

Advances in
Carbohydrate Chemistry
and
Biochemistry

Editors

R. STUART TIPSON

DEREK HORTON

Volume 38

1981

Advances in Carbohydrate Chemistry and Biochemistry

Editors

R. STUART TIPSON

DEREK HORTON

Board of Advisors

LAURENS ANDERSON

STEPHEN J. ANGYAL

GUY G. S. DUTTON

ALLAN B. FOSTER

DEXTER FRENCH

BENGT LINDBERG

HANS PAULSEN

NATHAN SHARON

MAURICE STACEY

ROY L. WHISTLER

Volume 38

1981



ACADEMIC PRESS

A Subsidiary of Harcourt Brace Jovanovich, Publishers

New York London Toronto Sydney San Francisco

Advances in
Carbohydrate Chemistry
and
Biochemistry

H. STUART THORSON
DORIS HORTON

COPYRIGHT © 1981, BY ACADEMIC PRESS, INC.
ALL RIGHTS RESERVED.

NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX



LIBRARY OF CONGRESS CATALOG CARD NUMBER: 45-11351

ISBN 0-12-007238-6

PRINTED IN THE UNITED STATES OF AMERICA

81 82 83 84 9 8 7 6 5 4 3 2 1

LIST OF CONTRIBUTORS

Numbers in parentheses indicate the pages on which the authors' contributions begin.

ROGER W. BINKLEY, *Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115* (105)

THOMAS C. CRAWFORD, *Central Research, Chemical Process Research, Pfizer Inc., Eastern Point Road, Groton, Connecticut 06340* (287)

HASSAN S. EL KHADEM, *Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931* (1)

JUKKA FINNE, *Department of Medical Chemistry, University of Helsinki, Siltavuorenpenger 10 A, SF-00170 Helsinki 17, Finland* (389)

PHILIP A. J. GORIN, *Prairie Regional Laboratory, National Research Council of Canada, Saskatoon, Saskatchewan S7N 0W9, Canada* (13)

JOHAN JÄRNEFELT, *Department of Medical Chemistry, University of Helsinki, Siltavuorenpenger 10 A, SF-00170 Helsinki 17, Finland* (389)

GEORGE A. JEFFREY, *Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260* (417)

JORMA KÄRKKÄINEN, *Department of Medical Chemistry, University of Helsinki, Siltavuorenpenger 10 A, SF-00170 Helsinki 17, Finland* (389)

TOM KRUSIUS, *Department of Medical Chemistry, University of Helsinki, Siltavuorenpenger 10 A, SF-00170 Helsinki 17, Finland* (389)

ANNA A. E. PENGLIS, * *Department of Chemistry, Queen Elizabeth College, Campden Hill Road, London W8 7AH, United Kingdom* (195)

HEIKKI RAUVALA, *Department of Medical Chemistry, University of Helsinki, Siltavuorenpenger 10 A, SF-00170 Helsinki 17, Finland* (389)

MUTTAIYA SUNDARALINGAM, *Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706* (417)

FRANK M. UNGER, *Sandoz Forschungsinstitut Wien, Brunner Strasse 59, A-1235 Vienna, Austria* (323)

* Present address: The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, United Kingdom.

PREFACE

In Volume 38, the thirtieth in this series that has been edited by the Senior Editor, a discussion of the ^{13}C -nuclear magnetic resonance spectroscopy of polysaccharides is provided by P. A. J. Gorin (Saskatoon). This technique has opened up a major, new avenue for determination of the structure of these macromolecular carbohydrates, and has proved much more fruitful than ^1H -n.m.r. spectroscopy, a methodology discussed largely in the context of simple sugars, by B. Coxon in Volume 27 and L. D. Hall in Volume 29. R. W. Binkley (Cleveland) complements and updates the article by G. O. Phillips in Volume 18 on the photochemical reactions of carbohydrates, with particular emphasis on organic-chemical aspects. A comprehensive treatment of fluorinated carbohydrates is contributed by A. A. E. Penglis (Oxford); this is a subject touched upon briefly in previous articles (by L. J. Haynes and F. H. Newth in Vol. 10; T. G. Bonner, F. Micheel, and A. Klemmer in Vol. 16; J. E. G. Barnett in Vol. 22; and H. Paulsen in Vol. 26). A review of the synthesis and reactions of the gulonic-1,4-lactones and related derivatives is provided by T. C. Crawford (Groton). F. M. Unger (Vienna) contributes an article on the biological significance of 3-deoxy-D-manno-2-octulosonic acid (KDO) and the chemical approaches for synthesis of this important compound. J. Järnefelt and coworkers (Helsinki) have written a detailed description of the use of the time-honored methylation technique, as adapted for modern, micro-scale work in the structural analysis of glycoproteins by J. Montreuil in Volume 37. A continuing article in the series of bibliographic surveys of crystal-structure work on carbohydrates, nucleosides, and nucleotides, covering the literature thereon for 1977-1978, is provided by G. A. Jeffrey (Pittsburgh) and M. Sundaralingam (Madison); these surveys not only present crystallographic results in a pictorial format readily comprehended by chemists and biochemists, but they correct errors found in the original-literature interpretations. H. S. El Khadem (Houghton) has written an interesting account of the life and work of Emil Hardegger, a Swiss sugar chemist whose work has been, perhaps, less well recognized than it might have been; a useful feature of this article is the citation of unpublished research that is available in doctoral dissertations.

