

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, ONTARIO RESEARCH FOUNDATION]

The Effect of Alkali on the Ultraviolet Absorption Spectra of Hydroxyaldehydes, Hydroxyketones and other Phenolic Compounds

BY H. W. LEMON

The ultraviolet absorption spectra for *p*-hydroxybenzaldehyde and vanillin have been reported by Purvis.¹ Hillmer and Schorning² have made an extensive study of the spectra of various phenols, both free and etherified. More recently the spectra for vanillin, syringaldehyde, acetovanillone and many related compounds have been reported by Patterson and Hibbert.³ The effect of alkali on the spectra is not mentioned in any of these papers, but Morton and Stubbs⁴ have determined the spectra of *o*-, *m*-, and *p*-hydroxybenzaldehydes, and of *o*- and *p*-hydroxyacetophenones in alkaline solution, and found that there is a displacement of the long-wave band in the direction of longer wave lengths. This displacement, they point out, is qualitatively in agreement with the effect of alkali on the spectrum of phenol.

In this Laboratory, the effect of alkali on the spectra of a number of phenolic compounds, particularly *p*-hydroxyaldehydes and *p*-hydroxyketones, has been investigated. This work was done in connection with the development of a spectrophotometric method for the determination of vanillin and related compounds, which will be reported elsewhere.

Experimental

Materials and Apparatus.—The compounds investigated are listed in Table I. Compound no. 8 was prepared by the method of Buckland, Tomlinson and Hibbert⁵; no. 9 by the method of Mauthner.⁶ The author is indebted to Dr. C. B. Purvis, McGill University, Montreal, Quebec, for no. 5, and to Dr. J. H. Fisher, Ontario Paper Company, Limited, Thorold, Ontario, for nos. 11, 12, 13 and 14. The others were purchased from Eastman Kodak Company and British Drug Houses, Limited.

The solvent used was absolute ethyl alcohol. A solution of potassium hydroxide was prepared as required by diluting a 4% stock solution to 0.2% with 95% ethyl alcohol. The absolute and 95% alcohols used were refluxed with zinc dust and potassium hydroxide before distillation, using all-glass equipment.

A Beckman spectrophotometer equipped with an ultraviolet accessory set was used for spectral absorption measurements.

Method.—Absolute ethyl alcohol solutions of the compounds to be investigated were prepared containing 0.100 g. in 100 ml. Further dilutions were made as required to bring the absorption readings within the range of the spectrophotometer. The alkaline solutions contained 7 ml. of the 0.2% potassium hydroxide solution in 100 ml. Absorption measurements were made with the slit-width adjusted to correspond to a band-width of about 1 m μ .

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Results

The absorption spectra of alkaline and non-alkaline solutions of a number of compounds are shown in Fig. 1, and the positions and absorption intensities of the long-wave bands of all of the compounds investigated are given in Table I. It will be observed that the absorption bands of all of the compounds are displaced in the direction of longer wave lengths by the addition of alkali and that the intensity of absorption of the long-wave bands is increased, except in the case of *m*-hydroxybenzaldehyde. The effect of alkali is greatest on the *p*-hydroxyaldehydes and *p*-hydroxyketones, both as regards displacement of the long-wave bands and the increase in their absorption intensities.

TABLE I

EFFECT OF ALKALI ON THE DISPLACEMENT AND INTENSITY OF THE LONG-WAVE BAND OF VARIOUS COMPOUNDS

Compound	Not alkaline		Alkaline	
	λ_{\max} .	$E_{1\text{ cm.}}^{1\%}$	λ_{\max} .	$E_{1\text{ cm.}}^{1\%}$
1. <i>o</i> -Hydroxybenzaldehyde	325	300	382	580
2. <i>m</i> -Hydroxybenzaldehyde	317	220	364	200
3. <i>p</i> -Hydroxybenzaldehyde	280	1380	336	2460
4. Vanillin	310	710	353	1980
5. Syringaldehyde	308	700	370	1530
6. 2,4-Dihydroxybenzaldehyde	318	595	334	2240
7. <i>p</i> -Hydroxyacetophenone	278	1030	328	1840
8. Acetovanillone	303	513	348	1450
9. Acetosyringone	302	574	362	1200
10. <i>p</i> -Hydroxypropionophenone	276	950	328	1570
11. 2-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	306	440	352	1280
12. 2-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	304	510	368	1060
13. 2-Acetoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	306	400	370	880
14. 1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione	324	380	370	1060
15. <i>p</i> -Hydroxybenzoic acid	254	1030	280	1350
16. Vanillic acid	286	245	298	792
17. Syringic acid	273	520	300	728
18. Vanillyl alcohol	281	190	294	245
19. Phenol	273	180	291	250
20. Guaiacol	277	220	289	300
21. 1,3-Pyrogallol dimethyl ether	270	70	285	180
22. <i>p</i> -Nitrophenol	312	720	400	1470

