

TABLE I (Continued)

R'	R''	R'''	Yield, %	M.p., °C.	[α] <sub>D</sub>	Empirical formula	Anal.		Recrystallization solvent
							Carbon, % Calcd.	Hydrogen, % Found	
			..	277-278	+ 5.2 <sup>a</sup>	C <sub>27</sub> H <sub>42</sub> O <sub>7</sub>	67.75	8.85	Methanol
			98	109.5-111.5	-10.8	C <sub>25</sub> H <sub>40</sub> O <sub>5</sub>	68.77	9.24	Acetone-hexane
			92	192.6-194.0	+21.3	C <sub>21</sub> H <sub>32</sub> O <sub>4</sub>	72.38	9.26	Acetone-water
			..	204.4-206.2	- 1.4	C <sub>23</sub> H <sub>34</sub> O <sub>5</sub>	70.74	8.78	Acetone-water

All rotations are in acetone, except those noted.

<sup>a</sup> Chloroform. <sup>b</sup> Dioxane. <sup>c</sup> Reported m.p. 116-118°, [α]<sub>D</sub> +91° (CHCl<sub>3</sub>) [O. Mancera, A. Zaffaroni, B. Rubin, F. Sondheimer, G. Rosenkrantz and C. Djerassi, THIS JOURNAL, 4, 3711 (1952)]; m.p. 102-105°, [α]<sub>D</sub> +83° (CHCl<sub>3</sub>) [H. Murray and D. Peterson, U. S. 2,602,769]. <sup>d</sup> Reported m.p. 148-149°, [α]<sub>D</sub> +65° (CHCl<sub>3</sub>) [Djerassi, *et al.*, ref. c].

ketal (IV, R = H) was converted to pregnan-11α-ol-3,20-dione (VI, R = H) without isolation of pregnan-11α-ol-3,20-dione 3,20-bis-ethylene ketal (V, R = H). Acetates were prepared by the usual procedure with acetic anhydride and pyridine. Physical constants and yield data are recorded in Table I.

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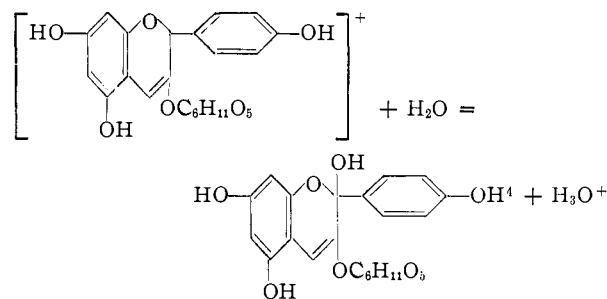
### On the Relation between Spectral Changes and pH of the Anthocyanin Pelargonidin 3-Monoglucoside<sup>1</sup>

BY ERNEST SONDSHEIMER

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The predominant effect of increasing hydrogen ion activity on the spectral properties of pelargonidin 3-monoglucoside is an increase in the intensity of absorption in the visible region.<sup>2</sup> Furthermore, on the addition of water to unbuffered benzopyrylium salt solutions a decrease in the light absorption in the visible range is observed which is greater than can be accounted for merely by dilution effects. These observations can be explained by the hypothesis that there is an equilibrium between hydronium ions, a red modification R<sup>+</sup> and a colorless form ROH of the anthocyanin. Evidence for this view is presented below. The method used here has previously been applied to many acid-base indicators but not to anthocyanins.<sup>3</sup>

The hydrolysis reaction may be shown as



then

$$pK = \log \frac{R^+}{ROH} + pH$$

In Table I the effects of changes in the pH on the light absorption at 500 millimicrons and on the pK values are shown. For the pH range in which the R<sup>+</sup> concentration varies between 98.4 and 10.8% the pK is constant within the experimental error. Thus one of the conditions necessary to consider this as an equilibrium reaction has been met. This evidence is strengthened by the observations that the pK is independent of the anthocyanin concentration and that the equilibrium may be approached from either side. The isolation of color-

(1) Journal Article No. 908, New York State Agricultural Experiment Station.

(2) E. Sondheimer and Z. I. Kertesz, THIS JOURNAL, 70, 3476 (1948).

(3) I. M. Kolthoff "Acid-Base Indicators," translated by Ch. Rosenblum, The Macmillan Co., New York, N. Y., 1937.

(4) Although the pseudo-base is here represented as a 2-chromenol it is not known whether this is the predominant tautomer. J. A. Berson, THIS JOURNAL, 74, 358 (1952), has shown that with some triphenylpyrylium pseudo-bases the open-chain 1,5-diketone was the only tautomer whose presence could be demonstrated.

less pseudo-bases on hydrolysis of several benzopyrylium salts by previous investigators<sup>5</sup> also supports the above results.