Kensington, Maryland
Columbus, Ohio
June, 1980

R. STUART TIPSON
DEREK HORTON

MEMBERS

The following is a list of the members of the Board of Directors of the American Society of International Law, as of January 1, 1978. The Board is composed of members elected by the Society for a term of three years. The Board is responsible for the general supervision and management of the Society and for the election of the Officers and the Executive Director.



E. Hardegger

1913 - 1978

Executive Director: [Name]
Secretary: [Name]
Treasurer: [Name]
Members: [List of names]

CONTENTS

LIST OF CONTRIBUTORS	ix
PREFACE	xi

Emil Hardegger (1913-1978)

HASSAN S. EL KHADEM

Text	1
Appendix I	4
Appendix II	10

Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polysaccharides

PHILIP A. J. GORIN

I. Introduction	13
II. Configurationally Dependent, ^{13}C Parameters	15
III. Identification of ^{13}C Signals of Monosaccharides: O-Substitution Shifts	19
IV. Identification of ^{13}C -N.m.r. Signals of Oligosaccharides and Polysaccharides	22
V. Molecular Motion	25
VI. ^{13}C -N.m.r. Spectra of Polysaccharides	37

Photochemical Reactions of Carbohydrates

ROGER W. BINKLEY

I. Introduction	105
II. Alkenes	106
III. Carbonyl Compounds	122
IV. Acetals	142
V. Unprotected Alditols, Aldohexoses, and Related Compounds	147
VI. Sulfur-Containing Compounds	150
VII. Nitrogen-Containing Compounds	160
VIII. Iodo Compounds	186
IX. Organometallic Compounds	190
X. Phosphates	192

Fluorinated Carbohydrates

ANNA A. E. PENGLIS

I. Introduction	195
II. Synthesis of Fluorinated Carbohydrates	199
III. Physical Methods	253
IV. Some Biological Applications of Fluorinated Carbohydrates	281
V. Addendum	284

**The Gulono-1,4-lactones: A Review of Their Synthesis, Reactions,
and Related Derivatives**

THOMAS C. CRAWFORD

I. Introduction	287
II. Synthesis	288
III. Crystal and Solution Structure, and Spectroscopic Properties of the Gulono-1,4-lactones and Derivatives	296
IV. Reactions of the Lactone Moiety in the Gulono-1,4-lactones	298
V. Reactions of the Hydroxyl Groups in the Gulono-1,4-lactones	302
VI. Deoxy and Anhydro Derivatives of the Gulono-1,4-lactones	305
VII. Amino Derivatives of the Gulono-1,4-lactones	308
VIII. Miscellaneous Derivatives of the Gulono-1,4-lactones	310
IX. Oxidation of the Gulono-1,4-lactones and Derivatives	314
X. Reduction of the Gulono-1,4-lactones and Derivatives	315
XI. Nucleophilic Additions to the Carbonyl Group of Derivatives of the Gulono-1,4-lactones	317
XII. Analytical Procedures	318
XIII. Biological Role of the Gulono-1,4-lactones and Gulonic Acids	320
XIV. Addendum	321

**The Chemistry and Biological Significance of
3-Deoxy-D-manno-2-Octulosonic Acid (KDO)**

FRANK M. UNGER

I. Introduction	324
II. Occurrence, Location, and Linkages of KDO Residues in Bacterial Polysaccharides	326
III. Elucidation of the Structure of KDO	357
IV. Chemical Synthesis and Monosaccharide Chemistry of KDO	365
V. Enzymes of KDO Metabolism	378
VI. The Design of Inhibitors of KDO Metabolism	387

**Methylation Techniques in the Structural Analysis of Glycoproteins
and Glycolipids**

HEIKKI RAUVALA, JUUKA FINNE, TOM KRUSIUS, JORMA KÄRKKÄINEN,
AND JOHAN JÄRNEFELT

I. Introduction	389
II. Permethylation of the Sample	390
III. Analysis of Permethylated Carbohydrates without Depolymerization of the Sample	392
IV. Degradation of the Permethylated Sample, and Analysis of the Partially Methylated Sugars	396
V. Methylation Analysis Combined with Specific Degradation	407

CONTENTS

vii

Bibliography of Crystal Structures of Carbohydrates, Nucleosides, and Nucleotides: 1977 and 1978

