OBITUARY NOTICES.

LAUNCELOT WINCHESTER ANDREWS.

1856—1938.

LAUNCELOT WINCHESTER ANDREWS was born in London, Ontario, Canada, on June 13th, 1856, and died at Belmont, Massachusetts, on April 14th, 1938, at the age of 81. After elementary and high school training at Springfield and Northampton, Massachusetts, he went in 1872 to Cornell University at Ithaca, New York; then to Yale University, New Haven, Connecticut, where he was awarded the Ph.B. degree in 1875. In the summer of 1876 he studied at Harvard University, Cambridge, Massachusetts. He was teacher of chemistry, physics, and mathematics in the High School of Springfield, Massachusetts, 1876—77. In 1878, he matriculated at the Georgia-Augusta University in Göttingen, Germany, and in 1880 he went to the University of Bonn, where he continued his studies and finished the thesis which he had begun in Göttingen. On February 21st, 1882, he took the oral examination before the philosophical faculty of the University of Göttingen, from which he received the Ph.D. degree.

Andrews was professor of chemistry at Iowa State College, Ames, Iowa, from 1884—85, and professor of chemistry at the State University of Iowa, Iowa City, Iowa, from 1885—1904. Then, until 1910, he was research and consulting chemist for the Mallinckrodt Chemical Works, St. Louis, Missouri. During 1910—13, he was president of the Andrews Chemical Works, Davenport, Iowa. From 1913—14 he served as special investigator in canning for the United States Department of Agriculture, and from 1915—21 was research chemist for the Victor Chemical Works. He retired in 1921 and lived at Williamstown, Massachusetts, until a few years ago. He then went first to Amherst, Massachusetts, and then to Belmont, Massachusetts, where he was living at the time of his death.

Andrews became a member of the Chemical Society in 1882. He was also a member of the American Chemical Society, the American Institute of Chemical Engineers, honorary member of the Contemporary Club (Davenport, Iowa), member of Davenport Academy of Science, American Academy of Political and Social Science, Iowa Engineering Society, St. Louis Academy, American Association for the Advancement of Science, and an ex-president of the Iowa Academy of Science. He was a charter member of the Iowa Chapter of the honorary scientific society, Sigma Xi, and an honorary member of the honor chemical fraternity, Phi Lambda Upsilon.

He published numerous articles and obtained many patents. His writings were in various fields of chemistry—analytical, physical, and organic. The Andrews Chemical Works at Davenport, Iowa, were established to manufacture oxalic acid by a method covered by his patents. The time was unfortunate, for during the years 1910—13 he could not stand foreign competition. If it had been a little later during the world war, 1914—18, when the price of oxalic acid was very high, his work would have been most remunerative.

According to one of Andrews's assistants, " his assistants were in constant awe of him, partly on account of his abrupt, concise manner of speech, and partly owing to his remarkable breadth of knowledge and the finality with which he expressed it. His assistants were intensely loyal, and the influence and impression exerted upon them was such that they unconsciously imitated his manner of speech and striding walk, a rare unconscious tribute, indeed, to a leader they loved. Dr. Andrews was a man of energy, action, a remarkable personality, and a genial host to his chosen friends."

According to a student at the University, who was later a colleague of Andrews at the State University of Iowa, " he was an outstanding personality among the faculty. He was a leader of the science group, but was a man of wide knowledge on general subjects. He took great interest in building up the university in an academic and in a social way. He had broad and liberal views on educational subjects."

EDWARD BARTOW

FRANK BAINBRIDGE.

1891—1938.

FRANK BAINBRIDGE was born in Middlesbrough in 1891, the younger son of George Bainbridge, Town Clerk of Middlesbrough for many years. He was educated at the High School, Middlesbrough, and then entered the laboratories of Messrs. Pattinson and Stead, the well-known analytical and consulting chemists, in 1906. There he received his metallurgical training under Dr. J. E. Stead, F.R.S., who had a great reputation as a metallurgist and metallographer. From him, young Bainbridge drew his inspiration for research.

On completing his training in 1911 Bainbridge entered the service of the Skinningrove Iron Co. Ltd. as chemist, and remained with the Company up to his sudden death in April, 1938. Shortly before Bainbridge was appointed chemist, the Skinningrove Iron Co. Ltd. had erected steelworks, and Bainbridge developed a knowledge of the metallurgy of steel and the chemical control of all operations in blast furnaces, coke ovens, open-hearth furnaces and rolling mills.

During the War Bainbridge undertook important research work, on the Company's plant, on hot blast stove efficiency with cleaned blast furnace gas, and on the recovery of potash from blast furnace dust. After the War the Company adopted a progressive policy in the operation of blast furnace and coke oven gas for the manufacture of steel, their plant being the first to make steel with a mixture of these gases only, and to heat their soaking pits with blast furnace gas. Bainbridge did much to perfect these methods. Under a grant from the Carnegie Research Fund of the Iron and Steel Institute, Bainbridge conducted the research and ultimately, in 1920, published a paper on "The Effect of Fluorspar Additions on the Phosphates in Basic Slag." For this paper he was awarded the Carnegie Medal of the Institute in 1927.

At the May Meeting of the Institute in 1930 he read a paper on the "Development of Fuel Economy at Skinningrove;" for this paper he was awarded the Williams Prize in 1931.

In 1936 he was appointed Works Manager at Skinningrove, a position which he filled with great ability. By his tragically sudden death the Skinningrove Company lost a valued servant, and the Cleveland District one of its most promising technical experts in the iron and steel trade.

Throughout his active business life Bainbridge was greatly interested in the work of various Technical Institutes. He joined the Cleveland Institution of Engineers in 1915, was appointed a member of the Council of that Institution in 1923, and was President in the years 1935 and 1936. Further, he was appointed to the Council of the Cleveland Technical Institute in 1936. He was elected a Fellow of the Chemical Society on December 5th, 1918.

Apart from his undoubted technical knowledge and ability he was gifted with a charming personality which endeared him to all who came in contact with him.

A. HUTCHINSON.

GLYN OWEN.

1901—1937.

GLYN OWEN, the only son of Mr. and Mrs. William Owen of Minffordd, Merionethshire, was born in Liverpool in 1901, but it would be true to say that by his parentage, upbringing and education he was in every sense a son of Wales. He received his early education at the County Schools of Towyn and Ffestiniog and entered the University College of North Wales, Bangor, in 1917. In 1921 he obtained the degree of Bachelor of Science with first class honours in chemistry. He subsequently carried out research work under the late Professor Orton and in 1923 was awarded the degree of Master of Science. During his career at Bangor he held numerous exhibitions and scholarships, including the Isaac Roberts Scholarship and a University Postgraduate Studentship. In 1924 he was awarded a Fellowship of the University of Wales and proceeded to Gonville and Caius College, Cambridge, where he worked for three years under the late Professor Lowry. In 1927 he was appointed Assistant Lecturer in Chemistry in the University of Manchester, which position he held for four years, the maximum tenure allowed him by the University regulations governing such appointments. In 1931 he was awarded a grant from the Sir Clement Royds Scholarship Fund, which enabled him to remain at Manchester University for a further year in order to continue the researches referred to later in this notice. In 1932 he was appointed on the staff of the Dyestuffs Group of Imperial Chemical Industries Limited, and from 1932 to 1934 acted as private research assistant to Professor Rowe at the Department of Colour Chemistry and Dyeing at the University of Leeds. In 1934 he returned to Manchester to work in the Dyehouse at the Blackley works of Imperial Chemical Industries Limited, where he remained until his death on July 21st, 1937, at the early age of thirty-six.

While at Bangor, Owen worked mainly on the freezing point curves of binary mixtures of anilides (J., 1923, **123**, 3392; 1924, **125**, 766). At Cambridge he carried out some investigations on mutarotation in the sugars, dealing in particular with the promotion and arrest of the mutarotation of tetra-acetyl glucose in ethyl acetate (*Proc. Roy. Soc.*, 1928, *A*, **119**, 505). He also carried out an extensive investigation on the absorption spectra of halogen and sulphonic derivatives of camphor (J., 1926, 606). In Manchester, at the suggestion of Professor Lapworth and with the assistance of a number of research students, he worked on the equilibrium and velocity constants for cyanohydrin formation from a wide range of aldehydes and ketones. This work, which included studies of the effect of variations in the solvent and catalyst, finally led to a comprehensive series of measurements of velocity constants parallel with the series of equilibrium constants previously determined and discussed by Lapworth and Manske (J., 1928, 2533; 1930, 1976), which Owen also augmented. One of the most interesting and definite conclusions which arose out of this work was the fact that the velocity of formation of cyanohydrins from substituted benzaldehydes, like their stability as shown in the equilibrium constants, is highest when the substituent (OH, OMe, NMe_2, Cl) is in the *o*-position. This conclusion must be one of importance in relation to the application of any theory of steric or " proximity " effects to kinetic problems. A complete account of this unpublished work remained in Owen's possession, but information about certain sections of it is to be found in theses presented to the University of Manchester for the degree of Master of Science by E. V. Casey (1930), G. A. Harding (1931), and R. J. B. Marsden (1932). In association with Professor Rowe at Leeds Owen worked on the reduction and dispersion of azoic dyes and similar substances in presence of lissolamine A (*J. Dyers and Col.*, 1936, **52**, 205), for which he was awarded a Diploma of the Worshipful Company of Dyers. He also investigated the constitution of some insoluble azo-colouring matters and the action of formaldehyde in imparting increased stability to arylamides of 2-hydroxy-3-naphthoic acid on the fibre. Among his other publications may be mentioned " Calculation of Dispersion Equations " (*Trans. Faraday Soc.*, 1930, **26**, 371), " The Effect of Concentration on Values of Dispersion and Rotation Constants for Solutions of Camphor in Ethyl Alcohol " (*ibid.*, p. 423), and " Additive Compounds of Phenylnitroamines and Anilines " (*Mem. Manchester Phil. Soc.*, 1931—1932, **76**, 11).