Examination of Fig. 1 and Table I will show that the absorption characteristics for the *p*-hydroxyal-

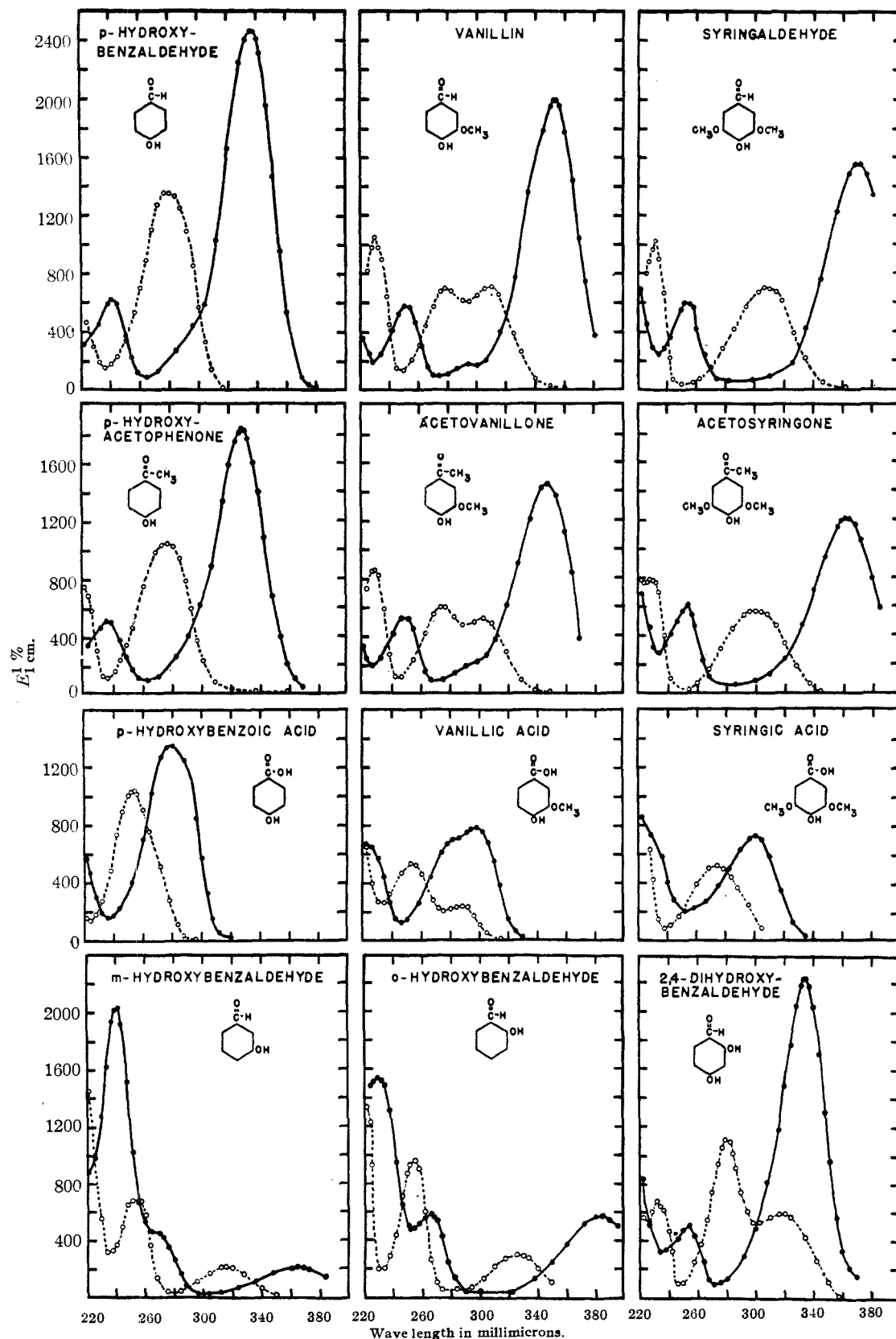


Fig. 1.—Ultraviolet absorption curves for alkaline and non-alkaline solutions. The curves for alkaline solutions are represented by continuous lines.