GEORGE A. JEFFREY AND MUTTAIYA SUNDARALINGAM

I. Introduction	417
II. Data for Carbohydrates	418
III. Data for Nucleosides and Nucleotides	485
IV. Preliminary Communications	526
AUTHOR INDEX	531
SUBJECT INDEX	554
ERRATA	577

EMIL HARDEGGER*

1913-1978

Emil Hardegger was born on November 25, 1913, in St. Gallen, Switzerland, to Emil and Anna Hardegger, both of whom were teachers in that city's school system. Soon after Emil's birth, his father was elected to the National Assembly, and he occupied a seat there for many years: he was also elected to the City Council of St. Gallen. He died at the age of 93, only a year before his son's premature death. Young Emil attended primary school and then the Kantonschule in St. Gallen. After passing the Maturität examination in 1934, he went to London, and spent a year there, learning the English language.

Early in his youth, Emil Hardegger showed a great interest in chemistry; he used to conduct chemical experiments in the attic of his home, much to his parents' distress. During one such experiment, fortunately conducted in an open field, an explosion occurred that burnt his hair and narrowly missed his eyes. It was therefore no surprise to his parents when Emil decided to study chemistry at the Eidgenössische Technische Hochschule (ETH).

In 1936, two years before receiving therefrom the degree of Diplom Ingenieur Chemiker, he met Olga Lüdi, the daughter of Albert and Marie Lüdi of Berne. They were married on February 16, 1940, after he had been named an assistant at the ETH. The Hardeggers lived in a furnished room until he received the doctorate in 1941, and then they rented a house on Toblerstrasse, overlooking the University. Their first son, Ivar, was born in 1947, and, three years later, they had a second son, Béat. As the house was "becoming too small," they rented another house, in Lufingen, 15 miles from Zürich. In 1948, after his Habilitation, he bought his first car, a small Volkswagen, which he would drive nonstop to Spain on vacations. Then, when Ivar started to attend school in Zürich, the Hardeggers bought a house in Gockhausen in order to be near his school. In 1968, they bought a country house in Toggenburg, near woods and meadows, and they spent all their week-ends and holidays there until Professor Hardeg-

* The author is indebted to Mrs. Emil Hardegger for her help and advice during the preparation of this article.

ger's sickness, Emil Hardegger loved to work on the land; he chopped wood and tilled the soil. Another hobby of his was collecting all types of engines. His pride and joy were two old Coronado jet-propulsion engines, which he used to operate in an abandoned factory-building on the property.

Emil Hardegger was very proud of his two sons. When they grew up, they used to visit him in Toggenburg on week-ends and holidays. At first, they came with their girl-friends; later, with their wives, and then, children. Ivar became a pharmaceutical wholesaler and married a bank employee, Marlys; they have two sons, Raoul and Gilles. Béat, who received a doctorate in pharmacy at the ETH, married Janine, a pharmacy student. They opened a pharmacy on Oberengstringen near Zürich, and have two daughters, Prisca and Andrea.

When Emil Hardegger enrolled as a student in the ETH, the most active research group in the Department of Chemistry was headed by Professor Leopold Ruzicka, who, at that time, was actively involved in the synthesis of sex hormones, work that earned him the Nobel Prize in 1939. It was not surprising that young Emil Hardegger was drawn to this group, and chose to work for Professor Ruzicka, both for his Diplomarbeit and his Doktorarbeit. His Diplomarbeit dealt with the synthesis of 1,10-dimethylpicene; it was published by Ruzicka and Hoffman, and Hardegger's name appeared in the Experimental section.

After Hardegger received his degree of Diplom Ingenieur Chemiker in the Autumn of 1938, he joined Ruzicka's sex-hormone research-team. His doctoral thesis comprised two parts; the first dealt with the elimination products of anhydro-oxyprogesterone in human urine, and the second, with the preparation and reactions of Δ^4 -17,20-oxypregnen-3-one. Despite lengthy interruptions in his research, caused by active duty during the war years, he finished his thesis in the winter of 1941, three years after he started it.

Hardegger, who had decided to make a career of teaching and research at the ETH, worked extremely hard to win an appointment at this prestigious institution and often stayed in the laboratory until 2 o'clock in the morning. The following three years were spent on research related to his doctoral work, carried out in collaboration with Professors Ruzicka and P. A. Plattner.

As Oberassistent, Hardegger supervised graduate students jointly with Professor Ruzicka. Klemens Scholz and Leo Blunschy were among his first graduate students, but Blunschy died before he could write his thesis.

