LANDMARKS IN THE BIOGRAPHY AND SCIENTIFIC ACTIVITY OF ACADEMICIAN S. A. HILLER. (ON HIS 90th BIRTHDAY)

On 14 January 2005, 90 years have passed since the day Academician Solomon Aronovich Hiller was born: famous organic chemist, founder and for many years director of the Latvian Institute of Organic Synthesis, organizer and first editor-in-chief of the journal *Khimiya Geterotsiklicheskikh Soedinenii* [Chemistry of Heterocyclic Compounds] (from 1965 to 1975). S. A. Hiller in his time became an authority as a brilliant organizer of science and new directions, as a multifaceted organic chemist seizing on and developing entirely new ideas in the chemistry of drugs and heterocyclic compounds, as an erudite group leader, as an indefatigable organizer of scientific conferences and symposia.

Some of the organic drugs he designed (*tegafur/ftorafur*, nitrofuran drugs, etc.) have remained important in the practical arsenal of modern drugs. Both the institute in Riga that he founded in 1957 and the journal continue to grow.

S. A. Hiller was born in Riga on 14 (1) January 1915. His father worked for various textile companies as a merchandising specialist (a wool expert) and a procurement agent. His mother studied dentistry. During a trip to visit her parents in Belostok in 1920, she died from typhus. The boy was then only 5 years old. He was raised by his grandmother, who fostered the development of Solomon Aronovich and taught him languages and literature. All the members of S. A. Hiller's family fell victim to Hitler's Holocaust: they were killed in the Riga ghetto in 1941.

In 1932, S. Hiller graduated from the business division of the Riga city German gymnasia in Riga. Even while back on the school bench, he was interested in various areas of natural science, in particular physics and chemistry. But his father, who despite his own business training could not achieve a proper social position, objected to his son's desire to become a student. He placed him as an apprentice in the Riga *Fel'dkhun* textile plant. Nevertheless, in fall of 1933, S. A. Hiller started at Latvian University in the Chemical Faculty, earning a living by tutoring and teaching various preparatory courses. One time he worked as a foreman in the *Emolip* glass factory.

Starting in his second year, S. Hiller participated in a seminar on organic chemistry led by university lecturer P. Kalninsh. Paul Kalninsh (1886-1955), who had been a student and laboratory assistant of the Nobel prize laureate F. Bergius, an organic chemistry of broad scope, was knowledgeable about both theoretical problems and technology issues. At that time, he was studying polyphenyl cyclobutanediones. Study of compounds in this class was the subject of S. A. Hiller's first scientific work. Under the supervision of P. Kalnin', S. A. Hiller studied *Langenbeck's compound*: an intensely colored crystalline material formed as a result of thermal decomposition of benzilic acid. Due to inadequate experimental resources, the correct structure of the compound could not be established at that time (this was done in 1954 by a group of chemists in the USA), but while carrying out the investigations he developed original ideas about the possibility of the existence of α-lactones. In 1937, S. A. Hiller was forced to discontinue his studies until 1940.

Combining his studies with working as a subassistant professor for Paul Kalninsh and actively participating in the social life of the division, S. A. Hiller carried out his degree research work on *Langenbeck's compound*. His defense occurred on one of the first days of the war, on 27 June 1941, and on that same day S. A. Hiller left Riga.

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During the evacuation, S. A. Hiller worked in Stalingrad at the Lenin Chemical Plant: first as a laboratory assistant, then as laboratory director, and finally as a production manager. At the end of 1942, S. A. Hiller found himself in Kazan, where until 1946 he worked as a technical director and chief engineer at a bakery plant. The years he spent at the plant gave him experience in organization and economics of production, which would later be useful in putting his own ideas into practice.

In July 1946, having returned to Riga, on the recommendation of his teacher P. Kalnin', S. A. Hiller became a junior scientist at the Institute of Forestry Problems, which had just been established by the Academy of Sciences of the Latvian SSR. This institute was founded by Academician A. Kalnin'sh to solve problems concerning the economical use of wood. Here S. A. Hiller worked on a previously little studied and undeservedly neglected problem, namely development of processes for chemical treatment of pentosans.

The major chemical product obtained from pentosan-containing raw material is furfuraldehyde. Chemical treatment of furfuraldehyde in turn yields on the one hand effective drugs and other biologically active substances, and on the other hand important monomers: intermediates in the production of polymer materials and solvents. Furfuraldehyde proved to be within the scope of S. A. Hiller's explorations, and two directions stood out: synthesis of new biologically active substances and new monomers. A third direction was subsequently added: theoretical studies in the chemistry of furan, and then in the chemistry of heterocyclic compounds in general. Consequently, solving the applied problem (study of the potential for using furfuraldehyde) led S. A. Hiller to furan chemistry, and then also to the chemistry of other heterocyclic systems.

