absorption spectra of tyrosine at shorter wave lengths and at various *p*H values has been made. Purified tyrosine was used throughout and the concentrations were verified by determination of Kjeldahl nitrogen and alpha amino nitrogen. The tyrosine was buffered in the region *p*H 5–9 with appropriate acetate, phosphate or borate buffers. Other *p*H values were obtained by adding hydrochloric acid or sodium hydroxide without the use of buffer. Values for *p*H approaching the *pK* were obtained by adding one-half equivalent of sodium hydroxide per equivalent of tyrosine. All of the ultraviolet readings were taken with the Beckman quartz spectrophotometer model DU.

As shown by the absorption curves in Fig. 1 the band at 240 mμ indicated by Sizer and Peacock[4] does not disappear in acid solutions but rather shifts to shorter wave lengths thus indicating the degree of ionization of the phenol group. A similar absorption curve was reported by Lemon[5] for vanillin.

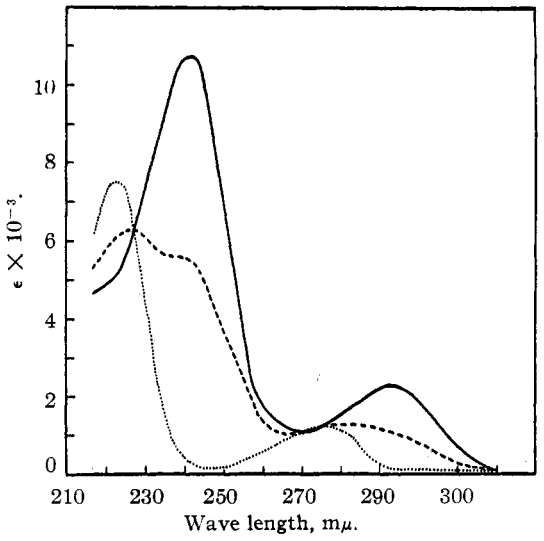

Fig. 1.—Ultraviolet absorption of tyrosine at various *p*H values: ....., *p*H < 8; - - -, *p*H = 10; ——, *p*H > 12; $\epsilon = D/cl$, c = concn. in moles/l., l = path length, D = optical density as read by Beckman spectrophotometer.

Our experimental data[6] show that the absorption curve in the "acid" range (*p*H 1 through 8) exhibits absorption maxima at 223 mμ (ϵ = 7600) and 275 mμ (ϵ = 1300). In the "alkaline" range (*p*H 12 and above) the absorption maxima are at 242 mμ (ϵ = 10,700) and 293 mμ (ϵ = 2400). At approximately the *pK* value there is an absorption band which is intermediate between that of "alkaline" solutions and "acid" solutions. The *pK* value calculated from these curves is 9.90, which is in approximate agreement with the *pK* 10.05 reported by Crammer and Neuberger.[3]

(5) H. W. Lemon, THIS JOURNAL, **69**, 2998 (1948).

(6) The authors wish to thank Miss Frances J. Cherot for her technical assistance.

The effect of "acid" and "alkaline" solutions on the far ultraviolet maximum of tyrosine is therefore essentially the same as that reported[3] for the near ultraviolet maximum in that the addition of acid shifts the maximum toward shorter wave lengths and decreases the molecular absorption coefficient. At the half ionization point for the phenolic group the observed values agree substantially with the theoretical half ionization absorption curve for tyrosine.

DEPARTMENT OF PATHOLOGY
LONG ISLAND COLLEGE OF MEDICINE
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An Improved Preparation of Gentisic Acid[1]

BY JULIUS LOWENTHAL AND J. M. PEPPER

Gentisic acid (2,5-dihydroxybenzoic acid), a metabolite of salicylic acid, has recently become of added interest because of its antirheumatic activity.[2] The reported oxidation of salicylic acid by potassium persulfate,[3] although it may be improved by a more careful control of the reaction time and temperature, gives a product which can only be purified with difficulty and great loss. A more recent publication[4] describes the preparation of gentisic acid by means of a four-step synthesis from hydroquinone diacetate in an over-all yield of 16%.

In connection with chemotherapeutic investigations attempts were made to find a more efficient synthesis for gentisic acid. Rakowski and Leppert[5] have reported the preparation of gentisic acid from 5-bromosalicylic acid by fusion with sodium hydroxide with an unspecified yield. It has now been found that this compound can also be prepared from 5-bromosalicyclic acid by heating in alkaline solution with copper powder as a catalyst.

From a series of experiments in which both temperature and time of reaction were varied, the following conditions were adopted. For the isolation of the required acid, the use of sulfur dioxide as acidifying agent, greatly facilitated the preparation of a pure product.

Experimental

The 5-bromosalicylic acid was prepared by the method of Hewitt and Kenner[6] in practically quantitative yield.

5-Bromosalicylic acid (21.7 g.) was dissolved in 500 ml. 8% sodium hydroxide solution and copper powder (20 g.) was added. The catalyst was prepared according to the method of Brewster and Groening.[7] The mixture was heated in an autoclave for one and one-half hours at 140–150°. The use of a rocking bomb did not increase the

(1) This research was conducted under a Public Health Research Grant from the Department of National Health and Welfare, Ottawa, Canada.

(2) Meyer and Ragan, *Science*, **108**, 281 (1948).

(3) Mauthner, *J. prakt. Chem.*, **156**, 150 (1940).

(4) Morris, THIS JOURNAL, **71**, 2056 (1949).

(5) Rakowski and Leppert, *Ber.*, **8**, 788 (1875).

(6) Hewitt, Kenner and Silk, *J. Chem. Soc.*, **85**, 1225 (1904).

