On pages 57–74 of this issue appear papers from the Symposium given in honor of Ernst Klenk, entitled "Glycolipids and the Nervous System," presented in April 1965, in Houston. Additional papers presented in this Symposium have appeared in Lipids. *Professor Klenk was further honored in Houston when he was named for the second AOCS Award in Lipid Chemistry.*

Printed here are personal notes about her husband's life, provided by Dr. Med. Grete Klenk, and a résumé of his extensive scientific achievements, provided by Hans Faillard, Bochum, Germany.

Professor Ernst Klenk

Personal Biography

MY HUSBAND, ERNST KLENK, was born October 14, 1896 in Pfalzgrafenweiler, a village near Freudenstadt in the Black Forest. His father owned a farm and a brewery. He grew up in a happy family and had a brother who was two years older.

When he started elementary school in his home village, the teacher inspired his father to send him to high school and to give him a good education. So he left home at the age of 8. Soon after he lost his brother. Even at that young age he had decided not to take over the brewery but to study, so that his father finally sold this part of his property. At school he was not very fond of languages but was extremely brilliant in mathematics. The schoolboys admired his dangerous experiments with rockets and montgolfieres.

Upon graduation from high school in Tübingen, and the outbreak of World War I, he entered the army as a volunteer. He belonged to the mountaineers and spent 4 difficult years. At least, these years were in beautiful surroundings: the Vogesen, the Dolomites, the Carpates and the mountains of the Balcany. Since that time he has enjoyed the mountains and spends all of his vacations there in summer as well as in winter.

After the end of the war he went to the University in Tübingen to study chemistry. It happened in one of his last terms that he could not get a laboratory space at the Institute of Chemistry, so he moved into the Institute of Physiological Chemistry of which Geheimrat Hans Thierfelder was in charge. The latter was very kind to him and took much interest in his studies. He wrote his thesis under the supervision of Percy Brigl. Before he had finished his thesis work, Thierfelder had made him an assistant. Although he (Klenk) nearly refused in the beginning, Thierfelder encouraged, almost pushed him, to take the academic career. He has always kept a feeling of deep gratefulness and respect towards his master.

After Thierfelder's death he went on working at the same institute under Franz Knoop, the discoverer of β-oxidation of fatty acids. I became acquainted with Ernst Klenk when he tutored me in two chemical courses. We married in 1937 and now have three sons.

Institute in Cologne, having refused to succeed Fr. Kutscher in Marburg. He started with two or three co-workers in a few rooms of the medical clinic. He had just moved into a

In 1936 he was made head of the Physiological Chemical building of his own when World War II broke out. The institute was bombed several times. By the end of 1944, it had become impossible to stay longer in Cologne. The institute was evacuated to Marburg and its suburb.

In the fall of 1945, Klenk returned to Cologne and again started to rebuild his Institute a fourth or fifth time under the greatest of difficulties and with the help of the Marshall Plan. Although the building looked rather poor from outside, the team working inside was always especially nice like a family. This family enlarged considerably in the course of the years. The laboratories became too small. In 1959 they moved into a fine modern building with very good working facilities.

In 1948 Klenk became dean of the medical faculty and the recipient of an honorary Doctor of Medicine degree by this faculty. In 1962 he was elected president of the University of Cologne. He was awarded the Norman medal of the Deutsche Gesellschaft für Fettforschung and the Heinrich-Wieland-Preis. He is a member of the "Leopoldina" der Deutschen Akademie der Naturforscher and a member in honor of the American Society of Biological Chemistry.

DR. MED. GRETE KLENK
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Scientific Achievements

IN 1932 ERNST KLENK began his scientific career under Thierfelder, a former student of Hoppe-Seyler. His initial investigations were concerned with the behavior (retention) of the aromatic fatty aldehydes and of carbohydrates in animals. In his work some information concerning their oxidative degradation was gained. Above all, it was made clear that the oxidation of the methyl group of n-propyl benzene and its higher homologues to a carboxyl group precedes β-oxidation. This finding stimulated his interest in fats and lipids and led him to investigate in detail a glucosamine-containing phosphatide which had previously been reported by Frankel and Kafka in 1920. In an attempt to purify this substance, he came to the conclusion that the isolated phosphatide did not contain hexosamine. He then became interested in the chemical nature of sugar-containing substances in the brain. He succeeded in isolating a cerebroside which had previously been unknown and demonstrated it to consist of a 24-carbon monocarboxylic acid with one double bond, sphingosine, and galactose. He gave to this cerebroside the name "nervon," and to the monoenoic acid with 24 carbons, "nervonic acid." In subsequent experiments he found an additional cerebroside containing a 24-C hydroxy acid. This acid was designated as oxynervonic acid and the cerebroside containing this hydroxy was designated as oxynervon. By oxidative degradation of this hydroxy acid, he found it to be a mixture of two isomeric α-oxy-n-tetracosanoenic acids in which the double bond was at either C-15 or C-17. Similarly, cerebronic acid was shown to be an α-oxy-n-tetracosanoic acid.