Later, after Professor T. Reichstein moved to Basel, Dr. Emil Hardegger was asked to take charge of the carbohydrate research in the

ETH, and he moved to Reichstein's laboratory in the basement of the chemistry building. Among the first group of his graduate students working in the carbohydrate field were Montavon, DePasqual, El Heweihi, and the present writer. This multinational group worked on a variety of topics, ranging from the partial *p*-toluenesulfonylation of D-glucose to 1,2-anhydrides, dithioacetals, and osazones. In 1948, Emil Hardegger presented his published work for the habilitation, and was appointed Privatdozent. At that time, Jucker, Robinet, Spitz, and Leemann joined his research group. Jucker worked on the *p*-toluenesulfonylation of D-glucose, continuing Montavon's project; Robinet, on the glycosides of steroids and triterpenes; and Spitz, on D-glucuronic acid; Leemann continued the work started by DePasqual on 1,2-anhydro sugars. Then, Schreier, Kreis, and Stöhr joined the group, and all three worked on anhydro-osazones, continuing the present writer's project.

The years 1945 to 1952 were mainly devoted to carbohydrate chemistry. During this period, Hardegger published some 25 papers, of which only two were on noncarbohydrate topics. In 1952, when Professor Plattner left the ETH, Emil Hardegger assumed part of his teaching responsibilities, and supervised research in the areas of alkaloids and antibiotics. The graduate students joining the Hardegger research group during the period from 1952 to 1966 were involved with such problems as the stereochemistry of tropine alkaloids, the synthesis of lysergic acid, and structural studies on plant and mushroom degradation-products, as, for example, lycomarasmine, muscarine, fusaric acid, and prostaglandins. A large team, composed of ten graduate students, was at one time working on the synthesis of the last-mentioned compounds. This period saw the promotion of Emil Hardegger to *Ausserordentlich* Professor in 1957, and to *Ordentlich* Professor in 1966.

During the following ten years, Emil Hardegger returned to his true love, the carbohydrates. He started to emphasize such topics as urea derivatives of 2-amino-2-deoxy-D-glycosides, the synthesis of monosaccharides, thio sugars, the electrochemical oxidation and reduction of sugars, the oxidation of D-glucose with oxygen, and the epimerization of aldonic acids.

Emil Hardegger was a man of average height and build, 172 cm tall and weighing 68 kilograms. He had dark-brown eyes and hair, the latter turning gray in later years. He was a very humane person of great warmth and kindness, but was never affiliated formally with a particular church. In December, 1975, at the peak of his scientific productivity, Emil Hardegger's health suddenly deteriorated, and his condition was diagnosed as a cirrhosis of the liver. Diazomethane poisoning was

suspected; he had worked for several years with this toxic reagent, which must have affected his system. After a short recovery, he soon relapsed, and had to undergo surgery. Finally, his condition worsened, and he died on the 18th of May, 1978.

During his short, but fruitful, academic career, from 1939 to 1975, Emil Hardegger published 123 papers and supervised 46 Doctoral dissertations. The results of some of his later students' work were never published, due to the decline of his health, and therefore the titles, authors, and year of doctoral theses he supervised are given in Appendix II.

Emil Hardegger always had a very good relationship with his many research students. They, in turn, admired not only his scientific knowledge, but also his overall warmth and human qualities. Emil Hardegger will long be remembered in the scientific community as one of the great carbohydrate and natural-products chemists.

HASSAN S. EL KHADEM

APPENDIX I

The following is a chronological list of the scientific publications of the late Professor Emil Hardegger.

"Umwandlung von 17-Aethinyl-androstendion-(3,17) in Pregnadienol-(3)," by L. Ruzicka, M. W. Goldberg, and E. Hardegger, *Helv. Chim. Acta*, 22 (1939) 1294-1300.

"Ueber die bei Verabreichung von Anhydro-oxy-progesteron im Ham ausgeschiedenen Steroide," by M. W. Goldberg and E. Hardegger, *Schweiz. Med. Wochenschr.*, 71 (1941) 1041-1042.

"Oxydation von $\Delta^{4,17}$ -Pregnadienon-(3) mit Phthalmonopersäure," by L. Ruzicka, M. W. Goldberg, and E. Hardegger, *Helv. Chim. Acta*, 25 (1942) 1297-1305.

"Die Umlagerung von Δ^4 -17,20-Oxido-pregnen-3-on durch Eisessig," by L. Ruzicka, M. W. Goldberg, and E. Hardegger, *Helv. Chim. Acta*, 25 (1942) 1680-1689.

"17 α -Oxy-20-keto-Verbindungen der Pregnen- und der Allopregnan-Reihe," by M. W. Goldberg, R. Aeschbacher, and E. Hardegger, *Helv. Chim. Acta*, 26 (1943) 680-686.

"Zur Kenntnis der unverseifbaren Lipoide aus arteriosklerotischen Aorten," by E. Hardegger, L. Ruzicka, and E. Tagmann, *Helv. Chim. Acta*, 26 (1943) 2205-2221.

