

Table 1. PROPERTIES OF RESORCINOL GLYCOSIDES

Compound	$R_F$		MSA* 0.1 M sodium borate buffer (pH 10.0)	$\lambda_{max}$ in H <sub>2</sub> O in NaOH		$\beta$ -Galactos- idase hydrolysis products†
	Solvent A	Solvent B†				
<i>m</i> -Hydroxy- phenyl- $\beta$ -D- glucopyran- oside I	0.56	0.49	0.50	271	285	Resorcinol, galactose Resorcinol, fucose
	0.53	0.46	0.68	270	285	
II	0.68	0.64	0.62	270	285	

\* Electrophoretic mobility relative to salicyelic acid.

† B, ethylacetate/acetic acid/water (9:2:2, by vol.).

‡ Hydrolysis products detected on paper chromatograms. Sugars, solvent B (silver nitrate/sodium hydroxide spray reagent); resorcinol, solvent A (diazotized *p*-nitroaniline/sodium hydroxide spray reagent).

The results show clearly that (I) and (II) are *m*-hydroxyphenyl- $\beta$ -D-galactoside and *m*-hydroxyphenyl- $\beta$ -D-fucoside, respectively, both glycosyl groups presumably occurring in the stable pyranoid form. The two higher molecular weight compounds produced from lactose and resorcinol were probably *O*-digalactosyl derivatives of the phenol.

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<sup>1</sup> Cardini, C. E., and Leloir, L. F., *Cienc. Invest.*, **13**, 514 (1957).

<sup>2</sup> Pridham, J. B., and Saltmarsh, M. J., *Biochem. J.*, **74**, 42 P (1960); **87**, 218 (1963).

<sup>3</sup> Yamaha, T., and Cardini, C. E., *Arch. Biochem. Biophys.*, **86**, 127 (1960).

<sup>4</sup> Dutton, G. J., and Duncan, A. M., *Biochem. J.*, **77**, 18 P (1960).

<sup>5</sup> Barber, G. A., *Biochem. J.*, **1**, 463 (1962).

<sup>6</sup> Cardini, C. E., and Yamaha, T., *Nature*, **182**, 1446 (1958).

<sup>7</sup> Anderson, J. D., Hough, L., and Pridham, J. B., *Biochem. J.*, **77**, 564 (1960).

<sup>8</sup> Pridham, J. B., *Biochem. J.*, **76**, 13 (1960).

<sup>9</sup> Pridham, J. B., *Chem. and Indust.*, 1172 (1961).

<sup>10</sup> Wallenfels, K., Zarnitz, M. J., Laule, G., Bender, H., and Keser, M., *Biochem. Z.*, **331**, 459 (1959).

<sup>11</sup> Swain, T., *Biochem. J.*, **53**, 200 (1953).

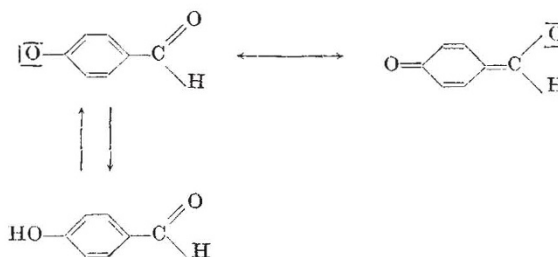
### Chalcon Formation of Different Substituted Acetophenones and *p*-Hydroxy-benzaldehyde

WE have already reported attempts to carry out the chalcon-forming condensation reaction of three isomeric nitro- and several nitro-hydroxy-acetophenones (2-nitro-3-hydroxy-, 3-nitro-4-hydroxy-, 4-nitro-2-hydroxy-, 4-nitro-3-hydroxy-, 5-nitro-2-hydroxy and 6-nitro-3-hydroxy-acetophenone) and *p*-hydroxy-benzaldehyde in presence of sodium hydroxide and hydrochloric acid catalysts<sup>1-3</sup>. It was shown that in absolute ethanol saturated with hydrochloric acid gas, *p*-hydroxy-benzaldehyde readily reacts at room temperature with three isomeric acetophenones. It also reacts with several nitro-hydroxy-acetophenones (3-nitro-4-hydroxy-, 4-nitro-2-hydroxy-, 4-nitro-3-hydroxy-, 6-nitro-3-hydroxy-acetophenone and with 5-nitro-2-hydroxy-acetophenone at high temperatures) as well as with 4-hydroxy-acetophenone. The same substituted acetophenones in the presence of sodium hydroxide as catalyst do not react with *p*-hydroxy-benzaldehyde at room temperature; moreover, on heating, condensation occurs only with 3-nitro-4-hydroxy-acetophenone. According to the reactions the greater reactivity of *p*-hydroxy-benzaldehyde in acidic medium can be interpreted as follows.

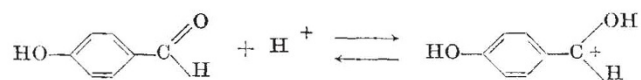
It is known that the rate of chalcon formation in alkaline medium depends on the electrophilic properties of benzaldehyde and on the nucleophilic properties of the

acetophenone component. The electrophilic and nucleophilic substituents exert a corresponding influence on reactivity.

The carbonyl group of phenolaldehydes and phenolketones, attracting *ortho*- or *para*-situated electrons, decreases the electron density of the oxygen of the phenolic hydroxyl group by a mesomeric effect, promoting the dissociation of hydrogen of the phenolic hydroxyl group. In alkaline medium the shift of the electrons is more pronounced, for example, *p*-hydroxy-benzaldehyde can be expressed by the following mesomeric extreme structures:



Taking into consideration that the mesomeric electron shift (+ *M* effect) changes in the order  $O < OR < O^+R_2$  (refs. 4-6), a chinoid structure and consequently a lower reactivity seem more likely. This phenomenon leads to the absence of chalcon formation. In acidic medium the proton catalysis renders the formation of the carbonium ion easier, and as the dissociation of the phenol is restricted, it probably reacts with the non-chinoid, that is, more reactive structure:



Results obtained in acidic medium support this assumption.

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<sup>1</sup> Sipos, Gy., and Széll, T., *Acta Phys. Chem.* (Szeged), **5**, 70 (1959).

<sup>2</sup> Sipos, Gy., Széll, T., and Várna, I., *Acta Phys. Chem.* (Szeged), **6**, 109 (1959).

<sup>3</sup> Sipos, Gy., Dobó, I., and Czukor, B., *Acta Phys. Chem.* (Szeged), **8**, 160 (1962).

<sup>4</sup> Jaffé, H. H., *Chem. Rev.*, **2**, 191 (1953).

<sup>5</sup> Ingold, C. K., *Structure and Mechanism in Organic Chemistry*, 77 (1953).

<sup>6</sup> Burkhardt, G. N., Horrex, C., and Jenkins, D. I., *J. Chem. Soc.*, 1654 (1936).  
Burkhardt, G. N., Ford, W. G. K., and Singleton, F., *ibid.*, 17 (1936).

### Note on Gas Chromatographic Injection

IN the course of investigations of the accurate determination of gas chromatographic retention times, several causes of errors in these measurements have been examined; this communication is concerned with the errors which may be due to the finite concentration of any one component observed, even when the isotherms are practically linear for that concentration.

The primary effect is that, as the flow of gas within the column is higher at the places where retained components are present, any given retained component will travel at a velocity greater than  $v_0/1 + k$ , where  $v_0$  designates the carrier gas velocity in the immediate vicinity of that component, and  $k$  the capacity ratio of the column for it.

Secondary effects are caused by the increased pressure gradient at the instantaneous location of the various com-