Advances in Carbohydrate Chemistry and Biochemistry

Editor
R. STUART TIPSON

Assistant Editor
DEREK HORTON

Volume 25

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PREFACE

With this twenty-fifth Volume, *Advances in Carbohydrate Chemistry and Biochemistry* has completed its first quarter-century. This serial publication was initiated with the dual objective of presenting definitive accounts of the status of matured fields and of providing, for areas of high activity, critical evaluations that would serve as guidelines for future research. The past 25 years have seen an acceleration of research unprecedented in the history of science, and the extent to which *Advances* has usefully fulfilled a need, and yet provided flexibility in accommodating to change, may be judged by the frequency with which many of the older articles are still cited.

Over its lifetime, *Advances* has developed into a permanent source of reference in organized form for practically all of the major subdivisions of knowledge in the field of carbohydrates. It has also stimulated, by means of timely articles on active and controversial areas of research, the exploration of important fields that might otherwise have been neglected or investigated in a more haphazard fashion. The breadth of coverage, as originally conceived and subsequently maintained, has allowed the discussion of carbohydrates from the viewpoints of many specializations. Structural and synthetic organic chemistry have certainly been highly influential, but biochemistry and physical chemistry have been no less important, and the techniques and ideas of agricultural chemistry, analytical chemistry, industrial chemistry and technology, microbiology, pharmacology, and many other disciplines have brought the full breadth of scientific inquiry to bear on this, the largest, class of natural products. In the present era, the idea of interdisciplinary research has become much in vogue, and it is therefore interesting to observe that the original Advisory Board for *Advances*, in setting a policy of studying a single major class of natural products by a broad spectrum of many classical disciplines, was instrumental in the achievement, over the years, of that very type of cooperation between specialists of different persuasions that is only now becoming properly recognized as an important trend in the future development of science. Bearing in mind the not infrequent asseverations in the past by certain classical specialists (especially, organic chemists) that the study of carbohydrates is a narrow specialization, the tenacity of the Editors and the Advisory Board in adhering to the original interdisciplinary concept is a fitting testimony to the soundness of their ideas in the face of changing opinion.

The present volume was in the planning stage at the time of the death of Professor Melville L. Wolfrom, but it is one of the few volumes in the history of this Series not to have received his editorial attention. His influence always reflected the precision and accuracy that he applied in his own writings, and the present Editors will endeavor to meet these criteria.

This volume includes an obituary, contributed by J. R. Turvey, of the late Professor Stanley Peat, F.R.S., who was for many years a member of the Board of Advisors of *Advances*, and who served as Associate Editor for the British Isles for a number of years.

The separation of macromolecules by molecular-sieve techniques constitutes a major technical advance, especially for biochemists. The principles of the method and applications in the carbohydrate field are surveyed by S. C. Churms (Rondebosch). The field of X-ray crystal-structure analysis is undergoing rapid evolution because of major advances in methodology; automatic diffractometers and computerized systems for data reduction have advanced the technique to the point where the solution of many simple structures is almost routine, and the chapter by G. Strahs (New York) surveys developments since the article by Jeffrey and Rosenstein in Volume 9 of *Advances*. The chapter marks a transition between the era of the classical crystallographer, who determined a structure for its own sake, and that of the newer generation of crystallographers concerned with the broader implications of a coordinated plan of attack, where crystallography provides the tool rather than the objective for the study of fine points of the molecular structure of carbohydrates in relation to their conformations and biological roles. The wide-ranging subject of anhydrides of sugars and their derivatives is treated from the organic chemical viewpoint in three separate chapters in this volume. Because of the extensive literature on sugar anhydrides of various types, it was found impossible to treat developments in this whole area within the confines of one chapter, or even in the three chapters here presented; other aspects remain to be treated in future issues. Oxiranes (epoxides) are discussed by N. R. Williams (London), and ring-forming reactions, of aldoses, that result in the formation of 2,5-anhydro rings are delineated in the chapter by J. Defaye (Gif-sur-Yvette). The anhydrides of alditols are considered separately by S. Soltzberg (Delaware).