In addition Ernst Klenk had directed his attention to the sphingosine moiety of the split products from the cerebroside. It was he who gave the first correct experimental formula $C_{18}H_{37}O_2N$ to sphingosine and thereby made an essential contribution to the elucidation of its structure. By oxidative degradation of triacetylsphingosine, an α, α-dihydroxy-β-amino-butyric acid derivative was obtained, which after its deacetylation with lead tetra-acetate and subsequent oxidation, gave L (-) serine. Thus the position of the amino group at C-2 of the sphingosine and the configuration around this asymmetric carbon was established, which had also been proved by Carter.

Of Klenk's numerous works on the cerebrosides, one deserving of special mention was the discovery of the substance deposited in Gaucher's disease. This substance was found to be a cerebroside containing glucose instead of galactose. He found that the very high content of phosphatide in the brain, liver and spleen in Niemann-Pick's disease (another lipodosis) is due to the enormous accumulation of sphingomyelin.

Even in his early days of investigation, Ernst Klenk was very much interested in phosphatides. Attracted by the abundance of acetalphosphatide in the cephalin fractions of the brain, he decided to work on this problem. In the meantime, it had become known that the formula for acetalphosphatide given by Feulgen did not account for a number of experimental findings. The data accumulated from various sources suggested that the substance isolated by Feulgen and Thanhauser is a secondary product derived from the genuine plasmalogen. No water-soluble phosphate was formed when the phosphatide mixture was treated with acid. After hydrogenation only 30% of the total phosphate could be easily split off with alkali, and 60–70% of the total phosphate was isolated in the form of chimyl or batylphosphoric acid. These findings led Klenk to propose a formula for the genuine plasmalogen. According to this formula the enol form of the C_{16} or C_{18} aldehyde is bound to the primary alcoholic hydroxyl group in an acetal-like fashion, and the unsat-

urated fatty acids with 18, 20 and 22 carbons are esterified with the secondary hydroxyl group of glycerol. The chemical constitution of acetalphosphatide is therefore very similar to the classical formula of ethanolamine-cephalin, which explains the close relationship in the physical properties of these two substances. When plasmalogen is hydrolyzed with alkali, the fatty acids are split off. The remainder of the molecule possibly is rearranged to the ether-insoluble acetalphosphatide to which the original formula of Feulgen may be ascribed.

A considerable portion of Klenk's work has been concerned with investigation of the structures of highly unsaturated fatty acids found in mammalian organs and in fish oils. From the work of Burr in 1930's a question arose concerning the essential nature of the polyenoic acids such as linoleic and linolenic acids in foods and of the more highly unsaturated C_{20} tetraenoic acid (arachidonic acid) in liver phosphatides. In the early 1930's, Klenk found a C_{22} polyenoic acid more highly unsaturated than arachidonic acid. This C_{22} acid was very similar to "clupanodonic acid" of fish oil and was assumed to be docosapentaenoic acid. He later found eicosapentaenoic and docosahexaenoic acids to be the most highly unsaturated. In his extensive work after 1950, Klenk found it possible to elucidate the structure of a large number of the highly unsaturated fatty acids, primarily by oxidative ozonolysis of the polyenoic acids and by quantitative chromatography of the resulting mono- and dicarboxylic acids. A general principle concerning the structure of these acids was established by this work. It was found that all the double bonds are arranged in a divinyl methane rhythm. They have the chain length of 18, 20, or 22 carbons and belong either to the so-called oleic-, linoleic-, or linolenic- type. Seen from the methyl end the first double bond is situated at the position which corresponds to that of the oleic, linoleic and linolenic acids respectively, i.e., C-9, -6 and -3. Some C_{16} polyenoic acids of fish oils are the only exceptions to the remarkable regularity mentioned above. The investigations by Klenk on the highly unsaturated acids made clear that the polyenoic acid of the oleic type are present in only small amounts in the mammalian phosphatides and that they are totally absent from fish oils. The principal polyenoic acids of fish oils are of the linolenic type.

