consistent with the expected diminution in the basicity of the carbethoxylated porphyrin.

## Experimental

**Mesohemin chloride** was prepared by the method of Corwin and Erdman.[7]

**1,4,5,8-Tetramethyl-2,3,6,7-tetracarbethoxyporphyrin** was prepared by the method of Corwin and Andrews.[8]

**1,3,5,7-Tetramethyl-2,4,6,8-tetracarbethoxyporphyrin** was prepared by the method of Kleinspehn.[9]

**Hemin.**—Introduction of iron by the method used for mesohemin is not applicable in this case because of the greater difficulty of securing the reaction. Air oxidation of the ferrous acetate is complete before there is appreciable conversion to the hemin. The reaction will proceed with an excess of ferrous acetate and some ferric ions by refluxing under an atmosphere of nitrogen for 2 hr. The addition of sodium chloride and subsequent air oxidation stabilizes the hemin.

*Anal.* Calcd. for $C_{26}H_{36}O_8N_4FeCl$: C, 58.12; H, 4.88. Found: C, 58.14; H, 4.77.

**Spectrophotometric Determinations.**—The determinations on mesoheme in acetic acid–water, 79:1 by volume, were made on a Cary Model XI. All others were made on a Beckman DK 2. The amounts of mesohemin and mesoporphyrin at the equilibrium point were determined in acetic acid without the addition of pyridine. With the tetramethyltetracarbethoxyporphyrin, 10 ml. of the glacial acetic acid solution was added to 25 ml. of pyridine to obtain sufficient solubility for measurement.

**Equilibration.**—A known weight of the hemin under study was added to a measured volume of solvent containing the desired salt in each of several small test tubes. A drop (0.05 ml.) of mercury was added to each of the tubes. These were then sealed under nitrogen to eliminate air. The contents were shaken vigorously for 15 min. The reaction mixtures in these sealed tubes were heated at 108° in an electronically controlled oil bath for reaction at various time intervals from 0.5 hr. to 3 hr. by 0.5-hr. increments. To determine the length of time required for equilibration, two tubes were withdrawn after each interval and were immediately immersed in an ice bath to freeze the reaction. The tubes were warmed to room temperature, opened, and mixed with 25 ml. of pyridine for measurement.

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(7) A. H. Corwin and J. G. Erdman, *J. Am. Chem. Soc.*, **68**, 2473 (1946).

(8) J. S. Andrews, A. H. Corwin, and A. G. Sharp, *ibid.*, **72**, 491 (1950).

(9) G. G. Kleinspehn, personal communication; See G. G. Kleinspehn, A. E. Briod, and W. S. Caughey, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., 1959, p. 350.

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# A Phenylosotriazole Rule for the Determination of the Configuration of Monosaccharides

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During the past two decades a sufficient number of monosaccharide phenylosotriazoles have been prepared to enable a correlation between their configuration and the sign of their optical rotation. This may be stated in the form of a "Phenylosotriazole Rule" as follows: "Whenever the hydroxyl group on C-3 of a monosaccharide is on the right in the conventional projection formula, the rotation of the derived phenylosotriazole is positive, and, conversely, when the hydroxyl group is on the left the rotation of the phenylosotriazole is negative."

TABLE I

SPECIFIC ROTATION OF KNOWN MONOSACCHARIDE PHENYLOSOTRIAZOLES

| Parent monosaccharide | Sign of OH on C-3 | on C-4 | $[\alpha]_D$ | Solvent[a] | Ref. |
|---|---|---|---|---|---|
| D-Arabinose | + | + | +23.1 | W | b |
|  |  |  | +26.0 | P | b |
| L-Arabinose | − | − | −22.8 | W | b |
|  |  |  | −25.8 | P | b |
| D-Xylose | − | + | −32.3 | W | c |
| L-Xylose | + | − | +32.5 | W | d |
| 6-Deoxy-D-glucose | − | + | −67.5 | E | d |
| 6-Deoxy-L-mannose | + | − | +101.5 | P | e |
|  |  |  | +67.5 | E | d |
|  |  |  | +49.4 | W | e |
| L-Fucose | + | + | +20.0 | W | e |
| D-Altrose | + | + | +28.0 | P | c |
| D-Glucose | − | + | −81.6 | P | f |
| L-Glucose | + | − | +82.0 | P | g |
| D-Galactose | − | − | −30.6 | P | c |
|  |  |  | −13.3 | C | c |
| L-Sorbose | − | + | −46.7 | P | c |
| 5-Desoxy-L-sorbose | − | + | −38.5 | M | h |
| D-Altroheptulose | − | + | −71.5 | P | i, j |
|  |  |  | −71.0 | P | k |
| D-Glucoheptulose | + | − | +46.9 | P | i |
| D-Mannoheptulose | − | − | −27.5 | P | i |
|  |  |  | −27.3 | P | k |
| D-Galaheptulose | + | − | +80.3 | P | i |
| D-Guloheptulose | + | + | +17.6 | P | l |
| L-Guloheptulose | − | − | −18.3 | W | .. |
|  |  |  | −15.9 | P | .. |
| D-Idoheptulose | − | + | −44.9 | P | m |
| D-Erythro-L-manno-octose | + | − | +77.3 | P | n |

[a] W = water, E = ethanol, C = chloroform, M = methanol, P = pyridine. [b] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **68**, 1766 (1946). [c] **67**, 939 (1945). [d] E. Hardegger and H. El Khadem, *Helv. Chim. Acta*, **30**, 900 (1947). [e] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **69**, 1461 (1947). [f] R. M. Hann and C. S. Hudson, *ibid.*, **66**, 735 (1944). [g] F. A. Kuehl, E. H. Flynn, F. W. Holly, and K. Folkers, *ibid.*, **69**, 3032 (1947). [h] P. Regna, *ibid.*, **69**, 246 (1947). [i] W. T. Haskins, R. M. Hann, and C. S. Hudson, *ibid.*, **69**, 1050 (1947). [j] D. A. Rosenfels, N. K. Richtmyer, and C. S. Hudson, *ibid.*, **73**, 4907 (1951). [k] V. Ettel and J. Liebster, *Collection Czech. Chem. Commun.*, **14**, 80 (1949). [l] L. C. Stewart, N. K. Richtmyer, and C. S. Hudson, *J. Am. Chem. Soc.*, **74**, 2206 (1952). [m] J. W. Pratt, N. K. Richtmyer, and C. S. Hudson, *ibid.*, **74**, 2210 (1952). [n] J. V. Karabinos, R. M. Hann, and C. S. Hudson, *ibid.*, **75**, 4320, 4324 (1953).

In Table I are recorded the specific rotations of the known monosaccharide phenylosotriazoles; these are all in agreement with this rule. The rule should, therefore, find application in the determination of the configuration of monosaccharides, in conjunction with the benzimidazoles rule[1] which gives the configuration of the hydroxyl group on C-2. Here as with benzimidazoles, when the hydroxyl group alpha to the heterocyclic ring is to the right, the compound is dextrorotatory and, when this hydroxyl group has a *cis* relationship with the following one, the rotation tends to be small.

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(1) N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 1612 (1942).