervals, samples of 10 ml were withdrawn and added to an excess (5–13 ml) of 0.02 N iodine solution, acidified with glacial acetic acid (3 ml). The excess iodine was titrated with 0.02 N sodium thiosulphate. A blank determination, where the solution of the alcohol was replaced by water, was also performed at each pH-value and the results were then corrected accordingly.

The rate constants were determined graphically from the following expressions between concentration ( $c$ ) and time ( $t$ ):

$$\ln \frac{c_0}{c} = k_I \times t \quad (1st \text{ order})$$

$$\frac{1}{c} - \frac{1}{c_0} = k_{II} \times t \quad (2nd \text{ order})$$

where  $c_0$  is the initial concentration of alcohol and sulphite and  $k_I$  and  $k_{II}$  are the rate constants. The rate expressions are valid under the assumption that any possible intermediates (*e.g.* quinone methide) appear in a low concentration compared with alcohol and sulphite.

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## Quantitative Fractionation of Low-Molecular-Weight Iodine-Containing Compounds in Thyroid Hydrolysates

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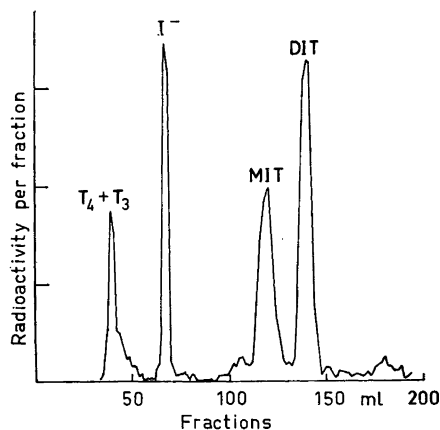
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There is a need of good and reliable methods for the quantitative fractionation of low-molecular-weight iodinated compounds which at the same time are suitable for automatic recording. The method to be described was developed in this laboratory to meet these demands. The method has already been in use for a long time for the routine fractionation of thyroid hydrolysates and has proved to give reliable results.

A chromatography column about 40 cm × 2 cm in size is packed tightly with a very pure dry cellulose powder

(J. H. Munktell's cellulose powder No. 400, Grycksbo Pappersbruk, Grycksbo, Sweden). The cellulose is applied as small discs about 0.5 cm thick. After packing, the column is wetted, starting from the bottom, with the eluent, a butanol-ethanol-ammonia-water solvent system,<sup>1</sup> by a hydrostatic arrangement. The solvent that has passed through is discarded, the direction of flow reverted and the column eluted with 200 ml of the solvent. Before the sample to be analysed is applied on the top of the column, the remaining solvent is sucked off and the column is allowed to drain until the top of the column is almost dry. Good results will be achieved if the volume of the sample does not exceed 0.5 ml. The effluent is collected with a fraction collector. The flow-rate is adjusted with hydrostatic pressure to about 5 ml per hour. A suitable volume for each separate fraction is about 1.5 ml.

If the sample contains radioactive material the radioactivity can be continuously recorded with the aid of a glass spiral passing through a well-type scintillation crystal in the way previously described.<sup>2</sup> Since the flow-rate is fairly constant it is not necessary to use a proportionating pump. The sample can be screened for stable iodine (<sup>127</sup>I) by the cerium sulphate method,<sup>3</sup> either automatically during the fractionation<sup>4</sup> or from aliquots taken from each separate fraction.



*Fig. 1.* Fractionation of a hydrolysate from human thyroid tissue. Ordinate: radioactivity in arbitrary units. Abscissa: volume of the eluent (50, 100, 150, and 200 ml).