S. A. Hiller rapidly advanced as a scientist. By 1949, he had become a senior scientist. By 1950, he was responsible for directing the furfuraldehyde section, and in 1951-1953 he was assistant science director of the Institute of Forestry Problems. In 1953, S. A. Hiller again became director of the furfuraldehyde section of that Institute. S. A. Hiller directed this section (subsequently the laboratory of heterocyclic compounds in the Institute of Organic Synthesis, it existed until December 1975) until the end of his life.

In December 1954, S. A. Hiller defended his Candidacy dissertation, "Study of the synthesis methods, physicochemical properties, and structure–biological activity relation for some substituted 5-nitrofurfurylidene imines," in which he correlated data from his own early research. The academic degree of Candidate of Sciences was awarded unanimously. Both the official opponents and the chemists who provided references as well as the medical scientists who had taken part in the discussion raised the question of awarding him the academic degree of Doctor of Chemical Sciences. The vote was repeated, but the proposal made by the Council to award the doctoral degree was turned down by VAK [Supreme State Certification Committee]. S. A. Hiller was awarded the academic degree of Candidate of Chemical Sciences. So S. A. Hiller did not defend a doctoral dissertation, although by the end of his life he had again started thinking about it. Even before defense of his Candidacy dissertation, in March 1951, S. A. Hiller was elected as a Corresponding Member of the Academy of Sciences of the Latvian SSR; and in May 1958, he was elected as a full Member of the Academy of Sciences of the Latvian SSR.

Along with the research work conducted within the Academy of Sciences, in 1947-1950 S. A. Hiller worked in the Organic chemistry department of the Chemical Faculty of Latvian State University as an assistant and senior instructor, where he taught a lecture course on "Theoretical problems of organic chemistry."

S. A. Hiller was an active popularizer of science. In 1947-1951, he supervised the science and technology section (which he had created) of the periodical *Padomju Jaunatne*, which at the time was the only source of regular information about the latest achievements in science for the Latvian reader.

Due to the increasing scope of work on synthesis of medicinal drugs and the favorable opportunities created by the N. S. Khrushchev era, S. A. Hiller proposed that a specialized institute be organized within the system of the Academy of Sciences of the Latvian SSR which would be concerned with targeted synthesis and study of physiologically active substances. The idea received support, and on 1 January 1957, the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR began operation under the direction of S. A. Hiller, and before long the Institute grew to become a widely known research institution.

From November 1963 to the end of his life, S. A. Hiller, as a member of the Presidium of the Academy of Sciences of the Latvian SSR and academic secretary of the Division of Chemical and Biological Sciences of the Academy of Sciences of the Latvian SSR, coordinated and directed all research by Latvian scientists in various areas of chemistry and biology.

We can identify four basic directions in the scientific research and scientific organizational activity of S. A. Hiller: 1) creation of the Institute of Organic Synthesis; 2) research in the chemistry of heterocyclic compounds and bordering fields; 3) search for new physiologically active compounds (diverse medicinal drugs and ways to use chemistry in agriculture); 4) development of studies in bioorganic chemistry and molecular biology.

Back while organizing the Institute, S. A. Hiller considered it necessary to establish a competent scientific group. In order to productively extend the search for new physiologically active compounds, it was necessary to have a multifaceted Institute where synthetic chemists would work side by side with microbiologists, pharmacologists, and medical scientists carrying out biological and sometimes also clinical testing of the synthesized substances: an Institute which would have its own production facility, an experimental plant for manufacture of a drug in amounts needed for clinical and field trials and development of technological regulations.

It was just such a structure that was given to the Institute of Organic Synthesis, which S. A. Hiller continuously directed until the end of his life. It began operation with a staff of 45 people, with no building of its own, with no laboratory space, with no equipment. Within 18 years, the Institute had grown to a scientific institution with 550 people (including about 100 Candidates of Sciences, 12 professors and Doctors of Sciences), with two experimental plants in which about 700 people worked, with a basic chemical laboratory corps and a biological corps, with new buildings for the experimental facility, with real prospects for constructing a building for molecular biology research, and mainly with an established scientific reputation and broad scientific contacts (and not only within the borders of the then Soviet Union).

