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# STUDIES OF HYDROXYL SUBSTITUTED GUAIACYL COMPOUNDS[1]

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## ABSTRACT

A new identification reaction for the distinction between $\alpha$- and $\beta$- or $\gamma$-substituted guaiacyl derivatives is described. Relations between structure and distribution coefficients are given and a deviation from Reichl's rule noted. The synthesis of 1-(3-methoxy-4-hydroxyphenyl)-2-propanol is described.

In continuation of the identification of spruce sulphite liquor components (3) it became of interest to develop a method for the identification of lignin degradation products which contain aliphatic hydroxyl groups. As a beginning, the series of 3-methoxy-4-hydroxyphenyl propane compounds containing hydroxyl groups in the side chain was selected. For this purpose 1-(3-methoxy-4-hydroxyphenyl)-2-propanol was prepared by the reduction of the corresponding ketone, 1-(3-methoxy-4-hydroxyphenyl)-2-propanone. The other members of the series were already available.

It was found that diazotized *p*-nitraniline fluoborate and diazotized sulphanilic acid give color reactions with this series which permit a distinction to be made between the $\alpha$-hydroxy compounds and the $\beta$- or $\gamma$-hydroxy compounds. Further, this color differentiation is not confined to the hydroxyl derivatives, but is valid also for compounds containing a carbonyl group in the $\alpha$, $\beta$, or $\gamma$ position in the side chain. These facts are illustrated in Table I.

TABLE I

COLOR REACTIONS OF SOME GUAIACYL DERIVATIVES

| Reagent | Color with $\alpha$-substituted derivatives | Color with $\beta$- or $\gamma$-substituted derivatives |
|---|---|---|
| Diazotized sulphanilic acid | Orange | Red |
| Diazotized *p*-nitraniline fluoborate | Purple | Gray blue |
| Derivatives tested (R = 3-methoxy-4-hydroxyphenyl group): | | |
| | $R{\cdot}CH_2OH$ | $R{\cdot}CH_2{\cdot}CHOH{\cdot}CH_3$ |
| | $R{\cdot}CHOH{\cdot}CH_3$ | $R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$ |
| | $R{\cdot}CHOH{\cdot}CH_2{\cdot}CH_3$ | $R{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ |
| | $R{\cdot}CHO$ | $R{\cdot}CH_2{\cdot}COOH$ |
| | $R{\cdot}CO{\cdot}CH_3$ | $R{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ |
| | $R{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ | |
| | $R{\cdot}CO_2{\cdot}H$ | |

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$R_F$ values for the hydroxyl substituted compounds were determined from a large number of paper chromatograms, and from these the corresponding values of the expression log $R_F/(1-R_F)$ were calculated. According to Reichl (4), in an homologous series such values consist of the sum of constants for each group in the molecule. Consequently, in such a series if the value for the first member in the series and the constants for each of the substituent groups be known, then the $R_F$ value for a particular member of the series can be calculated. For the series studied here this is only partially true, for, as shown in Table II, whereas the value of log $R_F/(1-R_F)$ changes uniformly as one and then two methyl groups are added to the side chain, as shown horizontally opposite "$\alpha$" and "$\beta$", it does not remain constant (as according to Reichl it ought to do) since the hydroxyl group is moved from the $\alpha$ to the $\beta$ to the $\gamma$ position, as shown by the two right-hand vertical columns. Probably this is because of interaction between the hydroxyl group and the substituted benzene nucleus.

TABLE II

RELATIONSHIP BETWEEN LENGTH OF SIDE CHAIN, POSITION OF HYDROXYL GROUP, AND VALUE OF LOG $R_F/(1-R_F)$ FOR CERTAIN GUAIACYL COMPOUNDS

| Position of hydroxyl group | Compound | $R_F$ | Log $\frac{R_F}{1-R_F}$ | Compound | $R_F$ | Log $\frac{R_F}{1-R_F}$ | Compound | $R_F$ | Log $\frac{R_F}{1-R_F}$ |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha$ | $R\cdot CH_2\cdot OH$ | 0.06 | −1.19 | $R\cdot CHOH\cdot CH_3$ | 0.17 | −0.69 | $R\cdot CHOH\cdot CH_2\cdot CH_3$ | 0.39 | −0.19 |
| $\beta$ | | | | $R\cdot CH_2\cdot CH_2OH$ | 0.10 | −0.95 | $R\cdot CH_2\cdot CHOH\cdot CH_3$ | 0.26 | −0.45 |
| $\gamma$ | | | | | | | $R\cdot CH_2\cdot CH_2\cdot CH_2OH$ | 0.20 | −0.60 |

Ultraviolet spectra failed to provide a means of differentiation. The compounds examined were (R = guaiacyl group): $R\cdot CH_2OH$, $R\cdot CH_2\cdot CHOH\cdot CH_3$, $R\cdot CH_2\cdot CH_2\cdot CH_2OH$, $R\cdot CH_2\cdot CO\cdot CH_3$, $R\cdot CH_2\cdot CH_2\cdot COOH$. All showed maximum absorption in 95% ethanol at 280.5–281.6 m$\mu$ which shifted to 294–297 m$\mu$ in $N$ potassium hydroxide. The isosbestic points were in the ranges 283.2–286.5, 267.7–269.2, and 231–231.8 m$\mu$.

## EXPERIMENTAL PART

### *Preparation of 1-(3-Methoxy-4-hydroxyphenyl)-2-propanol*

Vanillyl methyl ketone (6.5 g., 0.36 mole) was dissolved in 50 ml. methanol and 20 ml. 2 $N$ sodium hydroxide was added. The addition of 1 g. sodium borohydride caused a slight evolution of gas. The mixture was heated slowly and refluxed for 1 hour on the steam bath. After concentration under reduced pressure to 12–15 ml. the solution was cooled and 25 ml. water added slowly. Diluted hydrochloric acid was added and the mixture extracted four times with 25 ml. portions of chloroform. The extract was shaken twice with an excess of sodium bisulphite solution (21%), dried over sodium sulphate, and transferred to a bulb tube. After evaporation of the solvent under reduced pressure, the residue was distilled (air bath, 130–150° C., 0.5 mm.) to yield an almost colorless, viscous liquid which solidified after a few hours. Yield: 5.27 g. (80%); m.p. 36–37° C.

Found: C, 66.02; H, 7.82; $OCH_3$, 17.12. Calc. for $C_{10}H_{14}O_3$: C, 66.07; H, 7.71; $OCH_3$, 16.94.

### *Color Reactions*

(*a*) A 1% solution in acetone of diazotized *p*-nitraniline fluoborate was sprayed on the chromatogram, followed by treatment with alkali.

(*b*) Diazotized sulphanilic acid, prepared according to Koessler and Hanke (2), was sprayed on the chromatogram, followed by treatment with alkali.

$R_F$ values for the compounds listed in Table II, and the method of measuring them, are recorded by the authors (3), with the exception of the value for 1-(3-methoxy-4-hydroxyphenyl)-2-ethanol, which was found by the method used in the reference just cited to be 0.10.

U.V. spectra were determined with a Beckmann Spectrophotometer (Model DU). Isosbestic points were determined by superposition of the neutral and basic (1 g. KOH/l.) spectra and of several spectra of solutions with intermediate pH values (1).

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