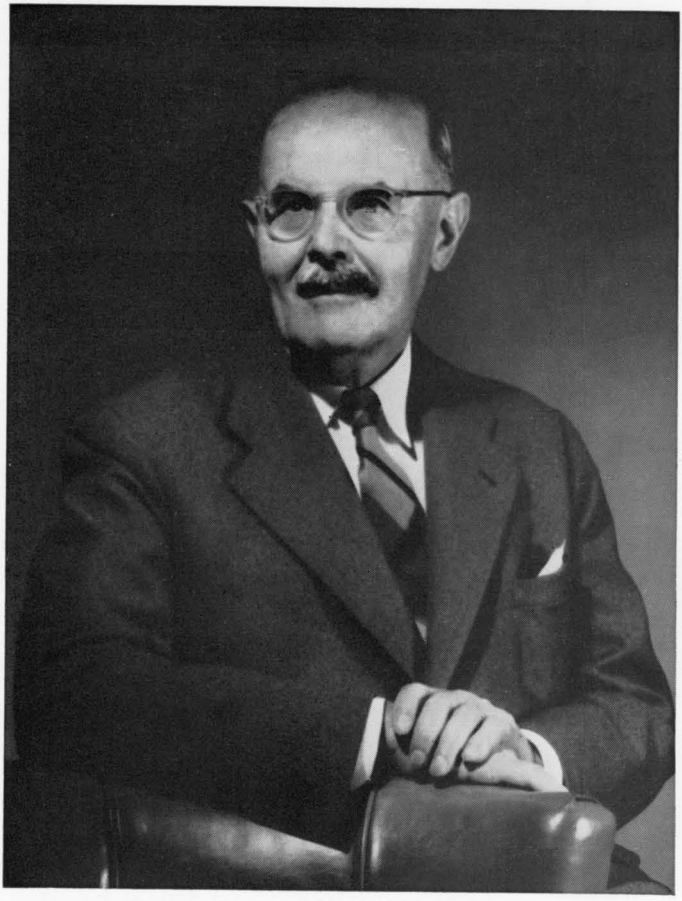
NATIONAL ACADEMY OF SCIENCES

HERMANN OTTO LAURENZ FISCHER

1888—1960

A Biographical Memoir by
W. M. STANLEY AND W. Z. HASSID

Biographical Memoir



Herman O. Finsler.

HERMANN OTTO LAURENZ FISCHER

December 16, 1888–March 9, 1960

BY W. M. STANLEY AND W. Z. HASSID

HERMANN OTTO LAURENZ FISCHER was born on December 16, 1888, in the university town of Würzburg in Bavaria and died on March 9, 1960, in the University of California Hospital in Los Angeles. He was the first of three sons of Emil and Agnes Fischer and was early exposed to academic surroundings since his father was Professor of Chemistry at the University of Würzburg. In 1892 the Fischer family moved to Berlin where Fischer's father, not yet forty years of age, succeeded to the chair of August Wilhelm von Hofmann and directed the activities of the Chemical Institute of Berlin University. Three years later Fischer's mother died and the three boys grew up in the rather lonely household of their widowed father who was greatly preoccupied with his teaching and research. However, Fischer remembered with pleasure the very informative conversations which the boys had with their father at lunchtime. During this period the Fischer boys went to the local *Gymnasium* where, Fischer recalls, "Latin, Greek, history and German were taught very well, mathematics somewhat and science very little." Fischer was given full freedom to select a profession but, of course, his early and continuing contacts with academic life and chemical research were quite influential. He retained early memories of a two-week visit within the Fischer household of Sir William Ram-

say, who told about the discovery of the noble gases—argon, helium, krypton, and neon. Fischer decided to become a chemist and his father, "conscious of the international aspect of science and deeply impressed with the philosophy of the English-speaking people," sent him in 1907 to Cambridge University in England for a year. He then returned to Germany where he spent a year in military service in the little town of Lüneburg. With his military service completed Fischer returned to the study of chemistry, first in Berlin and then in Jena, where he started his doctoral program under the direction of the eminent Professor Ludwig Knorr at the University of Jena.

