have shown that under suitable conditions, however, one mole of carbon dioxide is liberated per mole of ascorbic acid reacting with formaldehyde. Recently, Reithel and Wither[3] have presented data suggesting that ascorbic acid is oxidized by formaldehyde to dehydroascorbic acid, which slowly undergoes decarboxylation. Conclusive evidence concerning the origin of the carbon dioxide evolved during the reaction has not been presented. The availability[4] of L-ascorbic acid-1-C^{14}, however, has enabled us to show definitely that the carbon dioxide is derived entirely from the carboxyl carbon of L-ascorbic acid.

Experimental

Thirty milligrams of L-ascorbic acid-1-C^{14} (specific activity 130 counts per minute per milligram under our conditions of measurement[5]) was dissolved in 1 ml. of carbon dioxide-free distilled water in a test-tube (25 × 150 mm.) fitted with a dropping funnel and two side-arms so that any gases evolved could be swept with nitrogen into a saturated barium hydroxide solution. The test-tube was cooled to 0° in an ice-bath and 2 ml. of carbon dioxide-free distilled water was added, followed by 0.3 ml. of a 37% formaldehyde solution. The *p*H was adjusted to 7.5 by addition of 0.5 *N* carbon dioxide-free sodium hydroxide. The reaction was then carried out at 60° for a period of four hours. At the end of this time the reaction mixture was cooled to 0° in an ice-bath, acidified with 10 ml. of 1.8 *M* sulfuric acid, and the evolved carbon dioxide collected in the saturated barium hydroxide solution. The precipitated barium carbonate was prepared for counting as described previously.[5]

In preliminary experiments it had been shown that the yields of carbon dioxide corresponded closely to those obtained by Reithel and West.[1] When the experiment was carried out under the same conditions without adding formaldehyde, less than 0.3 mg. of barium carbonate was recovered.

The experimental data obtained with labeled ascorbic acid are summarized in Table I.

TABLE I

SPECIFIC ACTIVITIES OF ASCORBIC ACID AND BARIUM CARBONATE, IN THE ASCORBIC ACID–FORMALDEHYDE REACTION

Expt. number	Specific activity of carboxyl carbon of ascorbic acid (counts/min./mg. C)	Specific activity of barium carbonate (counts/min./mg. C)
1	1910	2070
2	1910	1950

Thus, within the over-all precision of measurement (±6%), the radioactivity of the carbon dioxide evolved was derived exclusively from the carboxyl carbon of L-ascorbic acid.

Acknowledgment.—The authors are indebted to the Nutrition Foundation, Inc., and to the National Institutes of Health, U. S. Public Health Service, for grants in support of the present investigation.

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[4] Burns and King, *Science*, **111**, 257 (1950).

[5] Burns, Ph.D. Dissertation, Columbia University, 1950.

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Some 7-Substituted Derivatives of 8-Quinolinol

BY J. P. PHILLIPS AND STANLEY PRICE

A substituent in the 2-position of 8-quinolinol has been shown to create enough steric hindrance to prevent the molecule from forming a chelate with aluminum.[1,2] Since it seemed possible that large substituents in the 7-position would also produce steric hindrance to chelate formation, the following investigation was carried out.

The compounds studied were 7-phenylazo-8-quinolinol-5-sulfonic acid (I), 7-*o*-tolylazo-8-quinolinol-5-sulfonic acid (II), 7-*m*-tolylazo-8-quinolinol-5-sulfonic acid (III), 7-*o*-tolylazo-8-hydroxyquinaldine-5-sulfonic acid (IV) and 7-*m*-tolylazo-8-hydroxyquinaldine-5-sulfonic acid (V). Since the complexes formed by these compounds with metal ions were water soluble, a spectrophotometric investigation of whether or not the compounds formed chelates with aluminum was employed. The compounds with a 2-substituent, IV and V, did not react; those having only the 7-substituent did react under the same conditions, as shown by a marked decrease in extinction from the value calculated for no reaction (Table I). Evidently the 7-substituents used in this study do not produce steric hindrance to chelate formation.