Possessing a very comprehensive knowledge of chemistry, Owen was particularly interested in the application of physical methods to the elucidation of problems in organic chemistry. He never guided his interests into the narrow channels of the specialist, but was rather at pains to keep within his grasp as wide a field as possible and his scientific interests included many aspects of pure mathematics, physics, and geology. His lectures in physical chemistry were the result of wide reading and careful preparation, and as a demonstrator in the laboratory he showed great enthusiasm and almost infinite patience, never sparing himself in his attempts to make the work clear to even the most backward students. He was a very neat and able practical worker, both in laboratory and in workshop, and his work was always characterised by meticulous care, accurate measurement, and precise observation. His output of research work was far greater than a list of his publications would indicate. This was in part due to a form of modesty characteristic of him, since his interest was first and last in the investigation in hand : he tended to regard the publication of his results as an irksome task for which he had no liking. It was also due to the very high standards at which he aimed : he would never consider the question of publication until he himself was perfectly satisfied that from every aspect the work was accurately executed to the smallest detail and the theoretical discussion carefully considered from every possible angle.

Owen had many interests beyond the realms of science. He showed a natural inclination towards the arts and humanities: he was a wide and critical reader and a great admirer of Samuel Butler. As a water colour artist he possessed considerable ability, and his interest in music and drama was very real. He possessed a great love of the countryside and of everything belonging to it, and hated the ugly northern industrial centres in which he was destined to spend the later years of his life. Although he did not enjoy vigorous health, he took a keen interest in mountaineering and knew intimately most of the climbs in Snowdonia. As a fervid Welshman, he was keenly interested in his beloved native land, its language and literature, its history, its music and its folklore. He made a special study of the old native crafts of Wales and their influence on the general culture of the democracy in bygone times, and, as a member of the Manchester Welsh Round Table Society, he contributed many valuable and illuminating papers and studies on these subjects. His political sympathy was with the aspirations of the Welsh Nationalist Party, which he sincerely believed is the only party to-day which seriously endeavours to grapple with the problems confronting modern Wales. His nationalism, founded on sincere conviction and supported by a well-balanced judgement and a liberal outlook, knew neither aggression nor fanaticism.

In England Owen was often conscious of being a foreigner in a friendly if sometimes unsympathetic land, and though he may have been misunderstood by some, his sincerity and ability were never doubted. Few of his friends and acquaintances were ever able to know, much less appreciate, the all-absorbing *hiraeth* which bound him to Wales and its people, for the word *hiraeth* defies translation into the English tongue. To those who were privileged to know and to understand something of this side of his personality his sudden and tragic death leaves a gap which cannot be filled. His many colleagues and associates have lost a friend whose life was imbued with unselfishness, unswerving devotion to duty, and the highest integrity of character. " Home, school and chapel, books, music and mountains: he had taken his fill of all they had to offer. . . . holding on to his own language and growing in it as his emotional horizon extended with the years, adding to it another language in which to think and carry out the business of the day, but remaining always, in his privacy, a son of Wales and its dark mountains "—these words, quoted from Wyn Griffith's " Spring of Youth," might have been written of Owen himself.

He had been married to Elinor Owen scarcely a year when she was left to mourn his loss with an infant son, born a few weeks after his father's death. D. H. HEY.

ARTHUR GEORGE PERKIN.

1861—1938.

ARTHUR GEORGE PERKIN was born at Sudbury, Middlesex, on December 13th, 1861. He was the second son of the late Sir William Henry Perkin, F.R.S., who discovered mauveine and thereby founded the coal-tar colour industry in this country. His elder brother was the late William Henry Perkin, jun., F.R.S., Waynflete Professor of Chemistry in the University of Oxford, and the late Dr. Frederick Mollwo Perkin, C.B.E., who was well known as a consulting chemist, was his half-brother.

A. G. Perkin's mother died of consumption shortly after his birth, and he was such a delicate child that he was not expected to live. At about the time of Sir William's second marriage to Miss A. C. Mollwo, Perkin, at the age of six, was sent to a boarding school at Margate and henceforth spent little time at home at Sudbury except during his holdiays. At about the age of ten, he entered the City of London School, where his brother William had already been a pupil for one year, this school having been selected for the boys, not merely because it was Sir William's old school, but also because it was the only one that he could find where science was taught at that period. The boys were fortunate to have as their science master there Henry Durham, who was an able and attractive teacher. It is said that one of the other masters, however, refused to have both Perkins in his class, so Arthur as junior had to give place to William and was transferred to another class.

During their holidays, the boys carried out crystallisations and similar work given to them to do by Sir William in a small hut which he had had fitted up as a laboratory for their use at the bottom of the garden at Sudbury. William used a bench beneath a window at one end and Arthur used a bench beneath a window at the other end.

Consequently, it is no more surprising that chemical research should have become the prime object of the working lives of both boys, than that music should have become the principal recreation of their leisure, for the Perkins were always an extremely musical family. Thus, during these holiday periods, nine members of the family constituted a small orchestra, in which William played second violin and Arthur the flute. The family concerts usually took place on Saturdays at the house of the late Thomas D. Perkin, Sir William's brother and partner, and more formal concerts were also given occasionally.

In October, 1877, William entered the Royal College of Chemistry at South Kensington, and one year later Arthur followed him there to study under Frankland and Guthrie. Arthur worked at a bench next to that of Leo Stern, who later became a well-known player on the violoncello, so William, Arthur, and Stern soon formed a trio to play on Saturdays, and the two Perkins were also leaders in gathering together an orchestra largely consisting of students.

It was at the Royal College of Chemistry that Arthur carried out the investigation that led to his first paper, " The Action of Nitric Acid on Di-*p*-tolylguanidine," communicated to the Chemical Society in 1880.

Up to this stage, the education of the two brothers had proceeded on similar lines, but their paths then diverged, for William at last received his father's permission to go to a German University and he went to Würzburg in October, 1880, whereas Arthur went for one year to Anderson's College, Glasgow, under E. J. Mills.

In 1881 A. G. Perkin heard that the Worshipful Company of Clothworkers had instituted a scholarship for one year tenable in the Dyeing Department of the Yorkshire College, Leeds, and applied for it, the only other applicant being Charles Bedford of Leeds. They became fellow students and friends, but the scholarship was awarded to Perkin, who was thus the first of many Clothworkers' Scholars in the Department of which he eventually became the Head. He worked with the then Head of the Dyeing Department, J. J. Hummel, on some new compounds derived from the colouring matters of brazilwood and logwood. Throughout his life Perkin lost no opportunity of paying a generous tribute to the ability and personality of Prof. Hummel, to whom he owed his first introduction to, and enduring enthusiasm for, the study of the chemistry of natural colouring matters.

When his scholarship expired, Perkin left the Yorkshire College to take up an appointment as chemist at the alizarin factory of Hardman and Holden, Ltd., Manchester.

In 1887 he married Annie, a daughter of James E. Bedford of Leeds and sister of Charles Bedford. As a bachelor he lived at Cheetham Hill, but after his marriage he lived at Eccles.

Perkin was promoted to the position of manager by Hardman and Holden, Ltd., in 1888 and continued in that capacity until 1892. During this period of ten years which he spent in industry, Perkin made time to carry out a number of scientific investigations and published papers on the action of nitric acid on anthracene, and, jointly with his brother William, on derivatives of anthraquinone, and on the Indian natural dyestuff, kamala.

In 1892 Perkin resigned his position with Hardman and Holden, Ltd., in order to join the staff of the Dyeing Department, Yorkshire College, as lecturer and research chemist. This position suited his tastes and temperament admirably, because, although he gave a course of lectures on the chemistry of natural colouring matters for one hour per week in the first and second terms of each session and also gave general supervision to the small number of senior students who did their practical work in the Clothworkers' Research Laboratory, he was able to devote all the rest of his time to his own investigations at a bench in this laboratory for the next twenty-two years. Nevertheless, there were not sufficient hours in a normal working day for him, so for a number of years at the outset he returned to the laboratory in the evenings, being then accompanied by his wife, who assisted him with his apparatus and with some of his experiments, and there they would usually remain until about 10 p.m. During this period of intensive research, with few exceptions, Perkin confined himself to the isolation of the colouring matters of a large number of natural products and the investigation of their constitutions, largely by degradative methods and by studying their dyeing properties. Synthetic work did not greatly appeal to him and he was content to leave to others the confirmation of his deductions. For example, the constitutions proposed by Perkin for apigenin, catechin, gossypetin, luteolin, morin, myricetin, and quercetagetin have since been confirmed synthetically by other workers.

The profound knowledge of natural colouring matters that Perkin gained by his brilliant researches established his international reputation in this field and brought many chemists from abroad, particularly from the East, to work at Leeds on natural products under his guidance

In 1905 the India Office, on behalf of the Government of India, selected the Clothworkers' Research Laboratory as the most suitable place for the continuation of the research work on natural indigo that had been carried out by W. P. Bloxam and two colleagues on behalf of the Government of Bengal at the Dalsingh Serai Research Station from 1902 to 1904. Bloxam, assisted by four other chemists, worked on this subject at Leeds from 1905 to 1907 under the general supervision of Perkin. In his Report to the Government of India published in 1908, Bloxam made it very clear that Perkin by no means confined himself to the official limits of general supervision, but that he also devoted much of his time to experimental work on this subject. Thus, his examination of the constituents of natural indigo and their isolation led to a method for the estimation of the glucoside indican either in the crystalline condition or in aqueous infusions of the leaf, established that indirubin present in natural indigo arises from the condensation of indoxyl with isatin, the latter being produced by air oxidation of the former, and that indigo yellow is identical with kæmpferol.