At that time Knorr and his students had succeeded in separating the pure keto form of ethyl acetoacetate by crystallization from alcohol, ether, or petroleum ether at —78°. The enol form had also been obtained by regenerating it from the sodium salt at low temperature. Fischer was able to apply somewhat similar methods to acetylacetone (2, 4-pentanedione) to obtain (*a*) the pure enolic tautomer, by direct crystallization at low temperature, and (*b*) a preparation rich in the ketonic modification. After receiving his doctor's degree in 1912 with a thesis entitled "Zur Kenntnis des Acetylacetones," Hermann Fischer decided to return to the Chemical Institute of Berlin University to continue his research studies with his father.

Under the direction of Emil Fischer the Chemical Institute was now one of the greatest scientific centers in Europe. There were experts in almost all fields of chemistry including such people as Diels, Franz Fischer, Gabriel, Otto Hahn, Lise Meitner, Leuchs, Wilhelm Traube, and Tiede. It was not surprising, therefore, that the Chemical Institute had a great attraction for the still somewhat lonely young chemist with his newly acquired doctor's degree. Here he rapidly laid the foundation of what was to represent his major interest for the remainder of his career, namely, synthetic organic chemistry with emphasis on compounds of biological interest.

Emil Fischer at this time was primarily interested in studying the structure and chemistry of the natural tannins, and his son Hermann was assigned to the problem of synthesizing certain of the naturally occurring depsides. In this endeavor, the carbomethoxy (methoxycarbonyl) group, which had been used so successfully in the earlier polypeptide synthesis by Emil Fischer, was used to protect the phenolic groups of hydroxyaromatic acids during their conversion to the acid chlorides. The latter were then employed for esterifying other hydroxyaromatic molecules to produce the didepsides. Hermann Fischer was thus able to prepare the *ortho-* and *para*-diorsellinic acids. This study resulted in the publication of four papers bearing the names of Emil and H. O. L. Fischer in the *Berichte* in the issues of 1913-1914. This two-year period of scientific collaboration between father and son that Hermann Fischer called the happiest of his life ended with the catastrophe of World War I.

His two brothers had studied medicine and the three had planned to work as a team on problems presented by the living cell. But with the outbreak of war all three brothers were drafted into military service, Fischer in a chemical warfare unit and his brothers into military medical service. Both brothers died in the line of duty; hence when the war ended after four and one-half years, Fischer had to plan his life anew.

Science in Germany suffered an almost complete collapse for several years after World War I, owing to lack of personnel and facilities and to the pervading disorganized economic condition in the country. Meanwhile, the United States and England had been forced by the war to develop their own organic chemical industries, with auxiliary programs in basic research. During the war, Emil Fischer had kept the Chemical Institute in Berlin functioning as well as possible under the adverse circumstances. At this difficult period, at the end of 1918, Hermann Fischer returned to begin the work of redeveloping his career in chemistry. The shocking loss of his father in July 1919, coupled

with the general political and chaotic economic conditions of the times, made this task all the more difficult. However, in spite of many frustrations and difficulties, in the ensuing five years Hermann Fischer gradually gathered together a small research group and established a research program.