Regarding research in the field of medicinal chemistry, after the technology was devised to produce the new drugs (furaciline and *p*-aminosalicylic acid (PASA)), production began for more than 60 medicinal drugs developed by the Institute: antibacterial, antitumor, antiviral, psychopharmacological, cardiovascular. Twelve of them were original and had also become well known outside the USSR. Most of the drugs were synthesized by students of S. A. Hiller under his direct supervision. Such drugs especially included derivatives of the 5-nitrofuran series: the effective chemotherapeutic drugs *furagin* and *solafur*, and also the antibacterial thread *letilan*, and the antifungal drug *nitrofurilene*. Among the derivatives of the aziridine series, *imiphos* turned out to be an effective means for treatment of erythremia. The muscle relaxant *dioxonium* was widely used in operations on skeletal muscles. But the greatest recognition was won by the original antitumor drug *ftorafur* synthesized by S. A. Hiller, M. Lidaks, and R. Zhuk. At the time, this drug was one of the most effective weapons in the arsenal of chemotherapy against malignant tumors and was a drug designed to treat breast cancer and cancer of the gastrointestinal tract. The drug underwent thorough biochemical and clinical study in Japan and the USA as well as in the USSR; there were several international symposia (1974, 1979, etc.) devoted especially to *ftorafur*. The drug is widely used in oncological practice. In Japan, *ftorafur* is known under 36 synonyms, among which the name most often used is *tegafur*, the international non-proprietary name of the drug proposed by WHO.

In the first period of his activity, S. A. Hiller thoroughly studied various reactions in the furan series: oxidation, nitration, alkylation, acylation, reduction, deuteration, ring opening, etc. (N. Saldabola, K. Venters, E. Lukevics and others).

The 5-nitrofurylpolyene aldehydes and their derivatives proved to be especially interesting from both a theoretical and a practical standpoint. Quantum-chemical calculations, the spectral characteristics, and the values of the polarographic reduction potentials made it possible to substantiate the effect of introducing an additional vinylidene group, increasing the antibacterial activity of the compounds. The drugs synthesized by

S. A. Hiller and his colleagues differ from previously developed drugs of the nitrofuran series in that they are derivatives of 3-(5-nitro-2-furyl)acrolein rather than 5-nitrofurfuraldehyde. Under the direction of S. A. Hiller, the mechanism of nitration of furan and its derivatives was studied and the structure of the intermediate nitration products was established, including for the vinyl derivatives of furan (K. Venters). The mechanism for electrochemical reduction of nitrofurans was studied on a mercury drop electrode, and a correlation was found between their electrochemical properties and biological activity (J. Stradins).

Subsequently S. A. Hiller and colleagues turned toward the chemistry of nitrogen-containing heterocycles, and carried out extensive research in the area of furanidyl pyrimidines and pyridazones; extension of this work led to synthesis of "model analogs" of nucleotides and development of the technology for the herbicide *phenazone*.

Back in the beginning of his activity, when studying synthesis of alkylating antitumor drugs together with M. Lidaks, S. Hiller also became involved with the chemistry of aziridine. This direction became one of the major directions in S. A. Hiller's scientific investigations during the last years of his life. When PMR spectroscopy was used in the case of N-aminoaziridine as an example, a slow inversion of the nitrogen atom in this molecule and other related compounds was observed even at room temperature and elevated temperatures. This phenomenon established by S. Hiller, A. Eremeev, M. Lidaks, and V. Pestunovich together with a group of colleagues at the Institute of Chemical Physics of the Academy of Sciences of the USSR (R. G. Kostyanovsky et al.), which was of interest from the standpoint of the stereochemistry of nitrogen compounds, was officially registered in the USSR as Discovery No. 110 under the name "Configuration stability of trivalent nitrogen in unbridged structures."

Under the direction of S. A. Hiller, his colleagues (M. Shimanskaya et al.) carried out investigations in the area of catalytic synthesis of heterocyclic compounds (contact vapor-phase decarbonylation and partial oxidation of furan and pyridine derivatives, liquid phase and vapor-phase deaminocyclization of aziridines to form piperazine, pyrazine, and triethylenediamine). A large portion of the work by S. A. Hiller's colleagues (J. Stradins, R. Gavars, I. Mazheika, and others) relates to the field of physical organic chemistry: polarographic reduction of heterocyclic nitro compounds, electrochemical generation of radical ions, calculation of the dipole moments of nitrogen-containing heterocycles. In the last years of S. A. Hiller's life, on his initiative and under his direction studies were begun that were aimed toward identification and prediction of the medicinal activity of organic compounds from their chemical structure (A. B. Rozenblit, among the colleagues of which we should then especially point out V. E. Golender).