TABLE I

REACTION WITH ALUMINUM AT *p*H 3.5 (WAVE LENGTH 530 mμ)

Compound	Calcd. extinction for no reaction	Obs. extinction
I	0.73	0.302
II	1.12	0.895
III	0.80	0.470
IV	1.10	1.13
V	0.9	1.0

Similar qualitative tests were run with magnesium, copper and ferric iron in both 0.1 *N* hydrochloric acid and a buffer of *p*H 3.5. No positive

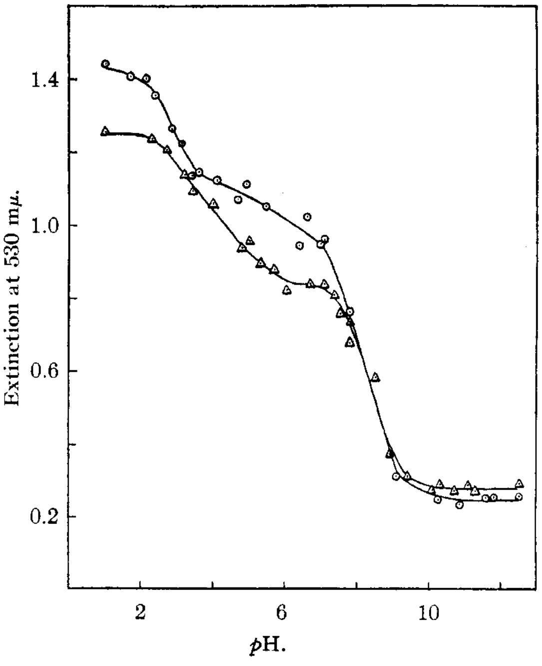

Fig. 1.—Structure changes with changing *p*H: ⊙, 7-*o*-tolylazo-8-quinolinol-5-sulfonic acid; ▵, 7-*o*-tolylazo-8-hydroxyquinaldine-5-sulfonic acid.

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[1] J. P. Phillips and L. L. Merritt, THIS JOURNAL, **71**, 3984 (1949).

[2] H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

TABLE II

ABSORPTION MAXIMA OF SOME 7-SUBSTITUTED-8-QUINOLINOLS IN THE VISIBLE

Cpd.	Solvent	Maxima (mμ)		Cpd.	Solvent	Maxima (mμ)
I	0.1 *N* HCl	500–510(4.21)[a]	530(4.24)	I	0.1 *N* NaOH	480(4.13)
II	0.1 *N* HCl	510(4.32)	540(4.32)	II	0.1 *N* NaOH	465(4.17)
III	0.1 *N* HCl	505(4.23)	535(4.25)	III	0.1 *N* NaOH	475(4.14)
IV	0.1 *N* HCl	510(4.29)	540(4.29)	IV	0.1 *N* NaOH	470–475(4.16)
V	0.1 *N* HCl	510(4.20)	530–540(4.20)	V	0.1 *N* NaOH	480(4.19)

[a] Figures in parentheses are logarithms of the molecular extinctions.

tests were obtained in the acid solution; in the buffer copper and iron reacted with all the compounds, magnesium with none.

The absorption spectra of all the compounds in acid and base solutions were determined in the visible region (Table II). Since the compounds are red in acid and yellow in base, it seemed possible that they could be used as acid–base indicators. Therefore, a study of the variations in spectra with changing *p*H was made with compounds II and IV. As shown by a graph of extinction against *p*H (Fig. 1) three different structures exist in acid, neutral and basic solution. It was not considered worthwhile to calculate an accurate indicator constant from these data, since the color transition is evidently more gradual than desirable for a practical indicator.

The compounds are capable of functioning as irreversible indicators for titrations with standard bromine solutions because they change from red to colorless with an excess of bromine. It is therefore possible to use these derivatives of 8-quinolinol as indicators for the well-known bromine titration of 8-quinolinol.