Between 1904 and 1918 the late E. R. Watson, while he was Professor of Chemistry, first at Sidpur Engineering College and then at Dacca College, usually worked in the Clothworker's Research Laboratory for a large part of his leaves in England in order to have the benefit of contact with Perkin, with whom he had so many research interests in common, and they became great friends.

During the War, Perkin carried out investigations for the Ministry of Munitions, and in 1916 he succeeded A. G. Green, F.R.S., as Professor of Colour Chemistry and Dyeing in the University of Leeds, at the same time also directing the work on intermediates and synthetic dyes carried out in his Department by the colony of research chemists of British Dyes, Ltd. It was this alteration in his position, with the consequent increase in his administrative and teaching duties, that gradually compelled Perkin to relinquish his work on natural colouring matters and to turn his attention again to the chemistry of anthraquinone derivatives, for which the starting materials were more readily accessible. Thus, a study of the migration of the acyl group in partly acylated phenolic compounds led to the preparation of interesting derivatives, many of which had not previously been obtained synthetically. The products of the reduction of hydroxyanthraquinone compounds also formed the subject of a notable series of papers published between 1922 and 1933. In the course of this work the constitutions of numerous hydroxyanthranols were established by conversion into corresponding benzanthrones and examination of the methylation products of the latter, whilst the formation of hydroxy-anthracenes, -dianthrones, -dianthraquinones, -dianthraquinonyls, and -helianthrones also was investigated and the constitutions of these compounds established.

During his professorship, Perkin did much to enhance the reputation of his Department as a scientific training ground for recruits for the dyestuffs, dyeing, and allied industries. In the immediate post-War years there was a very considerable increase in the number of students who entered for courses in colour chemistry and dyeing, and there is no doubt that they were attracted at least as much by the opportunity of working under him as by the popular appeal of these subjects at that period. His students were uniformly successful in securing appointments and most of them now occupy important positions in industry.

Perkin was elected a Fellow of the Chemical Society in 1884, a Fellow of the Institute of Chemistry in 1887, a Fellow of the Royal Society of Edinburgh in 1893, a Fellow of the Royal Society in 1903, and was awarded the Davy Medal of the Royal Society in 1924. Although he never took an active part in the affairs of scientific societies, he believed strongly in supporting them by membership: he was a vice-president of the Society of

Dyers and Colourists, and a member of the Biochemical Society, the Pharmaceutical Society, the Society of Chemical Industry, and the Textile Institute. He was also a Liveryman of the Worshipful Company of Leathersellers, of which his father was Master at one time, and thereby a Freeman of the City of London.

On his retirement in 1926, Perkin was accorded the title of Emeritus Professor, and in 1927 the University of Leeds conferred upon him the degree of D.Sc., *honoris causa*. An admirable portrait of him was painted by Richard Jack as a result of the subscriptions of Perkin's many admirers and presented to the University of Leeds, where it graces the wall of the Great Hall.

Perkin regarded his retirement merely as freedom from the burden of administrative and teaching work and the opportunity to concentrate once more on his experiments. From the autumn of 1926 he continued to prosecute his researches without any interruption in the writer's laboratory in the Colour Chemistry and Dyeing Department of the University of Leeds until his health began to fail in February of this year. He was then endeavouring to determine the constitution of a green vat dye which he had obtained some years previously by heating the hydroxylated anthranol, derived from alizarin, with tetrachlorothiophen and an alkylating agent (*Brit. Pat.* 353,422). In spite of the preparation of a very large number of individual specimens of this dye, however, Perkin was unable to interpret the analytical results obtained with them to his satisfaction, and this apparently insurmountable difficulty worried him greatly, as it was contrary to his whole nature to allow himself to be beaten by a mere compound.

Perkin's health continued to decline slowly for about three months, during which he welcomed visits from his colleagues and enjoyed entertaining them with his vivid recollections of chemists and their work, but he collapsed suddenly on May 26th and died at his residence, Grosvenor Lodge, Grosvenor Road, Leeds, on May 30th.

Many representatives of the leading scientific societies, of the University of Leeds, of industry, and of his students paid respect to Perkin at the funeral service in St. Chad's Church, after which the interment took place at Adel Church, Leeds.

Perkin was an indefatigable worker and delighted in carrying out experiments with his own hands, it being only within recent years that he became resigned even to entrusting the necessary analyses of his new compounds to others; in earlier years he would not allow students near his melting point apparatus or his analytical apparatus, so much did he dread interference with their adjustment. His technique was well-nigh flawless and his skill in isolating the required substance from a complex mixture almost uncanny. He appeared to be immune to any vapours; the atmosphere of his laboratory, often charged with the vapours of acetic anhydride, nitrobenzene, and pyridine, to an extent sufficient to induce nausea in the other occupants, left him unaffected, indeed it is doubtful whether his concentration on his work permitted him to notice this accumulation of odours. This deep absorption in his experiments and close attention to every detail, together with his infinite patience with difficult reactions or with tedious processes of purification of initially resinous materials, from which he would eventually isolate " beautiful crystals," gained for him the admiration of his colleagues and students. He made a deep impression on all who were privileged to work with him; he was eminently easy to approach, ever ready to discuss difficulties, and to offer from his great experience suggestions for new lines of attack, once he was satisfied that the lack of success was not attributable to " the personal equation " ! He was a great chemist in his generation, who always sought to encourage, to stimulate to fresh effort, and to set by his example a standard of application that all who came in contact with him were inspired to emulate. In addition, although a man of deep convictions, he was a very gentle man with a most charming and lovable personality. His attitude towards young men was always so fatherly that for over forty years all students of the Colour Chemistry and Dyeing Department showed their affection for him by referring to him amongst themselves solely as " Pa Perkin."

Perkin's work is recorded in some 270 memoirs, of which 12 were published in the *Journal of the Society of Chemical Industry*, 4 in the *Journal of the Society of Dyers and Colourists*, and the rest in the *Proceedings* or *Transactions of the Chemical Society*; his work is permanently illustrated by a collection of research specimens in the Museum of the Colour Chemistry and Dyeing Department of the University of Leeds, adjacent to a collection of his father's research specimens. In addition, he was concerned in 7 patents arising from his work since 1916. He was also the author of many articles on natural colouring matters in Thorpe's " Dictionary of Applied Chemistry," and, in collaboration with Dr. A. E. Everest, he published the classical monograph " The Natural Organic Colouring Matters " in 1918.

Perkin was completely happy in his home during his fifty years of married life and he owed a great deal to his wife. Some forty years ago they built a house at Bradda in the Isle of Man and ever since then they spent almost all the vacations there. Perkin was very fond of the Isle of Man and was a governor of King William's College.

Perkin was deeply attached to animals and especially to his dogs and ponies, and his tortoise. He first kept King Charles spaniels, but for the last twenty years or so he kept only a succession of Japanese spaniels, each of which he named after Japanese Professors who had worked with him in the past and who greatly appreciated this token of remembrance. He kept his ponies in the Isle of Man, and the surviving one is to remain there. He was very proud of the good health and steady growth of the tortoise, which he had had for the last twenty-five years and which usually accompanied him to the Isle of Man in the vacations.

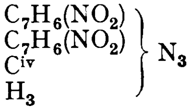
Although Perkin played golf and worked out exactly how it should be played, he had not the temperament to become a first class player. He remained a great lover of music throughout his whole life, and it was in music that he found his real recreation, devoting all his leisure to it. He was a very accomplished player on both the flute and the bassoon. Seldom a day passed, until a few weeks before his last illness, when he did not play one or other of these instruments for an hour or two. He played first bassoon in many amateur orchestras in Yorkshire until his retirement; subsequently he assisted the Leeds University Students' Orchestra, and his flute solos were a feature of the annual gatherings of past and present students of the Colour Chemistry and Dyeing Department until as recently as 1935.

F. M. ROWE.

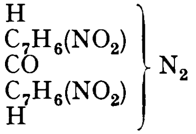
SCIENTIFIC WORK OF A. G. PERKIN.

Inclusive of Notes in the *Proceedings* of the Society, Perkin published about 270 original papers and more than 60 of his more substantial contributions are in his own name without collaborators. He worked best with his own hands and his sincere and simple nature is reflected in his writings. He possessed in full measure the family aptitude for experimental research and the singlehearted devotion to it which characterised his elder brother.* Nevertheless Arthur's method and attitude were individual and by no means the same as William's. He was a little the slower of the two and he did not aim quite so high, but he became the acknowledged master of his chosen field, which may roughly be defined as that of the natural colouring matters which have adjective dyeing properties. His chief contribution was doubtless the elucidation of the chemistry of the constituents of certain dye-woods and the development of the group of the flavones and flavonols. All his work was meticulous and accurate, most of his conclusions have been justified by later studies and his records have not been challenged.