By studying the metabolism of these acids he showed that the linoleic-type acids, for example arachidonic acid, arise from linoleic acid, and the linolenic-type acids, e.g., C_{20}- pentaenoic and C_{22}- hexaenoic acid, arise from linolenic acid. The chains of linoleic and linolenic acids are elongated by "active" acetate addition to the carboxylic end and additional double bonds are introduced in the carboxylic-end in a divinyl methane rhythm. On the other hand, all of the oleic-type polyenoic acids seem to be synthesized in the animal body. There exists presumably no fundamental difference among various vertebrates as regards the synthesis of the other polyenoic acids from the so-called essential fatty acids. This has been established by James Mead as well.

The investigations conducted on the lipidoses in the early days of Klenk's scientific career, provided him with another interesting field for research. He found a group of lipids in nerve tissue which had hitherto been unknown. In 1935 he describel a "substance x" which apparently was closely related to the cerebrosides. This substance appears in larger amounts in nerve tissue in amaurotic infantile idiocy and in Niemann-Pick's disease and in smaller amounts in the normal brain. He designated this substance *ganglioside.* In 1941 from this glycolipid he was able to isolate by methanolysis a previously unknown crystalline substance. This substance was characterized by Klenk as the methylglycoside of a hexosamine-free polyhydroxy-amino acid with 9 or 10 carbon atoms. He called this substance, which yields a red-violet color with Bial's orcinol-ferric chloride-HCl reagent, "neuraminic acid." Stimulated by the report of Blix of a similar color reaction of submaxillary gland mucin with Bial's reagent, Klenk succeeded in isolating for the first time the N-acetyl derivative of neuraminic acid from mucin, after having been

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able previously in isolating the crystalline methylglycoside of neuraminic acid from the same material. The N-acetyl form occurs in blood serum and together with N-glycolyl, N, O -di and tri-acetyl derivatives in all mucins of endodermal origin. In addition to his significant contribution to the elucidation of the structure of this very interesting substance he showed that the primary and one of the most important functions of neuraminic acid is to serve as the determinant group of the acceptorsite for the myxovirus of the mumps-influenza group. He has contributed further to the biochemistry of neuraminic acid by showing that the enzymic action of myxovirus is the same as that of the receptor destroying enzyme from the culture filtrate of various bacteria, by showing the role of neuraminidase in virus hemagglutination and panagglutination reactions, and by showing this acid to be the determinant group of the MN blood group system.

In the 1960's Klenk turned his attention once again to the gangliosides. Purification of the gangliosides and determination of their structures by partial hydrolysis, isolation of the oligosaccharides, permethylation, periodate oxidation and by the treatment with neuraminidase, resulted in the conclusion that the gangliosides are a mixture of substances which are very closely related in their chemical compositions. The difference in the fatty acid and sphingosine moieties are very slight, the main component of the former being stearic acid and that of the latter C_{18}- sphingosine. The C_{18}- sphingosine is replaced by its C_{20}- homologue with increasing age. However, there is extensive variation in the carbohydrate portion of the molecule. The carbohydrate sequence in all hexosamine containing brain gangliosides, is glucose- (4-1) galactose (4-1)-N-acetyl-galactosamine (3-1)-galactose with N-acetyl- neuraminic acid in a (3-2)-linkage at first galactose molecule and the glucose molecule is glycosidically bound to sphingosine. A second type of ganglioside which is devoid of the terminal galactose group exists in only small amounts in the normal brain, but appears in abundance in amaurotic idiocy of Tay-Sachs type. A third ganglioside has two molecules of neuraminic acid, one of which lies in the central galactose molecule and the other (3-2) glycosidically bound to the terminal galactose molecule. Of these two neuraminic acids only the latter can be split off with neuraminidase. A fourth type of ganglioside is composed of the same carbohydrate sequence but having two molecules of N-acetyl-neuraminic acid at the first galactose molecule, linked to each other in (8-2) position. An additional molecule of N-acetyl-neuraminic acid may be attached to the 3-position of the second galactose. The existence in small amounts of a hexosamine-free ganglioside which contains only glucose, galactose and N- acetyl-neuraminic acid, was also demonstrated. The configuration of the neutral sugar moiety corresponds to that of lactose. Another hexosamine-free ganglioside consists of 3 molecules of galactose with an N-acetyl-neuraminic acid in position 3 at the central galactose. (Of the extensive works of Ernst Klenk which have been presented in more than 160 publications, only the events of importance could be cited.)