Two main lines of research were developed by Hermann Fischer during the period of 1920-1932 in the Chemical Institute. One was the study of the constitution and configuration of the naturally occurring quinic acid. The other dealt with the difficult chemistry of the trioses, glyceraldehyde and dihydroxyacetone, and related two-, three- and four-carbon compounds. The first publication on quinic acid, which appeared in 1921, described certain new derivatives of this tetrahydroxycyclohexanecarboxylic acid but left the position of one of the hydroxyl groups doubtful. With Dr. Gerda Dangschat, his chief assistant, he continued the investigation of this problem and in 1932 had finally established the correct structure and configuration of quinic acid. This result led in turn to the correct structure for chlorogenic acid, the quinic acid ester of caffeic acid, that occurs naturally in the coffee bean. Up to this time little was known of the chemistry of glyceraldehyde, dihydroxyacetone, glyoxal, glycolaldehyde, and pyruvaldehyde, and the efforts of the Fischer group did much to clarify this difficult field. The outstanding achievement of this work in Berlin was the successful preparation by Hermann Fischer and Erich Baer of DL-glyceraldehyde 3-phosphate. It was subsequently established in the laboratories of Otto Warburg, Gustaf Embden, and Otto Myerhof that the D-enantiomorph of this ester is the key three-carbon intermediate in alcoholic fermentation and glycolysis. Thus, the Fischer-Baer ester took its place along with the Harden-Young, Neuberg, and Robison esters in the Embden-Myerhof fermentation-glycolysis scheme.

In 1922 a happy event occurred in Fischer's personal life.

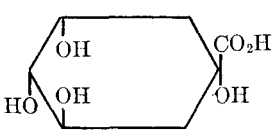
He married Ruth Seckels, in whom he found an understanding and devoted partner for life. This marriage resulted in three children, a daughter and two sons. About this time Fischer was appointed as Assistant Professor in the Institute, which was now under the direction of Professor Hermann Schlenk. This appointment gave him an opportunity to lecture to students and it was here that he acquired the ability that was to remain with him throughout his life to present really inspiring lectures. He remained at the Chemical Institute until 1932 when the threatening political situation in central Europe, coupled with an invitation to join the staff of the University of Basel, resulted in a move to Switzerland. The Fischer family found the Swiss university town of Basel a delightful place and were happy to leave the postwar turmoil of Germany.

The continuity of the triose research initiated in Berlin was assured when Erich Baer decided to accompany the Fischers to Basel, and their scientific collaboration produced many more outstanding results, both in Switzerland and, later, in Canada. Furthermore, although Gerda Dangschat remained in Berlin, she continued with Fischer their important work on the chemistry of the natural plant acids related to the inositols.

In pursuing the work on trioses, Fischer and Baer now developed a method of preparation for the enantiomorphous acetonated glyceraldehydes that was to lead later to their classical work on the asymmetric glycerides. The two collaborators succeeded in synthesizing the enantiomorphous acetonated glyceraldehydes from the mannitols. Inasmuch as the free glyceraldehyde could be readily obtained from these acetonated derivatives by mild acidic hydrolysis, the totally fermentable D-glyceraldehyde 3-phosphate and its mirror-image counterpart were made available for biochemical studies. The two investigators were able to show that the aldol reaction of unsubstituted D-glyceraldehyde with its ketonic isomer, dihydroxyacetone, leads in high yield

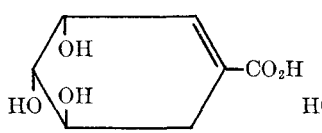
to D-fructose and D-sorbose, with practically a complete exclusion of the isomeric D-psicose and D-tagatose. Finally, the enantiomorphous acetonated glyceraldehydes provided, through reduction, the 2, 3-*O*-isopropylidine-D- and -L-glycerols, which opened up to Fischer and Baer, in their subsequent work in Toronto, the entire field of asymmetric glycerol derivatives.

During the Basel period the structural and configurational studies of quinic acid (1) by Fischer and Gerda Dangschat were extended to shikimic acid (2). This acid was first proved to be a 3, 4, 5-trihydroxycyclohexene-1-carboxylic acid by degrading it in a series of steps to both tricarballylic acid and aconitic acid. The configurational relationship of the three hydroxyl groups was then clarified through consideration of the chemical behavior and optical properties of the δ-lactone of dihydroshikimic acid. Ultimately, in a most outstanding series of experiments, the parent shikimic acid was converted to 2-deoxy-D-*arabino*-hexonic acid (3). Thus, the configuration of the acid and the precise location of its double bond were determined, and its relationship to quinic acid and to D-glucose was established. Some fifteen years later, this precise work by Fischer and Dangschat served Bernard D. Davis as the basis for identification of shikimic acid as a key intermediate in the biological transformation of carbohydrates into aromatic amino acids. The decisive biochemical experiments were performed by Davis with a sample of the acid contributed by Fischer and Dangschat.