"Herstellung des β -(trans-p-Oxy-cyclohexyl)- $\Delta^{\alpha,\beta}$ -butenolids," by E. Hardegger, P. A. Plattner, and F. Blank, *Helv. Chim. Acta*, 27 (1944) 793-800.

"Ueber die $\Delta^{5,16}$ -3 β -Oxy-ätiocoladiensäure und einige ihrer Umwandlungsprodukte," by L. Ruzicka, E. Hardegger, and C. Kauter, *Helv. Chim. Acta*, 27 (1944) 1164-1173.

"Ueber den sterischen Verlauf der Hydrierung von Doppelbindungen in 17,20-Stellung der Steroide," by P. A. Plattner, H. Bucher, and E. Hardegger, *Helv. Chim. Acta*, 27 (1944) 1177-1184.

"Ueber zwei weitere Homologe der digitaloiden Aglucone," by P. A. Plattner, E. Hardegger, and H. Bucher, *Helv. Chim. Acta*, 28 (1945) 167-173.

“Versuche zur Herstellung von 4,13-Dioxychrysen-Derivaten,” by E. Hardegger, D. Redlich, and A. Gal, *Helv. Chim. Acta*, 28 (1945) 628–637.

“Neue Derivate und Umwandlungsprodukte von Δ^5 -17-Aethinylandrosten-diol-(3 β ,17 α) und Δ^5 -Pregnen-20-on-diol-(3 β ,17 α),” by E. Hardegger and C. Scholz, *Helv. Chim. Acta*, 28 (1945) 1355–1360.

“Ueber Δ^2 -Androsten-dion-(6,17) und Δ^2 -Cholestenon-(6),” by L. Blunschy, E. Hardegger, and H. L. Simon, *Helv. Chim. Acta*, 29 (1946) 199–204.

“Herstellung des β -(cis-p-Oxy-cyclohexyl)- $\Delta^{\alpha,\beta}$ -butenolids,” by E. Hardegger, H. Heusser, and F. Blank, *Helv. Chim. Acta*, 29 (1946) 477–483.

“Herstellung weiterer Modell-Lactone für digitaloide Aglucone,” by E. Hardegger, *Helv. Chim. Acta*, 29 (1946) 1195–1198.

“Ueber die Herstellung von α - und β -Chinovose-tetraacetat aus Glucose,” by E. Hardegger, *Helv. Chim. Acta*, 29 (1946) 1199–1203.

“Versuche zur Herstellung von 3,4-Diacetyl-d-chinovanosan- α -1,2;1,5,” by E. Hardegger and R. M. Montavon, *Helv. Chim. Acta*, 30 (1947) 632–638.

“Osotriazole aus l-Xylose, l-Rhamnose- und d-Chinovose-phenylosazon,” by E. Hardegger and H. El Khadem, *Helv. Chim. Acta*, 30 (1947) 900–904.

“p-Tolylosotriazole einiger Monosaccharide,” by E. Hardegger and H. El Khadem, *Helv. Chim. Acta*, 30 (1947) 1478–1483.

“Glucoside und β -1,3,4,6-Tetraacetyl-glucose aus Triacetyl-glucosan- α -1,2;1,5,” by E. Hardegger and J. de Pascual, *Helv. Chim. Acta*, 31 (1948) 281–286.

“Herstellung und Hydrogenolyse von Benzhydylestern,” by E. Hardegger, Z. El Heweihi, and F. G. Robinet, *Helv. Chim. Acta*, 31 (1948) 439–445.

“Di-tosylierung der Glucose,” by E. Hardegger, R. M. Montavon, and O. Jucker, *Helv. Chim. Acta*, 31 (1948) 1863–1867.

“Umwandlungsprodukte von α -1,3,4-Triacetyl-2,6-ditosyl-glucose,” by E. Hardegger, O. Jucker, and R. M. Montavon, *Helv. Chim. Acta*, 31 (1948) 2247–2251.

“Derivate der 3,6-Anhydro-glucose und des Glucose-6-jodhydrins,” by E. Hardegger and O. Jucker, *Helv. Chim. Acta*, 32 (1949) 1158–1162.

“Herstellung von Derivaten des α -Methyl-D-glucuro-pyranosids,” by E. Hardegger and D. Spitz, *Helv. Chim. Acta*, 32 (1949) 2165–2170.

“Herstellung und Derivate des β -Methyl-D-glucuro-pyranosids,” by E. Hardegger and D. Spitz, *Helv. Chim. Acta*, 33 (1950) 337–342.

“ β -D-Quinonosides du cholesterol, de l'acide Δ^5 -hydroxy-3-cholenique et leurs produits d'hydrogenation,” by E. Hardegger and F. G. Robinet, *Helv. Chim. Acta*, 33 (1950) 456–462.