Modern methods of separation continue to reveal the complexity of mixtures of even simple carbohydrates in various natural sources, as demonstrated in the chapter by I. R. Siddiqui (Ottawa) on the sugars present in honey. The reactions of sugars with ammonia and amines, a field related to important problems in the food industry, constitute a subject of continuing interest, and are treated by M. J. Kort (Pietermaritzburg). The polyfunctional nature of sugars can be exploited in the synthesis of a multitude of types of heterocyclic derivative, but the uninitiated reader may find the literature confusing and disorganized because of the plethora of structural types possible, even from simple reactions; H. El Khadem (Alexandria) has performed a valuable service by organizing the facts, fictions, and paradoxes in this domain. In the final chapter, R. D. Marshall and A. Neuberger (London) explore the recent developments in our understanding of the structure and metabolism of glycoproteins, an area at the broad frontier of much advancing knowledge in modern biochemistry. The Subject Index was compiled by Dr. L. T. Capell.

A well-assorted, international representation of authorship is evident in recent volumes of *Advances;* the original British-American liaison on which the publication was founded has been substantially expanded to the international level. The present volume includes, in addition to contributions from North America and Great Britain, articles from continental Europe and, coincidentally, three separate chapters by authors based at different points on the African continent.

Kensington, Maryland
Columbus, Ohio
November, 1970

R. STUART TIPSON
DEREK HORTON

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STANLEY PEAT

1902–1969

On the 21st of February, 1969, Professor Stanley Peat, D. Sc., F.R.S., suffered a stroke at his home in Bangor, Wales, and he died 36 hours later without regaining consciousness. Thus ended the career of a scientist who, even as a child, displayed an unquenchable thirst for knowledge and who, all his life, regarded it as a duty to impart that knowledge to others.

His parents, Ada and John H. Peat, lived at Bolden, County Durham, but Mrs. Peat was staying with her sister Alice in South Shields when their first child, Stanley, was born in 1902. John Peat was a mining engineer, but, despite his status, the family was rather poor and the care of the infant boy was handed over to his Aunt Alice and her husband, James Gibson, who were childless. Unfortunately, despite their care and attention, the child developed bovine tuberculosis when only a few months old, and had to receive hospital treatment for some time. Possibly as a result of this illness, the child was left with a permanent curvature of the spine. This disability was to have a profound effect on the development of Stanley Peat, since, denied an outlet for his energies in active sports and games, he was thrown back onto his mental resources for amusement and interest.

The first consequence of this childhood illness was that Stanley was a rather frail child, requiring much attention from his aunt; this she gave unstintingly, often at the expense of her husband. Both Gibsons were keen members of the Salvation Army, the husband being a musician in the Army Band. The child was thus raised in a household where both Christianity and music were an important part of everyday life, and both were to influence him for the rest of his life. His frailty also resulted in a delayed start to his schooling; he did not attend a formal school until he was eight years old. Fortunately, he was blessed with an inquiring mind and this, coupled with the enforced idleness, resulted in his learning to read and write before he went to school. He became an avid reader, and the local library became an important point of call whenever he went out. From the library he was able to borrow books on travel, science, and a wide variety of other subjects. Two books in particular fired his imagination, one on chemistry and the other on photography. At the age of eight, he started a chemistry set with which to experiment, and, by the age of ten, he was developing and printing his own photographs in an improvized dark-room. This love for experimental chemistry and photography persisted throughout his schooldays and into College, when he still retained his private laboratory and dark-room at home. The lack of formal schooling in his early days had, however, left large gaps in his education which, in spite of his thirst for knowledge, he had been unable to fill by reading alone. Mathematics was a difficult subject to him and was to remain so for the rest of his life.

Once at school, Stanley Peat rapidly showed that he was a gifted pupil. He was never happy until he felt that he really understood a subject and, unable to follow active outdoor pursuits, he tended to devote much of his spare time to study and general reading. Not that he was completely debarred from all childish games; he used to play with the local children, and indulged in the usual boyish pranks. At the age of ten, he had returned to live with his parents at Station Road, Walker-on-Tyne, a mining community, and, as he subsequently used to relate with great glee, he was chased by the local policeman for "scrumping" apples from a nearby orchard. One other incident from this period is worth recording, as it throws some light on the boy's character. His maternal grandfather, then aged 60, was only semi-literate, and young Stanley took it upon himself to help his grandfather to write. Armed with a penny exercise book, a present from Stanley, the grandfather practised his writing under the watchful eye of his grandson. He made such rapid progress, that, within a short time, he was attempting to write an adventure story. This exercise book, with its spidery writing and frequent misspellings, was treasured by Stanley Peat all his life.