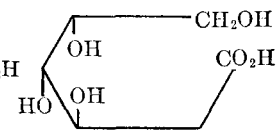
Quinic acid

(1)



Shikimic acid

(2)



2-Deoxy-D-*arabino* = hexonic acid

(3)

Unfortunately, the rumblings of war in Europe increased and by 1936 Fischer was convinced that war was coming again. His

two sons were approaching military age and Fischer was not happy about the prospect of their having to go off to war and to an uncertain future. So once again the political situation dictated a move, this time in 1937 to the Banting Institute of the University of Toronto in Canada. The previous year on a lecture trip to America Dr. and Mrs. Fischer had met Sir Frederick Banting and Dr. Charles Best, who were greatly impressed by the Fischers. Also on this trip the Fischers had their first experience with American hospitality at the hands of Dr. and Mrs. H. T. Clarke of Columbia University, Dr. and Mrs. H. B. Vickery of Yale University, and the great sugar chemist, Claude S. Hudson of Washington. The impressions gained by the Fischers during this trip were most influential, together with the political situation in Europe, in the decision to accept the offer from the University of Toronto. Fischer had anticipated the war by only two years, for World War II broke out in 1939. All during the war Fischer, despite his German origin, was able to continue his research work largely because of the very understanding attitude of the University of Toronto and the Canadian government and, of course, because of the actions of the Fischer family itself.

Dr. Erich Baer and a young Swiss chemist, Dr. Jean Grosheintz, followed Fischer to Canada. Later, another young Canadian chemist, John C. Sowden, joined them and with these able young men Fischer formed a small but stimulating and productive research group. The work of Fischer and Baer with enantiomorphous glyceraldehydes was now extended to the glyceride field. They succeeded in preparing the enantiomorphous α, β-diglycerides by benzlylation of the acetonated glycerides, followed by hydrolysis of the acetone group, acylation and hydrogenolysis of the benzyl blocking group. Of considerable interest was the observation that, although the asymmetric α-mono- and α, β-di-glycerides showed measurable optical activities, no rota-

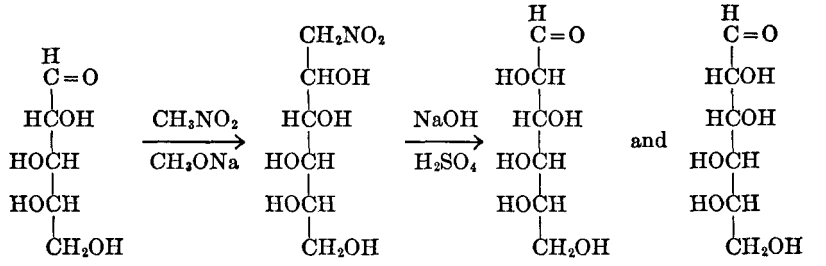
tion could be detected for any of the asymmetric, mixed triglycerides that contained only aliphatic ester groups. Thus, any failure to observe optical activity in natural fats does not necessarily mean that they are asymmetrical or racemic.

The enantiomorphous acetonated glycerols were also converted through phosphorylation, followed by hydrolysis of the acetone group, to the two α-glycerophosphoric acids (glycerol 1-phosphates). The L(—)-α-glycerophosphoric acid, obtained in this way from 2, 3-*O*-isopropylidene-D-glyceraldehyde, proved to be identical in every respect with the biological α-glycerophosphoric acid isolated from natural phosphatides and from fermentation and glycolysis media. Studies of the action of lipases on the enantiomorphous methylated α-monoglycerides, and of phosphatases on the two α-glycerophosphoric acids, demonstrated in each case that the enzymes act at markedly different rates on the two members of the antipodal pairs.