Early Investigations.—Whilst at the Royal College of Chemistry under Frankland and Guthrie, Perkin, at the age of 19, published his first paper " The Action of Nitric Acid on Di-*p*-tolylguanidin " (J., 1880, **37**, 696). He prepared the dinitro-derivative and in the presence of alcohol found that the product was dinitro-*p*-tolylurea. The corresponding diamines were obtained on reduction. It is interesting to note that the two nitro-compounds were formulated as condensed ammonia types as follows :



$$\left.\begin{array}{l} C_7H_6(NO_2) \\ C_7H_6(NO_2) \\ C^{iv} \\ H_3 \end{array}\right\} N_3$$



$$\left.\begin{array}{l} H \\ C_7H_6(NO_2) \\ CO \\ C_7H_6(NO_2) \\ H \end{array}\right\} N_2$$

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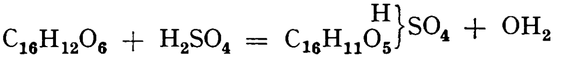
* The writer first heard of A. G. P. from W. H. P. and the description given was "a dab hand "; this was but one of many indications of the mutual respect that subsisted between the brothers. On many occasions William assisted Arthur in such matters as the preparation of papers for publication and it is within the writer's knowledge that Arthur's advice was frequently sought by William and found to be most valuable.

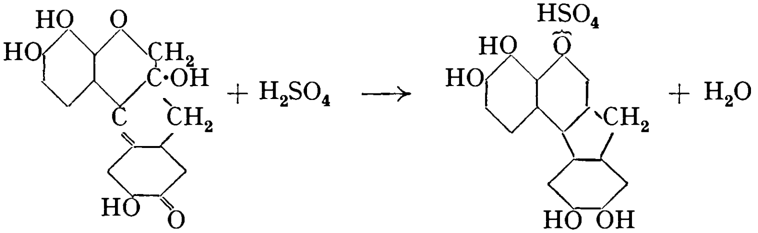
At the Yorkshire College he worked with J. J. Hummel and a joint paper published as a contribution from the Dye-House is of great interest. Perkin and Hummel (J., 1882, **41**, 367) improved the preparation of hæmatein and brazilein and showed that, when these substances were heated with sulphuric acid, a reaction occurred which was represented in the following manner :



$$C_{16}H_{12}O_6 + H_2SO_4 = \left.\begin{matrix}H\\C_{16}H_{11}O_5\end{matrix}\right\}SO_4 + OH_2$$

hæmatein iso*hæmatein sulphate*

*iso*Hæmatein sulphate (and the corresponding *iso*brazilein sulphate) was isolated as an orange crystalline powder by the addition of acetic acid to the solution. The sulphuric acid was found to be loosely combined and the substances were thought to be acid sulphuric ethers of a specially labile kind. We now know that the compounds in question are oxonium salts formed in accordance with the expressions :



Although Perkin and Hummel did not recognise the saline nature of the substances, they correctly stated that they were analogous to the acid compounds of the phthaleins which had been studied by Baeyer.

In 1883 Perkin followed up his father's work on xanthone, of which he prepared dinitro-, diamino-, and dibromo-derivatives (J., 1883, **43**, 187). A by-product from the distillation of a mixture of salicylic acid and acetic anhydride was thought to be $C_{14}H_8O_3$; it yielded xanthonecarboxylic acid when treated with alcoholic potash.

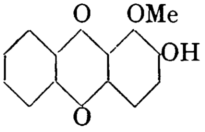
The first joint papers of the Perkin brothers deal with the products of the dry distillation of "silver salt" or sodium anthraquinone-2-sulphonate (J., 1885, **47**, 679; 1888, **53**, 831). They obtained in this way a red compound, which was examined in some detail, but the fact that it contained sulphur was overlooked ! The sequel to this curious and unique incident occurred 34 years later when A. G. Perkin disclosed that the substance is di-β-anthraquinonyl sulphide.

The action of nitric acid on anthracene under various conditions was the subject of some interesting work. In nitrobenzene solution the product was found to be nitrosonitroanthrone (J., 1891, **59**, 631), but in the presence of alcohol, nitroethoxydihydroanthracene was produced. The behaviour of these substances towards reagents was investigated and in collaboration with J. E. Mackenzie (J., 1892, **61**, 470) the formation of nitroalkyloxydihydroanthracenes was extended by the use of alcohols other than ethyl alcohol. With *iso*butyl alcohol the product was nitroanthrone and with *tert.*-butyl alcohol, nitrosoanthrone was produced, otherwise the formation of nitroalkyloxydihydroanthracenes was generalised. Other work of this period (partly at the Heriot Watt College) was concerned with derivatives of oxanilide, but the year 1893 may be taken as the starting point of Perkin's main work on natural colouring principles.

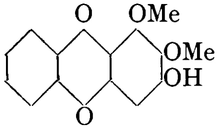
One of the first, if not the very first, problem selected was the nature of the constituents of the Indian dye, kamala, and preliminary work on this subject was published jointly with W. H. Perkin, jun. (*Ber.*, 1886, **19**, 3109). The more complete later papers (J., 1893, **63**, 975; 1895, **67**, 230) are by A. G. Perkin alone. Anderson had already isolated a crystalline colouring matter which he termed rottlerin and Perkin improved the method of extraction and obtained also the yellow homorottlerin, *iso*rottlerin and a resin. To rottlerin, which gave crystalline acetyl and benzoyl derivatives and a number of crystalline metallic salts, Perkin assigned the formula $C_{33}H_{30}O_9$. On fusion with alkali, phloroglucinol and acetic and benzoic acids were obtained; oxidation with hydrogen peroxide gave benzaldehyde and benzoic acid and treatment with nitric acid gave a variety of products, including *p*-nitrobenzaldehyde and *o*- and *p*-nitrocinnamic acids. Perkin concluded that rottlerin contains a phloroglucinol nucleus and a cinnamic acid residue. The difficult problem has not yet been completely solved, although the formula proposed by Robertson is doubtless a close approach to the truth. Perkin found that when the salmon-red rottlerin is heated with 2% sodium carbonate solution, garnet-red prisms of rottlerone separate. As the dyeing of silk to a bright orange shade is carried out with kamala in an alkaline bath, Perkin and Hummel (1895) point out that the colour fixed on the fibre is probably rottlerone.

Natural Colouring Matters of the Anthraquinone Group.

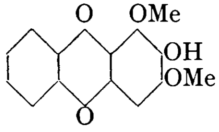
Largely in collaboration with Hummel, the constituents of dyeing materials similar to madder were examined. For example, Chay root or Indian madder was found to contain ruberythric acid, alizarin, rubichloric acid and sucrose, but no purpurin or its carboxylic acid, or purpuroxanthincarboxylic acid. The non-tinctorial constituents were distinct from those occurring in madder; they included alizarin methyl ether (I), anthragallol dimethyl ether-A (II), anthragallol dimethyl ether-B (III), hystazarin methyl ether (IV) and 2-hydroxyanthraquinone (Perkin and Hummel, J., 1893, **63**, 1160; 1895, **67**, 817; A. G. Perkin, J., 1907, **91**, 2066).



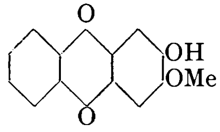
(I.)



(II.)



(III.)



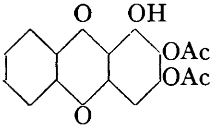
(IV.)

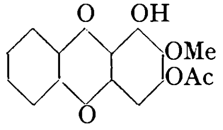
Much later a study of the partial acetylation of hydroxyanthraquinones and the action of diazomethane on the acetyl derivatives, with or without migration of an acetyl group, led to the syntheses of these compounds.

Oesch and Perkin (*Proc.*, 1914, 30) treated monoacetylalizarin with diazomethane in nitrobenzene solution and after hydrolysis isolated the isomeric alizarin monomethyl ethers. They interpreted this result as due to the fact that the monoacetyl derivative was a mixture, but in view of the later work it is probable that this was not so and that migration occurred. The *O*-methylalizarin from Chay root is the 1-methyl ether, because the 2-methyl ether is formed in the partial methylation of alizarin (and by analogy the hydroxyl ortho to carbonyl is protected) and also because it is very readily hydrolysed to alizarin, for example, by means of boiling aqueous baryta. In confirmation the alizarin 1-methyl ether is readily methylated with formation of alizarin dimethyl ether.

The syntheses of the isomeric anthragallol dimethyl ethers were effected in an interesting manner (Perkin and Kubota, J., 1925, **127**, 1889; Perkin and Storey, J., 1928, 229; 1929, 1399). Anthragallol 2 : 3-diacetate (V) was found to be methylated in position 2 by means of diazomethane; at the same time the acetyl group migrates to position 1. Hydrolysis and partial acetylation affords (VI), which is methylated by diazomethane with the formation of the acetyl derivative of anthragallol 1 : 2-dimethyl ether. Anthragallol 2 : 3-dimethyl ether can be obtained by direct methylation of anthragallol.

(V.)





(VI.)

Perkin and Hummel (J., 1893, **63**, 115) detected the presence of purpuroxanthin in *Rubia cordifolia* (Linn.) and found that the dyeing properties of *Rubia Sikkimensis* (Kurz) are due to its content of purpurin (*ibid.*, p. 1157). They also examined various species of *Morinda* and showed that the methylanthracene previously derived by Thorpe and Smith by zinc dust distillation of morindon is 2-methylanthracene (J., 1894, **65**, 851). *Polygonum cuspidatum* was found to be a source of a glucoside of emodin (Perkin, J., 1895, **67**, 1084).

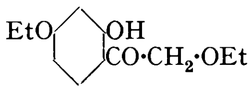
The root bark of *Ventilago madraspatana* (Gaertn.) was found to contain 8—10% of a resinous colouring matter, ventilagin, which is a derivative of 1-methylanthracene. Its composition was stated to be $C_{15}H_{14}O_6$ and the suggestion was made that it may be allied to alkannin (Perkin and Hummel, J., 1894, **65**, 923). This root bark also afforded an emodin monomethyl ether and two isomeric anthranols which yield the emodin derivative on oxidation.