dehydes and the corresponding methyl ketones are similar. It is also evident that the position of their long-wave bands in alkaline solution is influenced by the presence of methoxy groups on the benzene ring. The effect on the *p*-hydroxyaldehydes is as follows: With no methoxy group the absorption maximum is at 336, with one it is at 353 and with two methoxy groups it is at 370 $m\mu$. The corresponding wave lengths for the methyl ketones are 328, 348 and 362 $m\mu$, respectively. The positions of the long-wave bands of other ketones are given in Table I. Replacement of the methyl ketones with other alkyl radicals does not have much effect on the position of the maximum unless additional chromophoric groups are introduced (*cf.* acetovanillone and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione).

The position of the long-wave bands of the corresponding acids (*p*-hydroxybenzoic, vanillic and syringic) is not so greatly affected by methoxy groups, the maxima of alkaline solution being at 280, 298 and 300 $m\mu$. For the simple phenols (phenol, guaiacol and 1,3-pyrogallol dimethyl ether) the effect is small (see Table I).

The behavior of the *p*-hydroxyaldehydes and *p*-hydroxyketones in alkaline solution is similar to that of *p*-nitrophenol. Alkaline solutions of the latter are yellow as the displacement of the long-wave band is greater, maxima absorption being at 400 $m\mu$.

Summary

1. The ultraviolet absorption bands of phenolic compounds in absolute ethyl alcohol solution are displaced in the direction of longer wave lengths when the solutions are made alkaline. Usually the intensity of absorption of the long-wave band is increased.

2. The displacement and increase in intensity of the long-wave band is greatest for *p*-hydroxyaldehydes and *p*-hydroxyketones.

3. The position of the long-wave bands of alkaline solutions of *p*-hydroxyaldehydes and *p*-hydroxyketones is influenced by the presence of methoxy groups on the benzene ring.

4. The behavior of the *p*-hydroxyaldehydes and *p*-hydroxyketones in alkaline solution is similar to that of *p*-nitrophenol.

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The Solubilities of Four Amino Butyric Acids and the Densities of Aqueous Solutions of the Acids at 25^o

BY L. S. MASON

The solubilities of β -amino-*n*-butyric acid and γ -aminobutyric acid have not been determined heretofore. There are variations in the values of the solubilities of α -amino-isobutyric acid and α -amino-*n*-butyric acid reported by others.^{2,3} The densities of various concentrations of aqueous solutions of these compounds have not been available previously. A knowledge of these properties was of importance in connection with a study of the heats of dilution of aqueous solutions of these four acids.⁴ The latter investigation is a part of a systematic study^{5,6} of the heats of dilution of solutions of various amino acids in progress in this Laboratory.

The chief criterion of purity chosen for these materials was that a sample of an acid have essentially a constant solubility when saturated aqueous solutions were formed successively from the

residue from each preceding solution. This method of "constant solubility" has been found to be the most sensitive criterion of purity for compounds of this type.²

Materials

A quantity of glycine was purified at the same time for another purpose from a Merck and Company product. The α -amino-isobutyric and the α -amino-*n*-butyric acids were obtained from Eastman Kodak Company. The β -amino-*n*-butyric and the γ -aminobutyric acids were from the University of Illinois. The usual methods of purification were employed, with variations of conditions and solvents indicated by variations in the behavior of the compounds. All of the purified materials were ashed in a muffle furnace. In the case of the α -acids, the ash was less than 0.01%, and less than 0.02% for the β - and γ -acids. Formol titration was performed on the α -acids and the β -acid, using a Beckman pH-meter equipped with glass and calomel electrodes. In the case of the α -butyric acids, the percentage purity was determinable by formol titration with an error of 0.2-0.3%, and in the case of the β -acid with an error of about 1.0%.

The Solubilities.—The solids were equilibrated with water in a thermostat at 25 \pm 0.02^o, usually

(1) The generous support of the Buhl Foundation in this study is acknowledged.

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