Other investigations by Fischer and Baer in Toronto included the study of the asymmetric glycerol ethers, the development of syntheses for dimeric glycerose 1, 3-diphosphate, glyoxal semiacetate, L(+)-propylene glycol, the β-phosphatidic acids, and *O*-phospho-enolpyruvic acid. In collaboration with Dr. Jean Grosheintz, they also established conditions for glycol-cleavage reactions with lead tetraacetate in partially aqueous media.

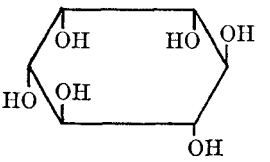
Then, in collaboration with Dr. Sowden, Fischer developed relatively simple conditions for the reaction of the sugars with nitromethane. For example, L-arabinose yielded L-glucose and L-mannose by way of the epimeric nitroalcohols, as shown in the accompanying formula. Thus, a new and general method of ascending the sugar series became available to supplement the classical cyanohydrin method of H. Kiliani and Emil Fischer.

An important adaptation of the aldose-nitromethane reaction was also made by Fischer and Jean Grosheintz. By addition of nitromethane to 1, 2-*O*-isopropylidene-D-*xylo*-pentodialdose and



L-Arabinose — Epimeric nitroalcohols — L-Glucose — and — L-Mannose

subsequent hydrolysis of the acetone group, they obtained a mixture of 6-deoxy-6-nitro-D-glucose and 6-deoxy-6-nitro-L-idose. A second, intramolecular reaction of these substances led to a mixture of deoxynitroinositols and, by reduction, to the related aminodeoxyinositols. One of the latter was successfully deaminated a few years later by T. Posternak to *myo*-inositol, thus completing a synthesis that started from D-glucose.



myo-Inositol

Hermann Fischer's laboratory in Toronto attracted a number of able young chemists. Among the postdoctoral fellows were Dr. Henry Lardy, who worked out a practical method for the chemical synthesis of D-glucose 6-phosphate, and Beat Iselin, who developed the first synthesis of *myo*-inositol 2-phosphate.

In spite of the productive scientific period at Toronto and the scientific and social climate which he enjoyed, the cold winters left much to be desired, especially now that Fischer was approaching his sixtieth year and his wife's health was affected by the weather.

One of us came to know and to admire Fischer during this

period, so when, in addition to planning and building a Virus Laboratory at the University of California at Berkeley, President Sproul added the obligation of starting a new Department of Biochemistry, Dr. Stanley's thoughts naturally turned to Fischer. Here was a gentleman and a scholar of the first order who in his own early life and through his father represented a relationship with the very beginnings of biochemistry, who over the years despite great difficulties had accomplished very important advances in carbohydrate chemistry, and who could undoubtedly provide a perspective of the real place of biochemistry in a unique way. It was, therefore, a pleasure to invite him to join the staff as Professor of Biochemistry in the newly established Department of Biochemistry of the College of Letters and Science.

The period in Berkeley from 1948 to 1960 was described by Fischer shortly before his death as one of the happiest in his life. In the stimulating environment of the Berkeley campus, Fischer, with the aid of junior staff members and visiting postdoctoral fellows, now turned his attention mainly to the carbohydrates and inositols. In addition to lecturing and the direction of his research program, he also assumed important administrative duties as chairman of the Department of Biochemistry from 1953 until his official retirement in 1956.

With Dr. Donald L. MacDonald he succeeded in working out a new and efficient method for descending the sugar series. This method was based on the sugar diethyl dithioacetals (mercaptals), which, on oxidation with peroxy acids, readily produced derivatives giving the corresponding sulfones. Upon treatment of these derivatives with mild alkali they were degraded in good yield to the next lower sugar and bis(ethylsulfonyl) methane. This new method proved to be a valuable supplement to the older, classical degradation methods of Ruff, Wohl, and Weerman.