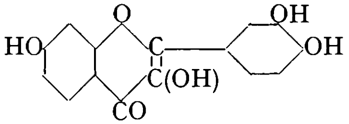
Flavones and Flavonols.

In 1864 Piccard isolated chrysin, $C_{15}H_{10}O_4$, from poplar buds and showed that on hydrolysis with alcoholic potash it yielded phloroglucinol, acetophenone, acetic and benzoic acids. These facts were confirmed in 1893 by v. Kostanecki, but the pioneering researches of Herzig on the constitution of fisetin and of quercetin gave the first real insight into the nature of this group of anthoxanthins. Herzig commenced his work in 1884 and determined the structure of fisetin in 1891. In the same year he established the composition of quercetin, which had been in some doubt, and suggested the formula at present accepted, partly by analogy with fisetin.

Herzig ethylated fisetin and showed that on hydrolysis with alcoholic potash the tetraethyl ether afforded fisetol diethyl ether (VII) and 3 : 4-diethoxybenzoic acid. Hence fisetin was regarded as a tetrahydroxyphenylbenzo-γ-pyrone (VIII) and quercetin, so similar to fisetin in all its properties, was considered to be the corresponding phloroglucinol derivative.

(VII.)



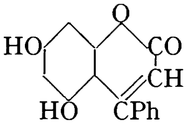


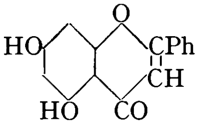
(VIII.)

v. Kostanecki's procedure with chrysin, two years later, was so logical and so well followed up in other cases that it has often been expounded as if it constituted the beginning of the subject and there has been a tendency to overlook the work of Herzig.

He pointed out that the products of hydrolysis of chrysin could be explained on the basis of two formulæ (IX and X). He therefore excluded (IX) by synthesis of this coumarin derivative, following the method of v. Pechmann. The comparatively recent work of Wilson Baker has shown that this step was necessary because coumarins constituted like (IX) do afford phloroglucinol on hydrolysis.

(IX.)





(X.)

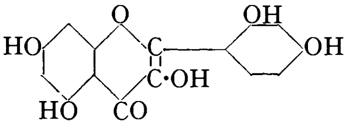
The synthesis of (X), which proved to be identical with chrysin, followed in 1898.

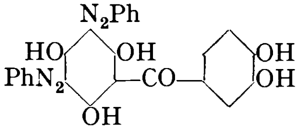
Accordingly when Perkin began his investigations (or rather when he published them) the nature of fisetin, quercetin, and chrysin was understood; his special contribution was the great extension of the group which he made and the development of new methods of investigation. One of the earliest of Perkin's researches in this field concerned the constitution of morin which had been isolated by Chevreul from the wood of *Chlorophora tinctoria* (Gaudich); this dye-wood is termed " old fustic " and until recently was largely used.

Perkin and Bablich (J., 1896, **69**, 792) improved the method of isolation of morin, determined its composition, and prepared numerous derivatives. On hydrolysis of the tetramethyl ether, 2 : 4-dimethoxybenzoic acid and phloroglucinol monomethyl ether were produced and hence the formula (XI) was assigned to the substance. This was proved to be correct by the synthesis of the substance by v. Kostanecki, Lampe, and Tambor in 1906 as well as by a study of morin pentamethyl ether by Herzig in 1909. The hydrolysis of this derivative gave the methoxyfisetol dimethyl ether which had previously been obtained from quercetin pentamethyl ether.

It may be mentioned at this point that Perkin and Pate (J., 1895, **67**, 649) examined the compounds formed by many members of the flavone group with mineral acids. The analysis of these substances often afforded valuable confirmation of the composition of the colouring matters themselves. In the case of morin the hydrochloride, hydrobromide, and hydriodide corresponded to the expression $C_{15}H_{10}O_7,HX$, but the sulphate was abnormal. Another type of derivative useful both for purposes of isolation and for analysis is represented by the monopotassium salt of morin, which separates when the substance is treated with potassium acetate in alcoholic solution (J., 1899, **75**, 437).

(XI.)



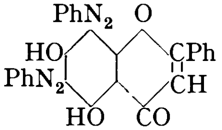


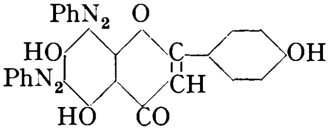
(XII.)

In addition to morin, old fustic contains a pentahydroxybenzophenone termed maclurin, and Perkin's brother-in-law, Mr. C. S. Bedford, found in 1887 (E.P. 12667) that a valuable dye could be prepared by coupling this substance with diazonium salts. By the action of diazotised aniline on the water-soluble constituents of old fustic a dye called "patent fustin" was produced; it gave orange-brown shades on chrome-mordanted wool. The dye is essentially bisbenzeneazomaclurin (XII) and the pure substance was prepared and examined by Bedford and Perkin (J., 1895, **67**, 933; 1897, **71**, 186); it yields a triacetate when treated with acetic anhydride, which is in harmony with the proposed constitution and the monoacetylation of bisbenzeneazophloroglucinol. The azo-derivatives of other natural colouring matters were prepared by Perkin (J., 1898, **73**, 665) and he found them useful for the diagnosis of the phloroglucinol nucleus. For example bisbenzeneazochrysin (J., 1896, **69**, 1439) (XIII) cannot be acetylated and bisbenzeneazoapigenin (J., 1897, **71**, 805) (XIV) forms a monoacetyl derivative.

Another use of azo-compounds made by Perkin was in the recognition of the oily phloroglucinol monomethyl ether in the form of its bisbenzeneazo-derivative. Perkin and Allison (J., 1902, **81**, 471) showed in this way that the quercetin tetramethyl ether obtained by direct methylation of quercetin is hydrolysed by alcoholic potash with formation of phloroglucinol monomethyl ether (and veratric acid).

(XIII.)





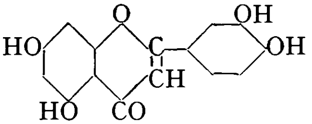
(XIV.)

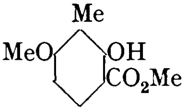
It is difficult to give the exact chronological sequence of Perkin's researches of this period because it is very probable that several investigations were proceeding simultaneously. It would appear, however, that the elucidation of the constitution of luteolin preceded that of apigenin.

Weld is the oldest European dye (prepared from *Reseda luteola*); it was used by the Gauls in the time of Julius Cæsar and its last surviving use was to produce lemon-yellow shades (aluminium mordant) on the silk facings of certain military uniforms.

Luteolin had been previously studied by Chevreul, Moldenhauer, Schützenberger, and Hlasiwetz, and the last-named assigned to it the composition $C_{15}H_{10}O_6$. Nothing was known, however, in regard to its constitution. Perkin (J., 1896, **69**, 206, 799; 1900, **77**, 1315) isolated the principle by a novel method and effected a final purification from a trace of apigenin by the preparation of the hydrochloride. From a study of the numerous derivatives (sulphate, hydrochloride, hydrobromide, hydriodide, monopotassium salt, dibromo-derivative, tetra-acetate, trimethyl ether and its monoacetate, ethyl ethers and bromo- and nitro-derivatives of the ethers, etc.) and the alkali-degradation to phloroglucinol and protocatechuic acid, Perkin (*loc. cit.*) assigned to luteolin the constitution (XV). The correctness of this view was later confirmed by synthesis (Kostanecki, Rozycki, and Tambor, *Ber.*, 1900, **33**, 3410). Perkin and Horsfall (J., 1900, **77**, 1322) showed that the decomposition of luteolin with 50% aqueous potassium hydroxide afforded 3 : 4-dihydroxyacetophenone in addition to phloroglucinol.

(XV.)





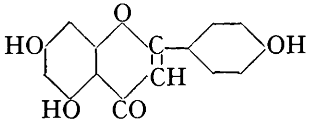
(XVI.)

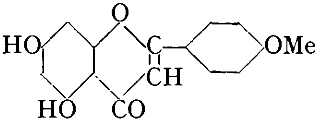
Perkin and Horsfall also observed that the methylation of luteolin with methyl iodide and alcoholic potash gives, in addition to the trimethyl ether, a methyl-luteolin trimethyl ether. The methyl group entered the phloroglucinol nucleus because alkaline degradation led to the formation of methylphloroglucinol methyl ether, identified as its bisbenzeneazo-derivative. Methyl-luteolin was prepared by demethylation of the methyl ether. Similar nuclear methylation was noted by Perkin in the cases of several other flavones and flavonols, and he made a special study of it in the resorcinol series (J., 1895, **67**, 990). Thus the methylation of methyl β-resorcylate by the usual process was proved to give rise to (XVI) in addition to the normal products.

The researches of von Gerichten on apiin, the glucoside occurring in the leaves, stem, and seed of parsley, rank in importance with those of Piccard on chrysin, but it was Perkin who showed that apigenin, the aglucone, is a member of the flavone group. As the result of the preparation of derivatives and their alkaline degradation he allocated the formula (XVII) to the substance and this was later confirmed by syntheses due to other investigators.

The natural flavone, acacetin (*ex Robinia pseud-acacia* Linn.), was examined by Perkin (J., 1900, **71**, 430) and shown to be apigenin methyl ether (XVIII). This substance was later synthesised.

(XVII.)