Starting from 1964, the problems dealt with by the Institute of Organic Synthesis increasingly included studies in bioorganic chemistry and molecular biology. Arising in the course of research conducted within classical organic chemistry, these studies over time took on an independent character. These include studies in the chemistry of peptides and proteins, nucleic acids and their synthetic model analogs, membrane-active compounds, and also on modification of antibiotics (G. Chipens, E. Grens, G. Duburs, R. Zhuk, R. Zhagats, G. Veinberg and others).

Back at the first All-Union Conference on physiologically active polymers (Riga, 1962), S. A. Hiller advanced the idea of creating model analogs of nucleic acids while retaining the natural pyrimidine and purine bases and the polyelectrolytic nature of the macromolecular chain, containing, instead of the sugar residue, the conformationally similar α,ω-polymethylenediol substituents. S. A. Hiller's opinion was that such model analogs, when they combined with nucleic acids, might affect certain functions of the latter and thus result in unusual biological effects. Colleagues of S. A. Hiller carried out a series of research projects on synthesis and study of the physicochemical and biochemical properties of model analogs of nucleosides and mononucleotides and polynucleotides (R. Zhuk, I. Goncharova, M. Lidaks, and others).

As a simplified model of a nucleoside, we may also consider the already mentioned drug *ftorafur*: 1-(2-furanidyl)-5-fluorouracil, which can be treated as a latent transport form of the antimetabolite 5-fluorouracil.

As a professor in the Fine Organic Technology Department of the Chemical Faculty of Riga Polytechnical Institute (1964-1972) and professor in the Organic chemistry Department of the Chemical Faculty of Latvian State University (1973-1975), he taught lecture courses on the chemistry of nucleosides, nucleotides, and nucleic acids.

The results of S. A. Hiller's research were described in more than 300 scientific papers and in many talks delivered at All-Union and international congresses, symposia, and conferences. A bibliography of his scientific publications up to 1976 was published in the journal *Khimiya Geterotsiklicheskikh Soedinenii*. S. A. Hiller held 80 inventor's certificates and 40 patents in the USA, UK, Japan, Sweden, the Federal Republic of Germany, France, and other countries. Thirty Candidacy dissertations were defended under his supervision, and he was the scientific advisor for 6 doctoral dissertations.

Among S. A. Hiller's students who defended dissertations under his direct supervision, we should mention Professor M. Shimanskaya (Honorary Member of the Latvian Academy of Sciences); Academicians M. Lidaks, I. Kalvin'sh, and E. Liepins (Latvian Academy of Sciences); Doctor R. Zhuk (Foreign Member of the Latvian Academy of Sciences); G. Veinberg (Corresponding Member); K. Venters, N. Saldabola, J. Polis, L. Avota, G. Sokolov, V. Slavinskaya, V. Egerts, A. Eremeev, I. Mazheika, R. Gavars, and others (Doctors of Chemistry); A. Kimenis and A. Zidermane (Doctors of Medicine). The author of these lines also considers it an honor to have been S. A. Hiller's dissertation student.

In 1951, S. A. Hiller together with his coauthors became a laureate of the Stalin Prize for development of the technology for the antitubercular drug *PASA*, and in 1957 and 1965 he was twice awarded the State Prize of the Latvian SSR for development of new medicinal drugs *(furacilin, furagin, imiphos, furazolidone, furadonin, Tio-TEPA, cyclophosphane)*. In 1965, he was named Honored Scientist and Engineer of the Latvian SSR. In 1972, S. A. Hiller was elected as a Member of the German Academy of Natural Scientists Leopoldina.

The activity of S. A. Hiller substantially contributed to the general rise of chemical sciences and the chemical industry in Latvia. He actively implemented the idea that Latvia lacked the raw materials for "large-scale chemistry", and so here we should develop fine organic synthesis and production of reagents for molecular biology and chemistry. It is precisely because of the collaboration between science and industry in Latvia that initially small pharmaceutical/chemical plants emerged and grew stronger in Riga, and after them came large plants for biochemical reagents and pharmaceutical/chemical production in Olaine, a new city which is a "chemical satellite" of Riga (subsequently the Biolar and Olainfarm companies). A number of technological processes developed by scientists of the Academy of Sciences of the Latvian SSR were adopted at the Olain and Riga plants, and then also in other republics of the USSR, for example production of the herbicide *phenazone*, the antihelminthic *piperazine*, the feed additive *furazolidone*, and various nitrofuran drugs. All this provided a basis for creating a fine chemical industry, and S. A. Hiller can truthfully be considered its initiator and founder.