“Kristallisierte Mercaptale von D-Ribose, von D-Lyxose und Derivate des Galactose- und Glucose-dibenzyl-mercaptals,” by E. Hardegger, E. Schreier, and Z. El Heweihi, *Helv. Chim. Acta*, 33 (1950) 1159–1164.

“ β -D-Quinonovoside de l'acide oleanolique,” by E. Hardegger and F. G. Robinet, *Helv. Chim. Acta*, 33 (1950) 1871–1876.

“D-Arabohehexose- β -naphthyl-osotriazol und p-Bromphenyl-osotriazole einiger Monosaccharide,” by E. Hardegger, H. El Khadem, and E. Schreier, *Helv. Chim. Acta*, 34 (1951) 253–257.

“Synthesen mit 3,4,6-Triacetyl-glucosan (Brigl-Anhydrid),” by E. Hardegger and H. Leeman, *Chimia*, 5 (1951) 108–109.

“Zur Kenntnis der D-, L- und DL-Erythron- und Threon-säurelactone,” by E. Hardegger, K. Kreis, and H. El Khadem, *Helv. Chim. Acta*, 34 (1951) 2343–2348.

“Die Konstitution des Diels'schen 'Anhydro-phenylosazons',” by E. Hardegger and E. Schreier, *Helv. Chim. Acta*, 35 (1952) 232–247.

"Oxydation einiger Mono- und Disaccharide mit Alkali und Sauerstoff," by E. Hardegger, K. Kreis, and H. El Khadem, *Helv. Chim. Acta*, 35 (1952) 618-623.

"Ueber das 3,6- und das 5,6-Anhydro-D-fructose-phenylosotriazol," by E. Hardegger and E. Schreier, *Helv. Chim. Acta*, 35 (1952) 623-631.

"Glucoside von Oleoanolsäure-estern und glykosidische Bindung im Zuckerrüben-Saponin," by E. Hardegger, H. J. Leemann, and F. G. Robinet, *Helv. Chim. Acta*, 35 (1952) 824-829.

"Oxydativer Abbau von Uronsäuren und Derivate der Trioxy-glutarsäuren," by E. Hardegger, K. Kreis, and D. Spitz, *Helv. Chim. Acta*, 35 (1952) 958-963.

"Ueber die Umwandlung des D-Fructose-phenylosazonen in das Diels-Anhydro-osa-
zon," by H. El Khadem, E. Schreier, G. Stöhr, and E. Hardegger, *Helv. Chim. Acta*, 35 (1952) 993-999.

"Beweis der Konfiguration des Pseudo-tropins, bzw. des Tropins," by E. Hardegger and H. Ott, *Helv. Chim. Acta*, 36 (1953) 1186-1189.

"Anhydroderivate der Tagatose- bzw. Sorbose-phenyl-osazone und -phenylosotriazole," by E. Schreier, G. Stöhr, and E. Hardegger, *Helv. Chim. Acta*, 37 (1954) 35-41.

"Abbau von vier 3,6-Anhydro-hexose-phenylosotriazolen zu kristallisierten antipoden Dialdehyd-hydraten," by E. Schreier, G. Stöhr, and E. Hardegger, *Helv. Chim. Acta*, 37 (1954) 574-583.

"Umsetzung von Nor- ψ -tropin und Nor-tropin mit Aldehyden," by E. Hardegger and H. Ott, *Helv. Chim. Acta*, 37 (1954) 685-690.

"Herstellung des Indol-4-aldehyds," by E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 37 (1954) 1826-1827.

"Derivate des Diäthanolamins und des N-Oxyäthyl-morpholins," by E. Hardegger and H. Ott, *Helv. Chim. Acta*, 38 (1955) 213-215.

"Konfiguration des Cocains und Derivate des Ecgoninsäure," by E. Hardegger and H. Ott, *Helv. Chim. Acta*, 38 (1955) 312-320.

"Herstellung und Umsetzungen der 4-Halogen-indole," by H. Corrodi and E. Hardegger, *Chimia*, 9 (1955) 116.

"Umsetzungen des o-Nitrophenylesterges und des 2-Chlor-6-nitrophenyl-brenztraubensäureesters," by A. Romeo, H. Corrodi, and E. Hardegger, *Helv. Chim. Acta*, 38 (1955) 463-467.

"Umwandlungsprodukte der 4-Chlorindol-2-carbonsäure und des 4-Chlorindols," by E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 38 (1955) 468-473.

"Die Konfiguration des Colchicins und verwandter Verbindungen," by H. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 38 (1955) 2030-2033.

"Die Konfiguration des Apomorphins und verwandter Verbindungen," by H. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 38 (1955) 2038-2043.

"Fusarinsäure-[carboxyl- 14 C] und quaternäre Derivate der Fusarinsäure," by E. Hardegger and E. Nikles, *Helv. Chim. Acta*, 39 (1956) 223-229.