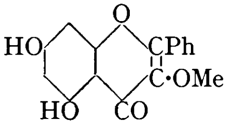


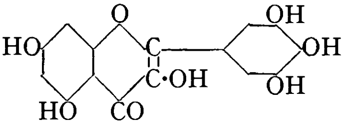


(XVIII.)

The flowers of the same plant were found to contain a remarkable glucoside termed robinin (Perkin, J., 1902, **81**, 473). On hydrolysis it furnishes two molecules of rhamnose, one of glucose, and kæmpferol. The last is the flavonol corresponding to apigenin. Both this substance and its monomethyl ether, kæmpferide, were studied by Perkin, who encountered them as constituents of various plants, but our knowledge of these flavonols is primarily due to v. Kostanecki. Incidentally it may be mentioned that the flavonol corresponding to chrysin is galangin (*ex* galanga root) and a congener is a galangin methyl ether (Testoni, *Gazzetta*, 1900, **30**, ii, 327). Perkin and Allison (J., 1902, **81**, 470) found that, when air was aspirated through an alkaline solution of the methyl ether, phloroglucinol and benzoic acid were obtained and hence the methyl ether is the 3-derivative (XIX). This was later confirmed by synthesis. Perkin made frequent use of this method of oxidation in order to distinguish between flavones, which are unattacked, and flavonols, which are degraded, and the case of galangin methyl ether is evidence that the distinction applies even to the 3-substituted flavonols.

(XIX.)

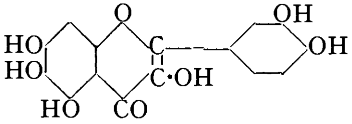


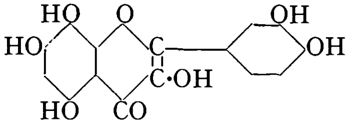


(XX.)

Employing similar methods Perkin in 1902 (J., **81**, 203; also 1911, **99**, 1721) showed that myricetin, isolated from *Myrica nagi* in collaboration with Hummel (J., 1896, **69**, 1287), is a flavonol of the constitution (XX). The constitutions of the isomerides of myricetin, namely, quercetagetin (XXI) from the African marigold and gossypetin (XXII) from cotton flowers were partly established by Perkin (J., 1899, **75**, 826; 1913, **103**, 209, 650), who regarded them as hydroxyquercetins and proposed the constitutions shown

(XXI.)



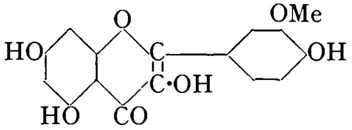


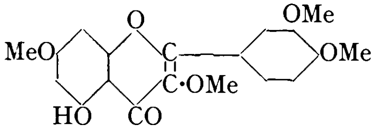
(XXII.)

above. The suggestion could only be tentative because a hydroxyquercetin which should be either (XXI) or (XXII) had been described and this substance differed from the two flavonols in question. The erroneous character of this work and the correctness of Perkin's views were later demonstrated by the syntheses of gossypetin and quercetagetin.

Finally, mention may be made of *iso*rhamnetin (XXIII), first isolated by Perkin and Hummel from yellow wallflowers (J., 1896, **69**, 1566) and later by Perkin and Pilgrim from *Delphinium zalil* (J., 1898, **73**, 268). Its constitution was determined by correlation with quercetin and by degradation to vanillic acid. The substance has been synthesised by an unambiguous method. Other quercetin methyl ethers were isolated from Persian berries (Perkin and Geldard, J., 1895, **67**, 500).

(XXIII.)

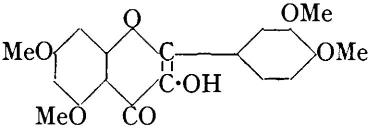




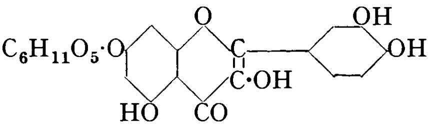
(XXIV.)

Quercetin Glucosides.—In addition to the aglucones Perkin studied the glucosides themselves in many cases and he extended the method of Herzig and Schönbach (*Monatsh.*, 1912, **33**, 678), who had shown that quercitrin is the 3-rhamnoside of quercetin. Direct methylation of quercetin affords the 3 : 7 : 3′ : 4′-tetramethyl ether (XXIV), whereas an intermediate in Kostanecki's synthesis is the 5 : 7 : 3′ : 4′-tetramethyl ether (XXV). Herzig showed that fully methylated quercitrin gives (XXV) on hydrolysis.

Perkin and Attree (J., 1927, 234) found in this way that rutin, xanthorhamnin, and *iso*quercitrin are also 3-saccharides of quercetin but quercimeritrin is the 7-glucoside (XXVI). By full methylation and hydrolysis it furnished the hitherto unknown 3 : 5 : 3′ : 4′-tetramethyl ether of quercetin. The transposition of sugar groups in this series has been effected by Zemplén. Acetylated quercitrin (rhamnoside) is subjected to cautious acid hydrolysis with formation of tetra-acetylquercetin; the free hydroxyl group in the 3-position is then glucosidated, and the product hydrolysed by alkali. The resulting quercetin 3-glucoside accompanies quercimeritrin in cotton flowers (cf. Perkin, J., 1909, **95**, 2181).



(XXV.)

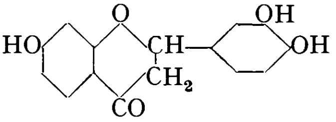


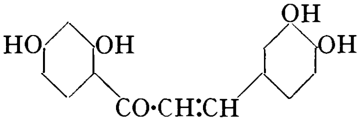
(XXVI.)

Natural Products related to the Flavones.

Perkin and Hummel (J., 1904, **85**, 1459) found in the flowers of *Butea frondosa* a colourless substance, termed butin, which was recognised as a flavanone of the formula (XXVII). On hydrolysis and in the dye-bath it is converted into the isomeric butein (XXVIII). Condensation of pæanol with veratraldehyde gave butein trimethyl ether and this was changed to butin trimethyl ether by the action of dilute alcoholic sulphuric acid.

(XXVII.)





(XXVIII.)

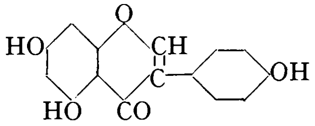
The occurrence of this simple flavanone in Nature is of considerable interest.

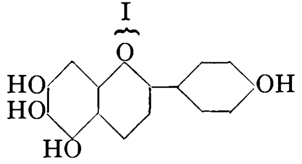
When a solution of butein in acetic acid is warmed with a few drops of sulphuric acid, a crystalline substance possessing beetle-green iridescence separates. This dissolves in alkalis to deep blue solutions and dyes mordanted fabrics in similar shades to those produced by anthragallol. The tentative explanation of Perkin is rather improbably correct and the matter is worthy of further investigation.

Genistein isolated along with luteolin from dyer's broom (*Genista tinctoria*) (Perkin and Newbury, J., 1899, **75**, 830; Perkin and Horsfall, J., 1900, **77**, 1310) was for some time considered to be a coumaranone derivative. Long before the syntheses demonstrated the fact, the late Professor told the writer that he knew that prunetin (Finnemore) was genistein methyl ether, but this idea was never published.

Perkin and Horsfall degraded genistein dimethyl ether by treatment with alkalis to phloroglucinol monomethyl ether and *p*-methoxyphenylacetic acid and these results are in harmony with the *iso*flavone constitution (XXIX).

(XXIX.)

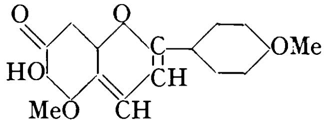


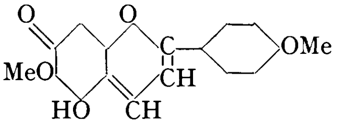


(XXX.)

A unique colouring matter from every point of view was isolated by Perkin from Chica Red (Perkin, *Proc.*, 1914, **30**, 212). This is a cosmetic pigment used by the natives of the Upper Orinoco and it is derived from a species of *Bignonia*. The main constituent is a red crystalline substance termed carajurin; it is a dimethoxy-compound of the formula $C_{17}H_{14}O_5$ and is the colour base of flavylium salts. On demethylation by means of hydriodic acid scutellareinidin iodide (XXX) is produced (Chapman, Perkin, and Robinson, J., 1927, 3015): the corresponding chloride was synthesised. As carajurin affords *p*-acetylanisole on degradation by alkalis, the only dubiety concerns the position of one methoxyl and the formulæ (XXXI) and (XXXII) are the alternatives. The red colour of the quinonoid colour base excludes the *o*-quinonoid structure (which by analogy would be associated with a violet or blue colour). Of these formulæ, (XXXI) is the more probable because the ferric reaction of carajurin salts suggests that two hydroxyls are in the *o*-position.

(XXXI.)



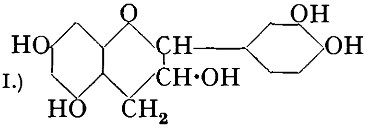


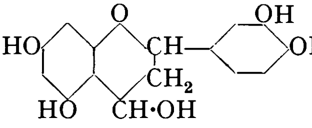
(XXXII.)

The form in which carajurin occurs in the plant is unknown, but from the method of isolation it must be as a saccharide of some kind. The substance may be regarded as a fission product of an anthocyanin. In parenthesis it may be remarked that the possibility exists that carajurin may be a derivative of 5 : 7 : 8 : 4′-tetrahydroxyflavenol, because opening and closing of the pyran ring in the course of the demethylation cannot be excluded in the absence of synthetical evidence.