Years after the death of S. A. Hiller, within the Experimental Plant of the Institute of Organic Compounds, one of Hiller's colleagues V. Jakobsons (now an Honorary Member of the Latvian Academy of Sciences) started the Grindex company (in 1991); and the Center for Biomedical Research of Latvian University, directed by Academician E. Grens, also evolved from the Institute.

The development of chemistry in Latvia was no less promoted by strengthening of bonds between Latvian scientists and scientists of the leading centers of the USSR. With the participation of S. A. Hiller, organization of conferences and symposia in Riga increased in scope, including: the Seventh International Symposium on the Chemistry of Natural Compounds, IUPAC, with four Presymposia (1970); the Third All-Union Biochemical Congress (1974); the Sixteenth All-Union Conference on High Molecular Compounds (1964); the First All-Union Conference on Chemotherapy of Malignant Tumors (1968), the First All-Union Symposium on Peptide Chemistry (1967); the Second All-Union Conference on the Chemistry and Physics of Organic Semiconductors (1966); the Seventh All-Union Conference on Electrochemistry of Organic Compounds (1973), the Twelfth Scientific Session on the Chemistry and Technology of Organic Compounds of Sulfur and Sulfur-Containing Oil (1971), and a number of other impressive conferences.

Up to the end of his life, S. A. Hiller headed up work on a number of All-Union scientific councils: the Science Council on the Chemistry and Technology of Organic Compounds of Sulfur, of the State Committee of the USSR on Science and Technology (starting in 1969); the chemical section of the Council on Automation in Scientific Research, of the Academy of Sciences of the USSR (starting in 1972), the All-Union Science Council on Use of Pentosan-Containing Raw Material, at the Academy of Sciences of the Latvian SSR (starting in 1956).

S. A. Hiller was the initiator for creation of the All-Union journal, *Khimiya Geterotsiklicheskikh Soedinenii*, and he was its organizer and editor-in-chief from the time it was founded in 1965 up to 1975. The creation of this journal was connected with the end of the era of the N. S. Khrushchev Administration in the history of the USSR, which on the one hand was characterized by increased attention to development of chemistry and on the other hand by some decentralization of the Soviet Union. Scientific centers and scientific journals were created not only in Moscow and Leningrad, but also in the capitals of the republics of the Union existing at that time. The favorable conditions could not even slightly bypass the ever-active S. A. Hiller. To be sure, he did not succeed in establishing the pharmaceutical chemistry journal in Riga; but he achieved a basis for the support of A. N. Nesmeyanov and Yu. K. Yur'ev for a specialized journal on heterocyclic chemistry. The first editorial board of the journal included, in addition to Riga chemists, the leading heterocyclic chemists of Moscow, Leningrad, Sverdlovsk, and Armenia. A special role in development of the journal in the first decade of its existence was played by Professor A. N. Kost of Moscow State University, and also the secretary of the editorial board I. N. Goncharova, but S. A. Hiller held the main controls over management of the journal firmly in his own hands. The traditions of the journal have been maintained by the successors of S. A. Hiller: since 1985, the editor-in-chief has been Academician E. Lukevics, who also began his work at the Institute of Organic Synthesis in S. A. Hiller's laboratory.

S. A. Hiller died on 7 June 1975 in Riga from a malignant tumor of the digestive tract, a disease against which he had worked hard to find effective drugs. He was buried at Rainis cemetery, where in 1977 a memorial was placed at the grave site (the work of the sculpture L. Novozhenets).

In 1990, the Institute established the Hiller medal as the highest award of the Institute, conferred for scientific work and scientific organizational service. In 2004, the Latvian Academy of Sciences, together with the Grindex company, the Center for Biomedical Research of Latvian University, and the Institute of Organic Synthesis, established the S. A. Hiller prize, awarded for outstanding achievements in biomedicine and development of new medicinal drugs. It is anticipated that the first award of this prize by the Latvian Academy of Sciences will be made on the 90th birthday of S. A. Hiller, in January 2005.

It is gratifying to see that S. A. Hiller's life's work has not faded away: the Latvian Institute of Organic Synthesis he founded and the scientific directions he established continue to grow, although under new political and economic conditions, and the journal that he organized continues to successfully publish papers by heterocyclic chemists of different countries.

J. Stradins

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