"Untersuchungen in der Pyridin-Reihe; ein neuer Weg zur Fusarinsäure," by E. Hardegger and E. Nikles, *Helv. Chim. Acta*, 39 (1956) 505-513.

"Herstellung von 4-Jod-oxindol, 4-Jod-indol, 4-Jod-skatolyl-aceton und verwandten Verbindungen," by E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 39 (1956) 514-517.

"Die Konfiguration des natürlichen (+)-Laudanosins, sowie verwandter Tetrahydro-isochinolin-, Aporphin- und Tetrahydro-berberin-alkaloide," by H. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 39 (1956) 889-897.

"Notiz über die β -Carboxy- γ -methylamino-buttersäure und den Methylamino-malonester," by E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 39 (1956) 980-983.

"Notiz über einige dem Tryptophan nanestehende Verbindungen und über das 4-

Cyan-indolyl-(3)-acetonitril," by E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 39 (1956) 984-986.

"Herstellung des racemischen Colchicins und des un-natürlichen (+)-Colchicins," by H. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 40 (1957) 193-199.

"Synthese von Stereoisomeren des Muscarins," by H. Corrodi, E. Hardegger, F. Kögl, and P. Zeller, *Experientia*, 13 (1957) 138-141.

"Synthese von S(+)-6,7-Dihydroxy-3-tropanon," by E. Hardegger and H. Furter, *Helv. Chim. Acta*, 40 (1957) 872-874.

"Diaporthin, ein Welketoxin aus Kulturen von *Endothia parasitica* (Murr.) And.," by A. Boller, E. Gäumann, E. Hardegger, F. Kugler, S. Naef-Roth, and M. Rosner (18. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 40 (1957) 875-880.

"Eine neue Synthese der Fusarinsäure," by E. Hardegger and E. Nikles (19. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 40 (1957) 1016-1021.

"Ueber induzierte Abwehrstoffe bei Orchideen I.," by A. Boller, H. Corrodi, E. Gäumann, E. Hardegger, H. Kern, and N. Winterhälter-Wild (20. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 40 (1957) 1062-1066.

"Präparative Herstellung der 2-Desoxy-D-ribose," by E. Hardegger, M. Schellenbaum, R. Huwyler, and A. Züst, *Helv. Chim. Acta*, 40 (1957) 1815-1818.

"Die absolute Konfiguration des (+)-Catechins," by E. Hardegger, H. Gempeler, and A. Züst, *Helv. Chim. Acta*, 40 (1957) 1819-1822.

"Ueber Muscarin, 7: Mitteilung. Synthese und absolute Konfiguration des Muscarins," by E. Hardegger and F. Lohse, *Helv. Chim. Acta*, 40 (1957) 2384-2389.

"Die Reaktion von 3-Butyl-pyridin mit Methylradikalen," by E. Hardegger and E. Nikles, *Helv. Chim. Acta*, 40 (1957) 2421-2427.

"Herstellung der Fusarinsäure aus 2,5-Lutidin," by E. Hardegger and E. Nikles (21. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 40 (1957) 2428-2433.

"Ueber Muscarin, 8: Mitteilung. Herstellung von racemischen Allomuscarin," by H. Corrodi, E. Hardegger, and F. Kögl, *Helv. Chim. Acta*, 40 (1957) 2454-2461.

"Ueber Muscarin, 9: Mitteilung. Ueber die Synthese von racemischen Muscarin, seine Spaltung in die Antipoden und die Herstellung von (-)-Muscarin aus D-Glucosamin," by H. C. Cox, E. Hardegger, F. Kögl, P. Liechti, F. Lohse, and C. A. Salemink, *Helv. Chim. Acta*, 41 (1958) 229-234.

"Ueber Muscarin, 10: Mitteilung. Herstellung des un-natürlichen 2R,3S,5R(-)-Muscarins aus 2-Desoxy-D-ribose," by E. Hardegger, H. Furter, and J. Kiss, *Helv. Chim. Acta*, 41 (1958) 2401-2410.

"Hydroxy-morphinane, 12. Mitteilung. Die Konfiguration der Morphinane," by H. Corrodi, J. Hellerbach, A. Züst, E. Hardegger, and O. Schnider, *Helv. Chim. Acta*, 42 (1959) 212-217.

"Relative Configurations of the Two 1-Keto-6-hydroxyspiro[4.4]nonanes and the Three 1,6-Dihydroxyspiro[4.4]nonanes," by E. Hardegger, E. Maeder, H. M. Semame, and D. J. Cram, *J. Am. Chem. Soc.*, 81 (1959) 2729-2737.

"Beiträge zur Stereochemie der Chitarsäure," by J. Kiss, E. Hardegger, and H. Furter, *Chimia*, 13 (1959) 336-338.

"2-Deoxy-D-ribose," by E. Hardegger, *Methods Carbohydr. Chem.*, 2 (1960) 177-179.