From Tyne Dock Grammar School, which he attended for some years, Stanley won a Scholarship in 1915 to the Rutherford College Boys' School in Newcastle. This school had a long tradition of excellence in its teaching of science subjects, and possessed some extremely able and inspiring science masters. Among these was William Carr, the chemistry master, who came to regard Stanley as one of his favorite and most able pupils. Certainly, the young boy spent nearly all his spare time studying, and he was regarded by his schoolfellows as a pleasant but extremely serious young fellow. In 1917, further hospital treatment for his back caused him some pain, but did not prevent him from winning the Form Prize at school. He obtained his School Certificate in 1919, and proceeded to the Sixth Form, where he specialized in Chemistry and Physics. In 1921, he was awarded the Higher School Certificate, with distinctions in chemistry and physics; at the same time he won a State Exhibition, an Entrance Exhibition, and an Earl Grey Memorial Scholarship to study at Armstrong College (now the University of Newcastle-upon-Tyne). It is interesting that fellow pupils of Peat at Rutherford College included Professor E. E. Aynsley, W. Charlton, R. Chirnside, and Sir James Taylor.

At Armstrong College, Peat read for Honours in Chemistry, with physics and mathematics as ancillary subjects. Once again, he proved to be an outstanding student, becoming Senior Pemberton Scholar in 1922 and Saville Shaw Medalist in 1923, and winning the Friere-Marreco Medal and Prize in 1924, when he graduated with First Class Honours in Chemistry. In addition to his normal studies at Armstrong College, Peat also found time to pursue a course of lectures and practical work in physiology, a fact that was to influence his subsequent career profoundly. The Professor of Chemistry at that time was W. N. (later, Sir Norman) Haworth who, with E. L. (later, Sir Edmund) Hirst, was carrying on pioneer research work, originated with Sir James Irvine at St. Andrews, on the use of methylation in the study of the ring structures of sugars. Both Peat and Charlton, who had graduated with him, were invited to conduct postgraduate work in Haworth's research school. While continuing to live with his aunt in South Shields, Peat joined this enthusiastic group of research workers, and rapidly immersed himself in the work on methylation and in the controversies surrounding it. An insight into his character comes from Professor R. Spence, then a junior student and a fellow commuter on the train from South Shields to Newcastle: "He was rather senior to me, but he was completely unpatronizing in his friendship. This readiness to help a younger man was, I am sure, strongly characteristic. He offered his collection of chemicals and apparatus to me when he left Newcastle . . . . Although a loyal co-worker, Stanley could, on occasion, make a pungent comment on the polemics in which Haworth was involved."

In 1925, Haworth was invited to the Chair of Organic Chemistry at Birmingham University, and he took with him Stanley Peat (as his research assistant), J. Avery, W. Charlton, E. Goodyear, A. Learner, and V. Nicholson. Peat, Charlton, and Learner were in the same lodgings in Birmingham until they were all awarded the Ph. D. degree in 1928. Stanley (or, as he was more generally known, "Sammy") Peat did not have many interests outside his work, not that there *was* much free time after an average 12-hour day in the laboratory. An occasional hand at bridge and listening to classical music were his chief amusements outside the laboratory. However, while waiting for experiments to "come to the boil," Peat would indulge in lengthy and fierce arguments on every possible subject with Learner and anyone else who cared to participate. It was usually Peat who took the orthodox viewpoint, which he would argue both logically and forcefully, while Learner upheld the revolutionary view. It is a measure of their characters that, though they argued vociferously they never quarrelled. They found common ground in reading the whole of Ibsen's and Shaw's plays, and in inviting lecturers on Psychoanalysis or Comparative Religion to address them on Sundays.