(7) Brewster and Groening, "Organic Syntheses," Coll. Vol. II, 446 (1943).

yield. The copper catalyst was removed by filtration, washed twice on the filter with water (50 ml.) and the combined filtrate and washings acidified with sulfur dioxide while kept in an ice-bath. The acidified solution was extracted with ether (500 ml.) in a continuous liquid–liquid extractor for twenty-four hours. The ethereal solution was concentrated on the steam-bath to a small volume (*ca.* 50 ml.), the gentisic acid precipitated by the addition of Skellysolve-C and recovered by filtration. The yield of a light tan colored product was 11.1 g. (72%), m. p. 190°.

Recrystallization from boiling water, after carbon treatment, gave a white crystalline material, m. p. 205°; mixed m. p. with an authentic sample of gentisic acid gave no depression.

DEPARTMENT OF PHYSIOLOGY AND
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SASKATCHEWAN
SASKATOON, SASK., CANADA

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Dielectric Constants of Methyl Alcohol–Benzene Mixtures

BY JOHN H. LAROCHELLE AND ARTHUR A. VERNON

In the course of solubility studies with non-aqueous solvents, it was necessary to determine the dielectric constants of methyl alcohol–benzene mixtures over the complete range. Williams, Rosenberg and Rothenberg[1] recently published density data for these same mixtures, and, therefore, it seemed worthwhile to calculate polarization values for methyl alcohol in benzene.

Materials.—Reagent grade benzene and methyl alcohol were dried over activated alumina and distilled with a fractionating column. The first and last 20% fractions were discarded and the purified product was stored in Pyrex flasks with sealed stoppers. The index of refraction of the purified methyl alcohol was 1.3277 at 25° compared to the "International Critical Tables" value of 1.32773; for benzene the index of refraction was 1.4977 at 25°, compared to the "International Critical Tables" value of 1.49779 at 25.2°.

Dielectric Constant Measurement.—The dielectric constants of a series of methanol-benzene solutions were measured on a wide range frequency bridge[2] using a cell holding 15 ml. and having a cell constant of 1.352 $\mu\mu$f/unit ϵ. Measurements were carried out at 500 kc. and 25° and dielectric constant values of the pure benzene and methanol compared very favorably with those reported.[3]

Results.—P_{12} values were calculated from the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\frac{f_1 m_1 + f_2 m_2}{\rho}$$

and P_2 values were obtained by use of

$$P_{12} = f_1 P_1 + f_2 P_2$$

The data of Williams, Rosenberg and Rothenberg[1] were used to make a plot of density *versus* mole per cent. Since the index of refraction of benzene reported by these authors does not agree with the "International Critical Tables" value, measurements of refractive index for various volume per cent. mixtures were made in this laboratory. A plot of data was used to determine compositions in volume per cent. Then the volume per cent. mole fraction data of Williams, Rosenberg and Rothenberg[1] were plotted to obtain mole fractions for any mixture made up.

Mole frac. MeOH	Dielectric constant	Density	Index of refraction	P_{12}	P_2
0.0	2.27	0.8724	1.4977	26.6	
.140	3.67	.8684	1.4859	38.9	114
.353	6.41	.8579	1.4643	46.4	82.6
.362	6.70	.8575	1.4637	46.9	82.8
.497	9.20	.8487	1.4459	47.6	68.9
.508	9.54	.8479	1.4439	47.7	68.2
.601	12.24	.8403	1.4281	47.36	61.13
.613	12.83	.8393	1.4264	47.40	60.51
.700	16.33	.8298	1.4092	47.22	54.62
.775	19.69	.8205	1.3924	44.53	49.73
.840	22.95	.8177	1.3762	42.72	45.78
.895	26.30	.8030	1.3595	41.06	42.75
.955	29.51	.7948	1.3420	38.83	39.41
1.000	32.65	.7865	1.3277	37.21	37.21

A plot of P_2 *versus* mole fractions of methyl alcohol is shown in Fig. 1.

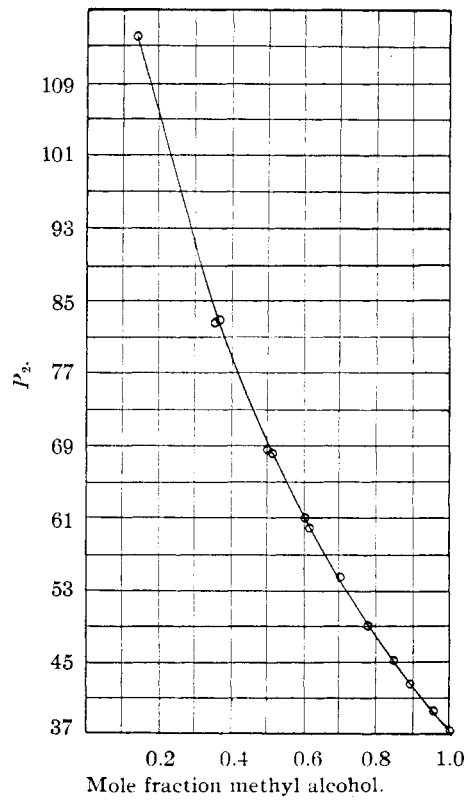

Fig. 1.—Polarization of methyl alcohol in benzene.

(1) G. C. Williams, S. Rosenberg and H. A. Rothenberg, *Ind. Eng. Chem.*, **40**, 1273 (1948).

(2) J. L. Oncley and N. R. S. Hollies, "A Wide Range Frequency Bridge, Dielectric Constants and Conductance Studies on Electrolytic Solutions," *Rev. Sci. Insts.*, in preparation.

(3) P. S. Albright and L. J. Gosting, THIS JOURNAL, **68**, 1061 (1946).