The idea that catechin should be regarded as a reduction product of quercetin was first advanced by Perkin (J., 1905, **87**, 398; cf. Perkin and Yoshitake, J., 1902, **81**, 1162). By oxidising catechin tetramethyl ether, he obtained veratric acid and, probably, phloroglucinol dimethyl ether. Hence the alternatives (XXXIII) and (XXXIV) were advanced.

(XXXIII.)





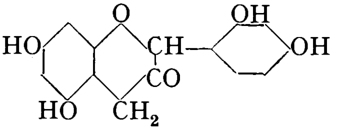
(XXXIV.)

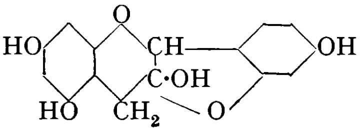
Acacatechin from *Acacia catechu* was proved to be an isomeride of catechin; it was subsequently shown by Freudenberg to be a mixture of *dl*-catechin and a little *l*-epicatechin.

The same author showed that the catechins are stereoisomerides having the constitution (XXXIII).

Perkin made many further researches, such as those on scoparin (1899, 1900), vitexin, and homovitexin (1898, 1900), fukugetin (1904), excoecarin and jacarandin (1902), carthamin (1910), santalin and deoxysantalin (1918), acertannin (1922), which were largely descriptive and the last substance to be mentioned in this section in more detail is cyanomaclurin, which he isolated from Jak-wood (*Artocarpus integrifolia*) (Perkin and Cope, J., 1895, **67**, 937; 1905, **87**, 715). This interesting substance is a kind of catechin related to morin rather than to quercetin and it contains two hydrogen atoms less than catechin. Perkin showed that it may be degraded to β-resorcylic acid and phloroglucinol and suggested the formula (XXXV). It was later found that the deep blue colour produced on warming an alkaline solution of cyanomaclurin (hence the name) is due to the formation of the colour base salts of morinidin and this confirms Perkin's hypothesis in essential respects. The slight modification (XXXVI) remains for consideration.

(XXXV.)





(XXXVI.)

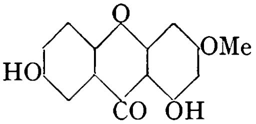
Other Natural Colouring Matters.

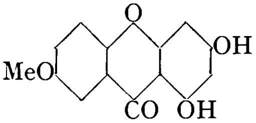
It is curious that Perkin took so little interest in plant colouring matters devoid of tinctorial properties, his sole contact with the carotenoids having been to show that the pigment of the Indian mahogany tree (J., 1912, **101**, 1538) is identical with nyctanthin, later found (Kuhn and Winterstein, 1929) to be identical with crocetin. He found several new sources of berberine (Perkin and Hummel, J., 1895, **67**, 414; Perkin, J., 1897, **71**, 1198).

In connexion with natural indigo he made more extensive researches (Perkin and Bloxam, J., 1907, **91**, 279, 1715; 1910, **97**, 1460; Perkin and Thomas, J., 1909, **95**, 793; Perkin, Thomas, and Bloxam, *ibid.*, p. 824; Perkin, *ibid.*, p. 847), the most important outcome being the method devised for the analysis of the indican content of the leaves of the indigo plant. The estimation depended on the formation of indirubin by the acid hydrolysis of the indican in a neutral atmosphere in presence of isatin. Indigo-yellow from the Java indigo plant (*Indigofera arrecta*) was shown to be kæmpferitrin, a rhamnoside of kæmpferol (J., 1907, **91**, 435).

Degradative evidence leaves two possible formulæ for gentisin, namely, (XXXVII) and (XXXVIII), and, as a result of the study of the properties of bisbenzeneazogentisin, Perkin was led to prefer the former.

(XXXVII.)





(XXXVIII.)

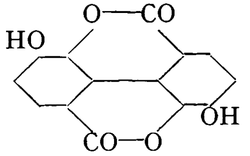
The correctness of this conclusion was later demonstrated by a synthesis of a substance corresponding to the alternative expression (Shinoda, J., 1927, 1983).

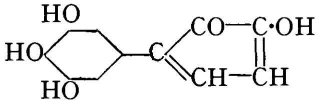
Although not strictly relevant, the opportunity may be taken here to mention the preparation of some analogues of ellagic acid by the oxidation of hydroxy-derivatives of benzoic acid.

For example, catellagic acid (XXXIX) was obtained from protocatechuic acid by oxidation with potassium persulphate and sulphuric acid. The oxidations were occasionally carried out electrolytically (Perkin and Nierenstein, J., 1905, **87**, 1417; Perkin, J., 1906, **89**, 251; A. G. Perkin and F. M. Perkin, J., 1908, **93**, 1194; Bleuler and Perkin, J., 1916, **109**, 629).

Related to this topic is the work which Perkin carried out on purpurogallin, the constitution of which (XL) was eventually established by Willstätter and Heiss (*Annalen*, 1923, **433**, 17). In collaboration with F. M. Perkin it was noted that purpurogallin could be obtained by the anodic oxidation of pyrogallol (J., 1904, **85**, 243), but for the preparation of the substance Perkin and Steven (J., 1903, **83**, 192) preferred the nitrous acid process of Nietzki; ferricyanide also was found to be applicable. The older formulæ,

(XXXIX.)





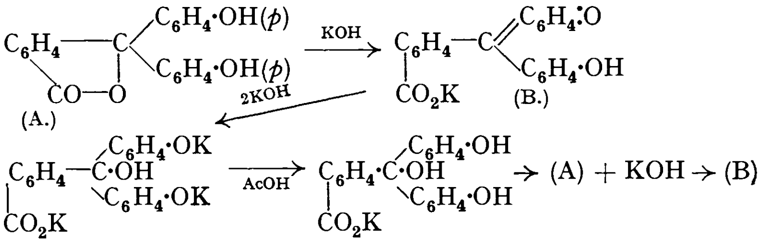
(XL.)

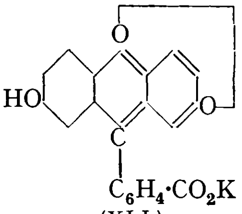
for example, $C_{20}H_{16}O_9$, were shown to be incorrect and were replaced by the formula $C_{11}H_8O_5$. Various derivatives (*e.g.*, tetra-acetate, dibromo-tetra-acetate, monopotassium salt, purpurogallone derivatives, and *iso*purpurogallone) were prepared and the formation of naphthalene by zinc dust distillation was confirmed. This proved a confusing factor, but Perkin suggested that one of the hydroxyl groups is in a side chain and he detected the presence of a carboxyl group in purpurogallone.

Work in Collaboration with Professor A. G. Green.

Some new polythiosulphonic acids of *p*-diamines were oxidised in the presence of aromatic amines and the products were shown to differ from known colouring matters of the sulphur class (J., 1903, **83**, 1201). A note on the constitution of cellulose was published in 1906. The behaviour of phenolphthalein and quinolphthalein was studied with highly interesting results (J., 1904, **85**, 398).

The first product of the action of alkali on phenolphthalein is the red quinonoid salt in which the lactone ring is broken. Then with more concentrated sodium hydroxide the quinone is hydrated and a colourless solution is obtained. Cautious neutralisation with acetic acid gives the free phenolic carbinol in which the carboxyl group alone is present in salt form. On heating, the lactone is probably regenerated with liberation of alkali-metal hydroxide (or the quinonoid phase is directly produced by dehydration). These changes are represented as follows :





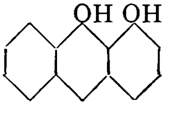
(XLI.)

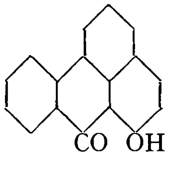
It was possible to follow these stages in the case of quinolphthalein and the formula (XLI) was suggested for the colour salt in this case. The hypothesis was analogous to the proposals of Kehrmann in connexion with the constitutions of members of the rosindone and oxazine groups.

Reduction Products of Hydroxyanthraquinones.

A long series of researches on this subject was Perkin's last interest and constitutes his major contribution to synthetic chemistry. Fourteen papers in this series were published between 1922 and 1933. It was found that the reduction of unsymmetrical hydroxyanthraquinones leads, as a general rule, to only one of the two anthranols which might theoretically be obtained. Thus 1-hydroxyanthraquinone gives (XLII) because the hydroxyl group of the corresponding benzanthrone (XLIII) is resistant to methylation by means of methyl iodide and alcoholic potassium hydroxide.

(XLII.)



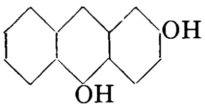


(XLIII.)

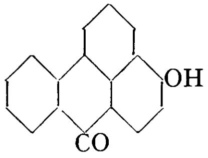
In a similar manner the constitutions of the anthranols (anthrones) from alizarin and its 2-methyl ether, anthrapurpurin, flavopurpurin, anthragallol and its methyl ethers, were determined (J., 1920, **117**, 696; Perkin and Spencer, J., 1922, **121**, 474; Perkin and Miller, J., 1925, **127**, 2684; Perkin and Cross, J., 1927, 1297; 1930, 292).

In the 1-hydroxyanthraquinones it was found that the carbonyl in the *o*-position to hydroxyl is protected from the action of the reducing agent, but if this hydroxyl is acetylated, then the carbonyl ortho to acetoxyl is the one attacked. Thus the isomeric anthranols could be obtained at will.