It is difficult to assess Peat's attitude towards religion. The Salvation Army influence of his childhood had been modified in his schooldays by regular attendance at a Methodist chapel with his mother. He had an exceptional knowledge of the Bible, being able to recite long passages from memory and, when older, he took pains to study most of the world's major religions. In spite of this knowledge, he never became an ardent member of any particular faith; he was too full of intellectual curiosity to accept blindly any dogma or principle that he could not subject to a scientific test. In his later dealings with colleagues and students, however, he was to display many Christian attributes, tolerance and understanding of their viewpoint, and a willingness to temper the wind to the shorn lambs among his undergraduates.

In those early days, Stanley Peat's contribution to carbohydrate chemistry was allied completely with Haworth's pioneering work on the constitution and ring structures of sugars. His first paper (with Haworth) in 1926 was a revision of the structural formula of D-glucose, in which it was established that the known methyl β-D-glucoside, and, hence, probably D-glucose itself, existed in the pyranoid ring-form. In 1926 also, his name appeared on two papers dealing with the structure of maltose, in which it was unequivocally shown that the linkage was $(1\rightarrow4)$ between two D-glucose residues, both of which were in the pyranoid ring-form. This was the "classical" type of research which was fast making Haworth's school the leading center of carbohydrate chemistry in Europe. In yet another paper, the importance of the synthetic approach to the structure of sugar derivatives was underlined by the preparation of D-glucono- and D-mannono-1,5-lactones from D-arabinose, by using a cyanohydrin synthesis.

Following the award of his Ph. D. degree in 1928, Peat was offered the post of lecturer in Biochemistry in the Physiology Department of the Medical School at Birmingham University. This department wished to expand its teaching on the biochemistry side, and Professor de Burgh Daly had appealed to Haworth to find him a suitable lecturer. Knowing of Peat's interest in physiology and of his potential as a teacher, Haworth nominated him. Peat threw himself with enthusiasm into the task of gathering material for his lectures to the medical students and of preparing experiments suitable for large classes in very limited laboratory space. To this problem of overcrowding, Peat brought an orderliness and precision that ensured that each student was able to carry out his allotted experiments without hindrance. A few well-chosen words from Peat were enough to quell the most mischievous prankster, thus ensuring the efficient working of the class. Accounts of such incidents were often related with obvious humor by Peat to his friends. To those who did not know him well, he appeared a shy and very earnest young man. Only with his colleagues and the many friends he made in the Founders' Room at the Edmund Street branch of the University did he show his tremendous sense of humor, his penchant for intellectual argument, and his deep humanity. During this period, he also taught himself German, and he subsequently made frequent trips to Austria and Germany. On these trips, he was able to indulge to the full a growing passion for grand opera and classical music. In Birmingham, he started playing golf, using specially shortened clubs, and was frequently to be seen practising on the University playing fields by the Bristol Road. His greatest enjoyment, however, came from the concerts given by the Birmingham Symphony Orchestra, from the plays at the local "Rep" theatre, and from learning to play the mandolin. Although a heavy teaching-load curtailed his research activities, in 1931 he collaborated in an investigation of a case of phenol poisoning and, with MacGregor, began a series of investigations on the physiological role of histamine in the animal body, subsequently publishing three papers on aspects of this topic. This experience with biological systems and the metabolism of compounds did much to influence his later work.

In 1934, Haworth invited Peat to return to the Chemistry Department as a lecturer. Peat thus joined a team which, during the next few years, was to include such eminent workers as E. L. Hirst, J. K. N. Jones, E. G. V. Percival, Fred Smith, M. Stacey, and L. F. Wiggins. In 1936, Haworth divided the direction of his rapidly growing research school among Peat (plant polysaccharides and amino sugars), Smith (plant gums), and Stacey (polysaccharides of microorganisms); these "compartments" were not, however "water-tight," and fruitful collaboration between the groups frequently occurred and often led to joint publications. Under Haworth's guidance, Peat began to develop two main lines of research. The first was a continuation and extension of the methylation method for investigating the structure of polysaccharides. Over the next few years, there appeared a steady stream of papers based on the use of this technique that described the constitution of agar, α-amylodextrin, cellulose, dextran, and xylan. Cellulose was the polysaccharide to which he frequently returned; its end-group assay by methylation, the importance of excluding oxygen during its methylation, and the properties of oxycellulose and hydrocellulose were among the aspects that he investigated.