Another significant contribution to the chemistry of carbo-

hydrates was the development, with Dr. C. E. Ballou and Dr. D. L. MacDonald, of methods for the preparation of the dialdoses. Starting with di-acetonated D-inositol, they were able to obtain *manno*-hexodialdose. *xylo*-Pentodialdose was produced by way of the disulfone to *myo*-inosose-2 and D-*gluco*-hexodialdose by use of the 6-deoxy-6-nitro-D-glucose.

Later Fischer, MacDonald, and Ballou prepared the biochemically important phosphorylated sugar D-erythrose 4-phosphate. The importance of this lower phosphorylated sugar was established when Srinivasan, Katagiri, and Sprinson demonstrated its condensation with *O*-phosphoenol-pyruvic acid to 5-dehydroshikimic acid by *Escherichia coli.*

In 1956 Fischer became Professor Emeritus, but he maintained an active and productive research laboratory at the Department of Biochemistry until the end of his life, early in 1960. During this period he became interested in the application of the aldehyde-nitromethane reaction, and particularly to its application for the synthesis of aminodeoxy sugars and aminodeoxy inositols. In collaboration with Dr. Hans H. Baer, making use of this reaction, he was able to synthesize 3-amino-3-deoxy sugars and, later with Dr. A. C. Richardson, a mixture of amino-anhydrodeoxy sugars. Working under the guidance of Fischer, Dr. F. W. Lichtenthaler obtained a mixture of 1,4-dideoxy-1,4-dinitroinositols, one of which, upon reduction, yielded *neo*-inosadiamine-1,4.

On the occasion of the official dedication of the Biochemistry and Virus Laboratory building in 1952, which fortunately could be arranged to coincide with the centennial of the birth of Emil Fischer, Dr. Fischer donated his personal cherished possession, the private library of his father, to the Department of Biochemistry. This was done as a gesture of appreciation and good will toward the University. The library now bears the name of the Emil and Hermann Fischer Library.

Hermann Fischer was the recipient of many honors and

awards. In 1949 he received the Sugar Research Award for his contributions to carbohydrate chemistry. Election to the National Academy of Sciences (United States) came in 1954 and a year later he was presented with the Adolf von Baeyer Medal, one of the highest scientific honors in Germany. In 1958 he was recipient of the Hudson Award of the Division of Carbohydrate Chemistry of the American Chemical Society. This award was particularly fitting in view of his close personal and scientific relationship with the late Claude S. Hudson, after whom the award is named. Also in 1958, to mark his seventieth birthday and his many services to biochemistry, Fischer was honored with an anniversary issue of the *Archives of Biochemistry and Biophysics* to which many of the world's foremost biochemists contributed. The following year, in 1959, he was presented with an honorary Doctor of Science degree by the Justus Liebig University in Giessen, Germany. He was an elected Fellow of the New York Academy of Sciences and of the Chemical Institute of Canada, and a member of the Society of Biological Chemists, the American Chemical Society, the Chemical Society (London), the Swiss Chemical Society, and the American Association for the Advancement of Science.

Professor Hermann Fischer had a combination of exceptionally fine and rare human attributes. He possessed an innate kindness and sincere concern for the welfare of others. He had a zest for life, a sense of humor, and a great capacity for friendship which won him innumerable devoted friends and admirers throughout the world. He was a gentleman and a scholar of the first order.

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KEY TO ABBREVIATIONS

Am. Chem. Soc. Meeting, Abstrs. = American Chemical Society Meeting, Abstracts
Ann. Rev. Biochem. = Annual Review of Biochemistry
Ber. = Berichte der deutschen chemischen Gesellschaft
Biochim. Biophys. Acta = Biochimica et Biophysica Acta
Can. J. Res. = Canadian Journal of Research
Helv. Chim. Acta = Helvetica Chimica Acta
J. Am. Chem. Soc. = Journal of the American Chemical Society
J. Biol. Chem. = Journal of Biological Chemistry
Naturwiss. = Die Naturwissenschaften

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