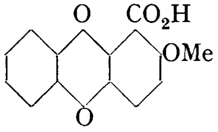
The reduction of 2-hydroxyanthraquinone was found to give 3-hydroxyanthranol (XLIV) and therefore a *p*-hydroxyl also protects a carbonyl from reduction. The corresponding hydroxybenzanthrone (XLV) was obtained also by the direct oxidation of benzanthrone by means of aqueous potassium hydroxide and some potassium chlorate at 230—240°, and its methyl ether afforded 2-methoxyanthraquinone-1-carboxylic acid (XLVI) on oxidation by means of chromic acid (Perkin and Spencer, *loc. cit.*; Perkin and Bradshaw, J., 1922, **121**, 911; misprinted 1911 in J., 1924, **125**, 231). The di-anthracene derivatives from 2-hydroxyanthraquinone were studied in very great detail and the results are of considerable scientific and technical interest. Perkin and Bradshaw treated 2-hydroxyanthraquinone with glucose, aqueous alkali, and potassium nitrate at 170—180° and obtained 2-hydroxybenzanthronecarboxylic acid together with substances at first considered to be $C_{28}H_{16}O_4$ (A) and $C_{28}H_{14}O_4$ (B). Perkin and Whattam (J., 1922, **121**, 289) reduced 2-hydroxyanthraquinone by means of zinc dust and ammonia to 3-hydroxynathranol (XLIV) and obtained as by-products, 2 : 2′-dihydroxydianthryl and 3 : 3′-dihydroxydianthrone. The latter on oxidation with permanganate gave a supposed dihydroxydianthraquinone identical with the product (A) of Perkin and Bradshaw.



(XLIV.)



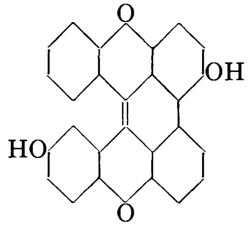
(XLV.)

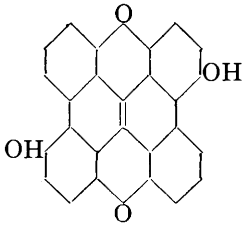


(XLVI.)

Later, Haller and Perkin (J., 1924, **125**, 231) oxidised dihydroxydianthrone with ferricyanide and obtained a 99% yield of (A) $C_{28}H_{14}O_4$, and a trace of (B). Because (A) is converted by iodine in pyridine solution into a monoiodo-derivative without further nuclear coupling, it was regarded as 3 : 6′-dihydroxyhelianthrone (XLVII). (B) was now recognised as $C_{28}H_{13}O_4$ and formulated as a dihydroxy*meso*naphthadianthrone (XLVIII).

(XLVII.)





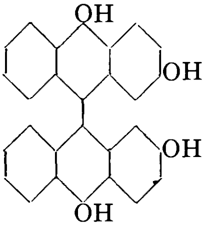
(XLVIII.)

The dihydroxyhelianthrone gives orange-red alkali salts and a bluish-green vat in which fibres are dyed bluish-green, becoming red and then orange on exposure to air.

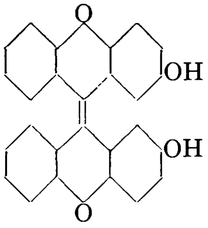
In later researches these conclusions were modified (Perkin and Yoda, J., 1925, **127**, 1884; Perkin and Hardacre, J., 1929, 180) and it was shown that on mild oxidation 3-hydroxyanthranol gives successively 3 : 3′-dihydroxydianthrone (XLIX), dihydroxydianthraquinone, dihydroxyhelianthrone (LI) and dihydroxynaphthadianthrone (LII).

The position of the hydroxyl groups was proved by synthesis (Perkin and Hardacre, *loc. cit.*). 1-Bromo-2-benzoyloxyanthraquinone was treated with copper powder according to Ullmann's method and after hydrolysis 2 : 2′-dihydroxy-1 : 1′-dianthraquinolyl (LIII) was obtained. This was reduced to dihydroxydianthranolyl (LIV) and then oxidised to the dihydroxyhelianthrone (LI).

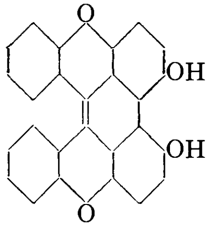
Somewhat different results were obtained by the oxidation of the anthranol (LV) from alizarin 2-methyl ether (Perkin and Attree, J., 1931, 144; Perkin and, in part, Haddock, J., 1933, 1512).



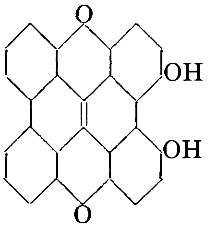
(XLIX.)



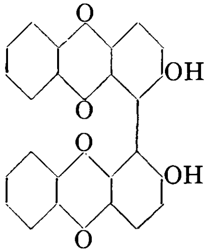
(L.)



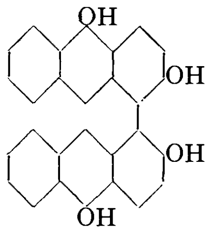
(LI.)



(LII.)

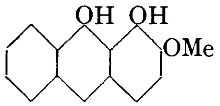


(LIII.)

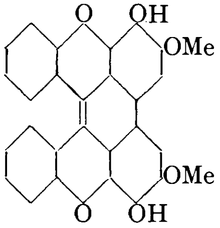


(LIV.)

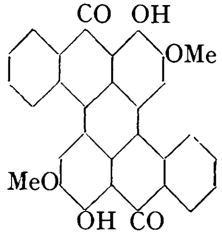
When iodine in pyridine solution was used as the oxidising agent, the product obtained was at first thought to be a dihydroxydimethoxyhelianthrone (LVI) analogous to that obtained from 2-hydroxyanthraquinone. This substance was, however, synthesised and proved to be a different compound. The oxidation product of the anthranol (also obtained by boiling a pyridine solution of 4-bromo-1-hydroxy-2-methoxyanthrone) was recognised as a dihydroxydimethoxydibenzperylenequinone (LVII).



(LV.)



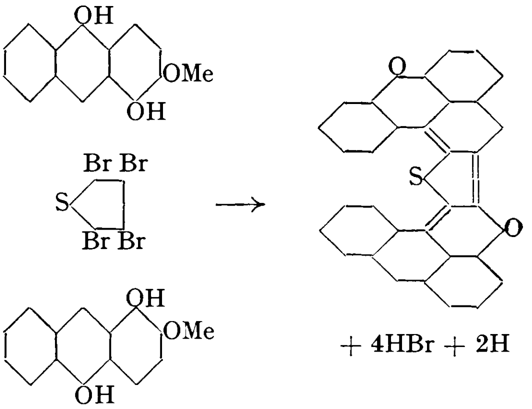
(LVI.)



(LVII.)

The last piece of work which engaged Perkin's attention showed that his powers as a discoverer were unimpaired. In attempting the methylation of 3 : 4-dihydroxyanthranol by means of methyl sulphate and anhydrous sodium carbonate in crude trichlorobenzene solution, the formation of a green vat-dye was observed. Further investigation showed that the presence of tetrachlorothiophen in the trichlorobenzene was responsible for the production of this interesting substance, and related products were obtained from 4-hydroxy-3-methylanthranol and from 4-hydroxy-3-methoxyanthranol (cf. B.P. 353,422, Imperial Chemical Industries Ltd., A. G. Perkin, A. Shepherdson, and N. H. Haddock). The dyes applied to cotton from a hyposulphite vat yield green shades of considerable beauty but of only moderate fastness to light and hypochlorite; they may nevertheless be of technical interest.

In a posthumous paper (Perkin and Haddock, this vol., p. 541) it is shown that the dyes can be oxidised by chromic acid with formation of the anthraquinone corresponding to the anthranol employed. The formation of the dye from the 4-hydroxy-3-methoxyanthranol is represented as follows :



Perkin was a very great chemist and a man of characteristic and lovable personality. His gentle, unassuming, and to a certain extent, retiring nature prevented him from taking a large part in national scientific affairs, but his laboratory activities gave him an international reputation second to none as an ardent and successful seeker of the truth. He was an ideal colleague, completely unselfish, a giver not a taker, a man who craved no recognition and sought no reward other than the joy of accomplishment.

R. Robinson.

SHIN-ICHI SAKO.

1892—1936.

Shin-ichi Sako, who died on June 20th, 1936, in his forty-fourth year, was born in Mié Prefecture, Japan, on March 14th, 1892. He was educated at the Technical School of Mié, and at the Higher Polytechnic School of Osaka, afterwards proceeding to the Imperial University of Tohoku, Sendai, where he received his training in organic chemistry under the guidance of Prof. Riko Majima. After the completion of the University course, he became lecturer at his mother university, where he stayed for two years. In 1919 he was appointed Assistant Professor of Organic Chemistry at the Imperial University of Kyushu, Fukuoka, under Prof. Tahara, whose sudden and unexpected death took place shortly afterwards. The next year Sako proceeded to England to study organic chemistry in the laboratory of Prof. J. F. Thorpe, where he published a paper on hydantoins in collaboration with Ingold and Thorpe. In December, 1922, he returned to the Imperial University of Kyushu and after two years was elected Professor of Organic Chemistry. He took his Doctor's degree in October, 1930, the title of his thesis being " The Formation of Cyclic Compounds from Diphenyl Derivatives." From that time until his death he was engaged in research on the derivatives of diphenyl.

He was a diligent and skilful practician; most of his researches were carried out alone, but in a few cases he had the assistance of Mr. T. Ono. From early morning to late in the evening he worked hard in his laboratory, and that was one of his greatest pleasures. Committee work or meetings which took him away from his laboratory he hated. It is not too much to say that his health, which was by no means poor, was ruined by the overwork and love of chemistry.

He is survived by his widow and three sons and one daughter, who now live in his native place.

He was elected a Fellow of the Chemical Society on February 17th, 1921.

H. Shiba.