"Die absolute Konfiguration des (-)-Epicatechins," by A. Züst, F. Lohse, and E. Hardegger, *Helv. Chim. Acta*, 43 (1960) 1274-1279.

"Verwendung radioaktiver Fusarinsäure und Synthese von Fusarinsäure-[2,5'-¹⁴C]," by H. Biland, F. Lohse, and E. Hardegger (22. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 43 (1960) 1436-1440.

"Ueber die Isolierung von Culmomasamin, einem peptidartigen Welkstoffe aus dem Kulturfiltrat von *Fusarium culmorum* (W. G. Sm.) Sacc.," by J. Kiss, S. Naef-Roth, E. Hardegger, A. Boller, F. Lohse, E. Gäumann, and P. A. Plattner (23. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 43 (1960) 2096-2101.

"Ueber Muscarin, 11. Mitteilung. Synthese von bisquaternären, dem Muscarin ähnlich Verbindungen," by J. Kiss, H. Furter, F. Lohse, and E. Hardegger, *Helv. Chim. Acta*, 44 (1961) 141-147.

"Konfigurationsbeweis für L-Tryptophan durch erschöpfende Ozonisierung," by E. Hardegger and H. Braunschweiger, *Helv. Chim. Acta*, 44 (1961) 1125-1127.

"Ueber Muscarin, 12. Mitteilung. Synthese des DL-2-Methyl-muscarons, des DL-2-Methyl-muscarins und des DL-2-Methyl-epimuscarins," by H. Corrodi, K. Steiner, N. Halder, and E. Hardegger, *Helv. Chim. Acta*, 44 (1961) 1157-1162.

"Ueber Muscarin, 13. Mitteilung. Synthese von Salzen des DL-Muscarons und DL-Allomuscarons über die Norbasen," by E. Hardegger, H. Corrodi, and N. Chariatte, *Helv. Chim. Acta*, 44 (1961) 1193-1198.

"Die absolute Konfiguration des Aglucons im Neosperidin," by E. Hardegger and H. Braunschweiger, *Helv. Chim. Acta*, 44 (1961) 1413-1417.

"Die Konstitution des Lycomasamins," by E. Hardegger, P. Liechti, L. M. Jackman, A. Boller, and P. A. Plattner (24. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 60-74.

"Präparative Herstellung von Krist. 6-Desoxy-6-amino-D-glucose-hydrochlorid und Konstitution einiger Zwischenprodukte," by E. Hardegger, G. Zanetti, and K. Steiner, *Helv. Chim. Acta*, 46 (1963) 282-287.

"Synthese der natürlichen Dehydrofusarinsäure," by K. Steiner, U. Graf, and E. Hardegger (25. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 690-694.

"Synthese der Anhydrolycomarasminsäure," by E. Hardegger, J. Seres, R. Andreatta, F. Szabo, W. Zankowska-Jasinska, A. Romeo, C. Rostetter, and H. Kindler (Vorläufige 26. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 1065-1067.

"Ueber induzierte Abwehrstoffe bei Orchideen II," by E. Hardegger, M. Schellenbaum, and H. Corrodi (27. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 1171-1180.

"Synthese von 2,4-Dimethoxy-6-hydroxy-phenanthren und Konstitution des Orchinols," by E. Hardegger, H. R. Biland, and H. Corrodi (28. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 1354-1360.

"Synthese von 2,4-Dimethoxy-6-hydroxy-9,10-dihydrophenanthren," by E. Hardegger, N. Rigassi, J. Seres, C. Egli, P. Müller, and K. O. Filtz (29. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 46 (1963) 2543-2551.

"Synthese des 5,6,7-Trimethoxy-indols und des 6,7-Dimethoxy-bufotenin methyläthers," by E. Hardegger and H. Corrodi, *Pharm. Acta Helv.*, 39 (1964) 101-107.

"Ausgangsprodukte zur Totalsynthese des Javanicins," by E. Hardegger, K. Steiner, E. Widmer, H. Corrodi, T. Schmidt, H. P. Knopfel, W. Rieder, H. J. Meyer, F. Kugler, and H. Gempeler (30. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 47 (1964) 1996-2017.

"Bicyclische Zwischenprodukte zur Synthese des Javanicins," by E. Hardegger, K. Steiner, E. Widmer, and T. Schmidt (31. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 47 (1964) 2017-2026.

"Synthese von Javanicin-5,8-dimethyläther und Konstruktion von Javanicin und Fusarubin," by E. Hardegger, K. Steiner, E. Widmer, and A. Pfiffner (32. Mitteilung, Welkstoffe und Antibiotika), *Helv. Chim. Acta*, 47 (1964) 2027-2030.

"Selektion Spaltung der Aether Chelierter Phenole und Synthese von Javanicin," by