Most of his work has been conducted at the University of Cologne following his appointment as director of the Institute for Physiological Chemistry in 1936. Here his works have been accomplished in cooperation with nearly 100 associates to which group the author of this biography has the honor to belong.

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increasing chain length of the alkyl sulphates. The deposition of carbon black particles from alkyl sulphate solutions with concentrations corresponding to the c_k values decreases in absolute magnitude with increasing chain length, while the change in adsorption with time remains unaffected. On the other hand, a definite increase in desorption rate was observed at the c_k value of the alkyl sulphates with increasing chain length. The optimum effectiveness of the alkyl sulphates does not, according to these experiments, lie within the range of critical micelle concentration.

CATIONIC SURFACTANTS AS LEVELLING AGENTS IN DYEING ANIONIC POLYACRONITRILE FIBERS. R. Rokohl (BASF, Ludwigshafen/Rhein, Germany). *Tenside* 2, 76–83 (1965). Cationic surfactants are effective levelling agents for dyeing anionic polyacronitrile fibers with selected basic dyestuffs. The rate of uptake of the dyestuff is diminished because of the blocking effect of the agent and the ability of the dyestuff to migrate during the process is also increased. This retarding effect is dependent upon the chemical constitution of the cationic surfactant.

NOTES ON THE DOCUMENTATION OF SURFACTANT SPECTRA. K. Bey (Düsseldorf, Germany). *Tenside* 2, 105–11 (1965). The reference spectra of a large number of commerical surfactants have been prepared in the form of punched cards. This useful collection of spectra is an excellent aid in interpreting infrared spectra of unknown surfactants, when used in conjunction with a spectrum list similar to the Spec-Finder system by Sadtler.

THE DETERMINATION OF PERBORATE CONTENT IN SYNTHETIC DETERGENTS. E. Heinerth (Düsseldorf, Germany). *Tenside* 2, 180–1 (1965). The active oxygen content of modern detergent compositions can be determined by reaction with an arsenite solution and iodometric titration of the excess arsenite. This method is effective even in cases where the permanganate and iodine titrations fail.

SPRAY DRYING EQUIPMENT FOR THE PRODUCTION OF SYNTHETIC DETERGENTS AND SOAP-SYNTHETIC POWDERS. E. Jury (Lurgi Gmbh, Frankfurt/Main, Germany). *Tenside* 2, 209–16 (1965). The principles of design and construction for a detergent spray drying plant are reviewed, with special regard to slurry preparation and its effect on the end product specifications. Besides a description of the actual spray drying equipment, the after treatment of the powder, storage and transport of the finished product, automatic control equipment and economic considerations on material and labor costs are also discussed.

ODORIFEROUS COMPOUNDS IN POLYPROPYLENE BENZENE SULFONATE. I. ISOLATION AND SEPARATION OF VOLATILE OIL. W. K. Seifert (Calif. Res. Corp., Richmond, Calif.). *Tenside* 2, 150–6 (1965). Nitrogen blowing of large batches of polypropylene benzene sulfonate slurry and condensation of the gas in cold traps led to the isolation of 0.2% (active basis) of an odoriferous volatile oil, with no indication of decomposition during the blowing step. Separation and qualitative identification of this oil, which contains about 200 compounds were done by preparative GLC and silica gel chromatography combined with instrumental analysis. Olefins and carbonyl compounds were found to be present in the most odoriferous fractions. Isolation and analysis of the volatile oil of unsulfonated polypropylene benzene showed that all the compounds causing the sulfonate odor are produced in the sulfonation process.

II. IDENTIFICATION. *Ibid.*, 182–90. Infrared analysis of the carbonyl compounds and reduction with sodium borohydride combined with odor panel tests showed that saturated ketones (less than 1 ppm) are the largest contributiors to the odor of polypropylene benzene sulfonate slurries. The second largest contributions came from about 50 ppm of substituted terpene-type diolefins, whose structure was investigated by mass spectroscopy, IR, UV, Raman Spectra and NMR before and after selective and total catalytic hydrogenation. The small odor contribution of sulfur compounds and the absence of mercaptans were demonstrated by gas chromatography combined with microcoulometric titration and chemical microreactions combined with odor panel tests. A number of branched chain paraffins and substituted cyclohexanes were directly identified by mass spectroscopy, however the contribution of these compounds to the over-all odor was found to be negligible.

III. REMOVAL OF ODOR BY CHEMICAL TREATMENT AND CONTROL OF SULFONATION CONDITIONS. *Ibid.*, 216–20. Removal of the ketone odor from polypropylene benzene sulfonate slurries is

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