TABLE I

THE EQUILIBRIUM BETWEEN HYDRONIUM IONS, AND THE BENZOPYRYLIUM SALT AND THE PSEUDO-BASE OF PELARGONIN 3-MONOGLUCOSIDE AT 25°

pH	Optical density at 500 m $\mu$	R <sup>+</sup> , %	pK
1.18	1.075	98.4	2.99
1.42	1.050	96.2	2.82
1.74	1.025	93.7	2.92
1.99	0.980	89.7	2.93
2.16	.928	85.0	2.91
2.49	.855	78.3	3.05
2.58	.775	71.0	2.97
2.77	.665	60.9	2.96
3.08	.490	44.9	2.99
3.36	.338	30.9	3.01
3.62	.227	20.8	3.04
3.83	.159	14.6	3.06
4.01	.118	10.8	3.09

Av. pK 2.98  $\pm$  0.06

The anthocyanin was isolated from strawberries by a previously described method.<sup>2</sup> It was purified by recrystallizing the picrate six times and then converted to the chloride. The values in Table I were obtained with a  $4.27 \times 10^{-6}$  molar anthocyanin solution in Sørensen's disodium citrate-hydrochloric acid buffers. Measurements were taken at 500 m $\mu$  with a Beckman spectrophotometer, model C, using 1 cm. Corex cells, at least one hour after the solutions had been prepared. The pH values were determined with a Beckman pH meter, model G. All measurements were made at 25°.

(5) P. Karrer and C. Trugenberger, *Helv. Chim. Acta*, **28**, 444 (1945); I. M. Heilbron and A. Zaki, *J. Chem. Soc.*, 1902 (1926); D. W. Hill and R. R. Melhuish, *ibid.*, 1161 (1935).

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### A New Synthesis of Oxindole

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While evaluating known<sup>1,2</sup> and potential methods for preparing oxindole, it was found that the synthesis used by Meyer and Beer<sup>3</sup> to prepare 3,4-dihydrocarbostyryl from 2-chlorodihydrocinnamic acid could also be used for the synthesis of oxindole. The method consisted of heating *o*-chlorophenylacetic acid with concentrated ammonium hydroxide and copper powder in a sealed tube at

(1) See W. C. Sumpter, *Chem. Revs.*, **37**, 443 (1945), for a review of the methods for preparing oxindole.

(2) At the time that this work was begun the method by which R. Stolle and R. Bergdoll, *J. prakt. Chem.*, **128**, 1 (1930), cyclized  $\alpha$ -chloroacetanilide with aluminum chloride was found to be unsuccessful. Subsequently the work of S. Sugassawa, I. Satoda and J. Yanagisawa, *J. Pharm. Soc. Japan*, **58**, 139 (In English 29) (1938), showed that a ratio of 1.8 parts of aluminum chloride to one part of  $\alpha$ -chloroacetanilide was necessary for the reaction instead of a ratio of one to one as reported by Stolle and Bergdoll. Similar results have been reported recently by P. L. Julian in "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p. 144.

(3) H. Meyer and R. Beer, *Monatsh.*, **34**, 1179 (1913).

155–165° for eight hours whereupon cyclization to form oxindole took place.

#### Experimental

*o*-Chlorobenzyl cyanide was prepared in a 91–94% yield from *o*-chlorobenzyl chloride by a method similar to that given in "Organic Syntheses" for the preparation of benzyl cyanide.<sup>4</sup>

*o*-Chlorophenylacetic acid was prepared in an 85–88% yield from *o*-chlorobenzyl cyanide by a method similar to that given in "Organic Syntheses" for the preparation of phenylacetic acid.<sup>5</sup>

**Oxindole.**—The best yields of oxindole were obtained by using the following conditions. A mixture of 5.3 g. (0.031 mole) of *o*-chlorophenylacetic acid, 0.56 g. of copper powder or 1.0 g. of cupric acetate and 28 ml. of concd. ammonium hydroxide was heated in a sealed pressure tube at 155–165° for 8 hours in a Carius oven. After allowing the tube to come to room temperature in the oven, the tube was opened, and the crystals which formed were filtered, dissolved in hot water and treated with Darco. On cooling, the white crystals which formed were filtered and dried. A yield of 1.4 to 1.8 g. (34 to 43%) of oxindole melting at 126–127° was obtained. A mixed melting point of this compound with an authentic sample of oxindole prepared by the method of Di Carlo<sup>6</sup> showed no depression.

(4) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 107.

(5) Reference 4, p. 437, note 3.

(6) F. J. Di Carlo, *THIS JOURNAL*, **66**, 1420 (1944).

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### Urea-Formaldehyde Kinetic Studies. IV. Reactions of Methylenebisureas

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In the course of studies of the reaction of dilute solutions of urea and simple N-alkylureas with formaldehyde at pH 7.15 it was observed that certain methylenebisureas once formed, showed no sign of hydrolysis, further condensation or polymerization.<sup>1</sup> Methylene compounds have been postulated as important units in urea-formaldehyde plastics and it was desirable that the reactions of methylenebisureas be studied further. It was found that the polarographic method of analysis used previously<sup>1</sup> was more suitable for this study than titration methods. The use of titration methods for the estimation of formaldehyde when working with more concentrated solutions must receive careful consideration, since condensation products have been shown to influence the estimation.<sup>2</sup> Preliminary studies have indicated that methylol compounds,<sup>2</sup> methylenebisureas and more highly condensed systems each have separately different effects on the usual titration methods. Consequently, the study of later stages of condensation in more concentrated solution must await reliable analytical methods. Borzee and Smetz<sup>3</sup> have recently used titration methods in a study of condensation reactions of urea and formaldehyde in concentrated solution but do not state whether errors were introduced by the condensation products.

The present work concerning the formation<sup>1</sup> and reactions of methylenebisureas requires further

(1) L. E. Smythe, *THIS JOURNAL*, **75**, 574 (1953).

(2) L. E. Smythe, *J. Phys. Colloid Chem.*, **51**, 396 (1947).