Experimental

Preparation of Compounds.—8-Quinolinol-5-sulfonic acid or 8-hydroxyquinaldine-5-sulfonic acid was coupled with diazotized anilines in alkaline solution according to the directions of Matsumura.[3] The sodium salts were converted to the free bases by addition of acetic acid and recrystallized from alcohol in which they are sparingly soluble. The purity of the compounds was tested by running a Beer law check in acid solution at 530 mμ on 5 or 6 known concentrations by weight and extrapolating the straight lines obtained to zero concentration. Since the corresponding extinctions did not differ from zero by a significant amount (less than 0.05 unit), the compounds were considered sufficiently pure.

Absorption Spectra.—The extinctions of solutions containing 0.0240 g./liter of each compound were determined at 5-mμ intervals from 400–700 mμ with a Beckman model DU spectrophotometer using 1.00-cm. cells. (The measurements in acid solutions on compound V required a 0.0160 g./l. concentration because of the insolubility of this compound.) The *p*H of the solutions was measured with a Beckman *p*H meter to the nearest 0.1 unit, adjustment of *p*H to the desired values being made by the use of standard phthalate, phosphate and boric acid buffers. A check on possible interference with the color from these buffer constituents was obtained by adjusting the *p*H of several of the solutions with standard acid and base only; no differences were noted. Variations in ionic strength of the many solutions used were not large enough to make significant differences in extinction.

Qualitative Tests.—Fifteen ml. of a solution containing 0.040 g./l. of each compound was treated with 1 ml. of an approximately 1% solution of the desired metal ion, buffered with potassium acid phthalate and acid to a *p*H of 3.5, and diluted to 25 ml. As blanks solutions containing 15 ml. of the reagent solution in the buffer, and 1 ml. of the metal ion in the buffer, were used. A positive test was claimed if the extinction of the test solution differed by more than 0.1 unit from the combined values for the blanks. The tests were run at 7 wave lengths between 400 and 550 mμ.

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[3] K. Matsumura, THIS JOURNAL, **49**, 810 (1927).

The Structure of Sedoheptulosan[1]

BY JAMES W. PRATT, NELSON K. RICHTMYER AND C. S. HUDSON

In 1938, one of us[2] marshalled the available evidence and presented what appeared to be an unequivocal proof that sedoheptulosan possessed the unusual structure I, with one of its rings having an ethylene oxide form and the other a septanoid form. The evidence behind this reasoning stemmed from three different sources: (1) Ettel's proof,[3] which has since been confirmed by other researches, that sedoheptulose is D-altroheptulose; (2) Hibbert and Anderson's preparation[4] of a crystalline tetramethylsedoheptulosan which upon oxidation with warm concentrated nitric acid yielded a trimethoxyglutaric acid; the latter was characterized as a dimethylamide melting at 145–146°, and was assumed to have the ribo configuration because it was optically inactive (the inactive xylo derivative could be excluded because of its higher melting point, 167–168°); and (3) Levene and Compton's oxidation[5] of 2,3,4-trimethyl-D-ribose similarly to a trimethoxyglutaric acid whose optically inactive dimethylamide also melted at 145–146°. From these results it was concluded that only formula I could apply to sedoheptulosan.

However, recent investigations in this laboratory have produced evidence that is not in accord with the formulation I. Oxidation of sedoheptulosan with periodate indicated the presence in its molecule of three contiguous secondary hydroxyl groups,[6] and restricts the possible formulas to I, II, and III. We have now found that the catalytic hydrogenation of the dialdehyde obtained from the periodate oxidation of sedoheptulosan, followed by acid hydrolysis of the product (IV, V, or VI), produced a non-reducing, water-soluble liquid which

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[1] A portion of this material has been taken from the thesis to be submitted by James W. Pratt to the Chemistry Department of the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] C. S. Hudson, THIS JOURNAL, **60**, 1241 (1938).

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[5] P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 169 (1936).

[6] W. T. Haskins, R. M. Hann and C. S. Hudson, unpublished results. *Cf.* N. K. Richtmyer, *Advances in Carbohydrate Chem.*, **1**, 52 (1945).