

**CORNELL UNIVERSITY,
DEPARTMENT OF CHEMISTRY. ON
BILIRUBIN: THE RED
COLORING-MATTER OF THE BILE.
A DISSERTATION**

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A Dissertation by John Edgar Teeple

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JOHN EDGAR TEEPLE

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DEPARTMENT OF CHEMISTRY

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On Bilirubin, the Red Coloring-Matter
of the Bile

A DISSERTATION

Submitted to the University Faculty for the Degree of
Doctor of Philosophy

BY

JOHN EDGAR TEEPLE

Ithaca, New York
1903

PREFACE.

The gall stones used in this work were furnished free of charge by Mr. F. M. Bell of Armour & Co. of Chicago. I desire to record my appreciation of their generosity in this respect as the material is rather rare and difficult to obtain and commands a good price on the market. The photographs of crystals were made by Professors Gage and Chamot; the crystal descriptions were given by Professor Gill; Professor Benedict of Wesleyan University, Middletown, Connecticut, and Professor Cavanaugh of this University kindly made the analyses which are credited to them in the text: I wish to express my thanks to all these gentlemen for their courtesy as well as to the not small number of members of the chemical department who have given advice in places where the subject matter touched their respective fields of work. My greatest debt of thanks is to Professor Orndorff, who suggested the field of study and outlined the work, and whose constant oversight of and participation in the work has made it possible to carry the investigation as far as it has gone.

ABBREVIATION OF PERIODICALS USED.

- | | |
|----------------------------|---|
| 1. Ann. Chem. | Annalen der Pharmacie.
Annalen der Chemie und Pharmacie.
Annalen der Chemie (Liebig's). |
| 2. Ber. | Berichte der deutschen chemischen Gesellschaft. |
| 3. Berzelius' Jahresh. | Jahresbericht über die Fortschritte der physischen Wissenschaften.
Jahresbericht über die Fortschritte der Chemie und Mineralogie (Berzelius'). |
| 4. Bull. Acad. Cracovie. | Bulletin de l'Académie des sciences de Cracovie. |
| 5. Bull. soc. chim. | Bulletin de la société chimique de Paris. |
| 6. Compt. rend. | Comptes rendus de l'Académie des sciences de Paris. |
| 7. Jahresh. Thierchemie. | Jahresbericht über die Fortschritte der Thierchemie, (Maly's). |
| 8. J. Chem. Soc. | Journal of the Chemical Society (London). |
| 9. J. Chem. Phys. | Journal für Chemie und Physik (Schweigger's). |
| 10. J. prakt. Chem. | Journal für praktische Chemie. |
| 11. J. Physiol. | Journal of Physiology. |
| 12. Liebig's Jahresh. | Jahresbericht über die Fortschritte der reinen, pharmaceutischen und technischen Chemie, Physik, Mineralogie und Geologie.
Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften (Liebig's). |
| 13. Monatsh. Chem. | Monatshefte für (Chemie.) |
| 14. Pflüg. Arch. | Archiv für die gesammte Physiologie des Menschen und der Thiere (Pflüger's). |
| 15. Poggendorff's Ann. | Annalen der Physik und Chemie (Poggendorff's). |
| 16. Proc. Roy. Soc. | Proceedings of the Royal Society of London. |
| 17. Sitzb. Akad. Wien. | Sitzungsbericht der Kaiserlichen Akademie der Wissenschaften, mathematisch-naturwissenschaftlich Classe (Wien). |
| 18. Virchow's Arch. | Archiv für pathologische Anatomie und Physiologie und für klinische Medicin (Virchow's). |
| 19. Ztschr. anal. Chem. | Zeitschrift für analytische Chemie (Presenius'). |
| 20. Ztschr. Biol. | Zeitschrift für Biologie. |
| 21. Ztschr. physiol. Chem. | Zeitschrift für physiologische Chemie (Hoppe-Seyler's). |

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I. INTRODUCTION

About the beginning of the nineteenth century the composition of bile was thoroughly investigated by such men as Berzelius, De-Marcay, Tiedemann, Gmelin, Thenard and Liebig, but the bile pigments, causing the characteristic yellow or green color, exist in such small quantities that they received only passing attention at that time.

Before this the color of blood had been generally attributed to iron. Now the belief was becoming more common that a specific animal pigment caused the color, and from this it was but a step to ascribe the various appearances of normal and pathological bile and urine to similar specific pigments, possibly to the blood pigments themselves or closely related substances¹. The exact nature of this relationship of blood, bile, and urine pigments is still unknown; even the positive proof that any one of them is derived from any other in the body may be said to be still wanting, although it has been earnestly sought in many directions.

As one of the bile pigments, bilirubin is obtainable in comparatively large quantities, can be well crystallized and seems to have a comparatively simple formula, $C_{42}H_{66}N_4O_6$, it was determined to attempt an investigation of its structure with the idea that this would throw some light on the much discussed relationship to other pigments.

II. HISTORICAL

I. FORMULA, PREPARATION AND PROPERTIES OF BILIRUBIN

Fourcroy¹ and Thenard² early stated that specific yellow pigments were characteristic of the bile. Tiedemann and Gmelin³, however, in their prize dissertation, could not isolate the coloring matters from the bile direct, but acting on Thenard's observation that the pigment occurred in large quantities in gall stones, they prepared it from that source. A little later Loir⁴ observed that the gall stones of cattle were particularly rich in pigment.

1. Bizio, *J. Chem. Phys.* (Schweigger's) 87, 129 (1822).
2. Gamgee, *Physiological Chemistry*, 2, 313; Hermann *Handbuch der Physiologie*, 2, 154.
3. Berzelius' *Jahresb.* 7, 313 (1826).
4. *Ann. Chem.*, 18, 213 (1834).