The second line of research was a detailed study of the formation and reactions of anhydro sugars. In 1938, with Wiggins, he described the base-catalyzed elimination of the *p*-tolylsulfonyloxy group from methyl 3-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside, with consequent formation of various methyl anhydrohexosides. The fact that Walden inversion frequently accompanied this type of elimination was stressed, and the opening of the anhydro ring by alkaline reagents, again with inversion, was described. Other *p*-toluenesulfonic esters were then investigated, and the opening of the anhydro ring by methanolic ammonia to produce aminodeoxy sugars was reported. Peat readily appreciated the importance of these reactions in the synthesis of the rarer sugars, and, particularly, in the preparation of amino sugars. The synthesis of "chitosamine," and the proof that this sugar is 2-amino-2-deoxy-D-glucose, followed from this work. Also of importance was the recognition, by Peat, Hands, and W. G. M. Jones, that the labile sugar present in agar is 3,6-anhydro-L-galactose. Much of this work and later contributions were elegantly summarized by Peat in an article in Volume 2 of *Advances in Carbohydrate Chemistry*. During this period, he was also a regular contributor to the *Annual Reports of the Chemical Society*.

At this time, Haworth asked Peat to take over from him the teaching course to first-year students, a course which both regarded as the most important of the syllabus. Peat was desirous of introducing into the teaching the new concepts of "electronic mechanisms" as a help to students in understanding why chemical reactions occur. He designed such a course and, in his meticulously careful way, delivered it with obvious enthusiasm. The students responded to this new approach, and all who attended the course agreed that it was outstanding in its clarity and mode of presentation. This avenue to the teaching of elementary organic chemistry was, with suitable modification, continued by Peat for nearly twenty years in Birmingham and Bangor.

In the teaching laboratory, he strove to instil into students the importance of neatness, accuracy, and precise observation. An accomplished experimentalist himself, and second only to Fred Smith in his ability to produce crystals from syrups, he would not tolerate untidy or careless work.

His private life, which had pursued an even tenor for several years, was also due for a change. During his days in the Medical School at Birmingham University, he had gone to lodge in Station Road, Harborne, with a Mr. and Mrs. Barnes. Mr. Barnes, a dental surgeon, had been forced by ill health to curtail his practice and, in 1937, to retire completely. Stanley Peat bought a house in Edgbaston, and the Barnes family moved in with him. Their daughter Elsie, several years younger than Stanley, would sometimes accompany him on his frequent visits to concerts or the theatre. In the spring of 1939, following a sharp bout of influenza during which Elsie was his faithful nurse, he proposed to her, and they were married in the summer. Peat threw himself wholeheartedly into the business of being a married man; and he planted a garden, but his early efforts were not an outstanding success. To his great joy, a daughter, Gillian, was born to them in 1940, and another daughter, Wendy, in 1942. He derived tremendous pleasure from the company of these children.

Unfortunately, the Second World War had brought an end to the happy state of the Chemistry Department. Haworth had agreed to turn much of the research potential in his department over to a study of uranium compounds, a project contributing in no small measure to the production of the atomic bomb. After six months of research on uranium carbonyls, Peat found that he could generate little enthusiasm for the work itself, and none at all for the project to which it was contributing. He persuaded Haworth that he could contribute more to the war effort by carrying out selected research in carbohydrates, with a view to increasing food production. With Haworth's approval, he took over from M. Stacey a project aimed at producing D-glucose directly from potatoes, and saw this process through to the stage of commercial production. His knowledge of cellulose and its derivatives was called for as a member of the Cellulose and Cordite Panel of the Ministry of Supply, and his interest in agar was used on the Committee charged with finding from among the British seaweeds a suitable substitute for Japanese agar. The eventual collection of seaweeds and their processing to afford a product acceptable to microbiologists, even if somewhat inferior to agar, was a direct result of the work of this Committee. In addition, members of his research team undertook work on Asdic recordings for the Admiralty.