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"OXFORD HOUSEWIFE" OR THE ONLY BRITISH WOMAN TO HAVE EVER WON THE NOBEL PRIZE IN SCIENCE? - DOROTHY HODGKIN

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Dorothy Crowfoot Hodgkin, a British chemist and Nobel Prize winner, who extended the method of X-ray crystallography to determine the structure of biomolecules that furthered the development of structural biology. In 1964, she was awarded the Nobel Prize in Chemistry " for the determinations by X-ray techniques of the structures of important biochemical substances", particularly vitamin B_{12} and antibiotic penicillin. Five years after winning the Nobel Prize, Dorothy Hodgkin also established the structure of insulin. Although The Daily Mail headlined her as an "Oxford housewife", Dorothy Hodgkin overcame gender inequality to become the third woman in history to win the Nobel Prize in Chemistry and remains the only British woman researcher to be awarded the most prestigious prize in the sciences.

K e y w o r d s: Nobel Prize in Chemistry, Dorothy Hodgkin, X-ray crystallography, structures of penicillin, vitamin B_{12}, insulin.

Dorothy Mary Crowfoot Hodgkin was born on May 12, 1910 in Cairo, Egypt, in the family of John Winter Crowfoot (1873-1959), a philologist and archaeologist who was working in the Egyptian Education Service, and Grace Mary (1877-1957). Grace Mary Crowfoot had wide-ranging interests. She was actively involved in charity work and was a good botanist, making a large collection of Sudanese flora and many drawings of wild plants, which are now in the Royal Botanic Gardens. She also loved weaving and textiles and became an expert in ancient weaving techniques [1-3].

When World War I broke out in 1914, Dorothy's mother left her (then aged 4) and two younger sisters, Joan and Elizabeth, with their grandparents near Worthing, England, and rejoined her husband in Egypt. Although the children spent much of their childhood apart from their parents, they were always supportive from afar. Thus, Dorothy's mother encouraged her interest in crystals, which was first sparked in her at age 10. With a portable mineral analysis kit, Dorothy and her sister tried identifing minerals in pebbles from nearby streams.

Dorothy Mary Crowfoot Hodgkin(1910–1994) [2]

In 1918, her parents moved to Khartoum, Sudan, where John Crowfoot worked as Director of Education and Antiquities until 1926, and where their fourth daughter was born [4].

Education

After the war, in 1918, the Crowfoot sisters and their mother settled in Lincoln, Lincolnshire. Dorothy and her sisters spent a year learning history, geography and literature at home under their mother's tutoring. At the age of 11, Dorothy was enrolled at the Sir John Leman School. Even at this young age, she showed a keen interest in the natural sciences, particularly chemistry. Her mother fostered Dorothy's enthusiasm, allowing her to conduct experiments at home. When Dorothy turned 15, her mother presented her with several books written for schoolchildren by Sir William Henry Bragg, a Nobel Prize laureate in physics – "Concerning the Nature of Things" and "Old Trades and New Knowledge" based on the Royal Institution Christmas Lectures. From these books, Dorothy gained her first knowledge about crystal structures and X-ray diffraction. Dorothy was also fascinated by biochemistry, inspired by Parsons's "Fundamentals of Biochemistry" [4].

From time to time, Dorothy and her sister Joan visited their father in Sudan. During one visit in 1922, Dorothy met Dr. A. F. Joseph, a chemist working in the Wellcome Laboratories and a close friend of her father. On a subsequent visit in 1924, Dr. Joseph guided Dorothy in her first chemistry experiments analyzing minerals in garden sand. This experience in the Wellcome laboratories deepened her passion for science. Dorothy's father believed that his children should attend local Sudanese schools, so Dorothy then studied at a local school. Her first steps in chemistry class began with a project on growing crystals, which captivated her [4].

In 1926, her father moved to Palestine to work as the director of the British School of Archeology in Jerusalem. Visiting him, Dorothy joined an archeological expedition to Jerash in Trans-Jordan (now Jordan) to excavate Byzantine churches [5]. She was fascinated by the ancient mosaic pavements and made detailed sketches of them. Despite her interest in archeology, she remained focused on chemistry, and eventually decided to pursue X-ray crystallography. Dorothy's father intended for her to study at Oxford.

After returning to England, Dorothy excelled academically, graduating at the top of her class. She passed successfully the college entrance exam, and in 1928, entered Somerville College, Oxford University, to study chemistry. She graduated in 1932 with a first-class honors degree, becoming the third woman in Oxford's history to receive this great distinction [6].

Carrier and Discoveries

In the fall of 1932, Dorothy began her PhD program at Newnham College, Cambridge, under the supervision of John Desmond Bernal, an Irish pioneer in the use of X-ray crystallography for biomolecular analysis [7]. It was then that she recognized the potential of X-ray crystallography for determining protein structures. In collaboration with J. D. Bernal, she first applied this technique to analyze the structure of pepsin. While the pepsin experiment is largely attributed to Dorothy, she consistently credited Bernal for taking the initial photographs and providing her crucial insights [8]. Together, they developed a method for analyzing single crystals of proteins immersed in mother liquor [7].

While working at Cambridge University, Dorothy was offered a two-year research fellowship from her alma mater, Somerville College, Oxford. It was hard for her to leave her current place where she was part of an exceptional and active group. Somerville was sympathetic and allowed her to split the fellowship, spending one year at Cambridge and second at Oxford. In 1934, she ultimately decided to return to Oxford, where she soon organized a research group with the help and support of the renowned organic chemist, Nobel Prize laureate in chemistry in 1947, Sir Robert Robinson, and began investigating the structures of insulin, cholesterol and other sterols.

In 1935, Dorothy raised funds to acquire an X-ray apparatus for her laboratory, enabling her to continue research on the analysis of sterols, particularly cholesterol iodide. For this work, she was awarded PhD degree in 1937 [9].

Cholesterol iodide was selected for the study for a reason. The iodine atom, being the heaviest in the molecule whose scattering would dominate the total scattering from the crystal, was a kind of "reference point" for electron density calculations, helping to identify the skeleton framework of complex molecules. At the time, crystal structure determination was performed by calculating the Patterson function* and plotting two-dimensional electron density maps.

(* If you plot a Fourier series with the X-ray amplitudes as coefficients and include phase information, you can determine the distribution of the electron density, the maxima of which correspond to the centers of the atoms.

Additionally, other functions related to atom positions in the crystal, such as the Patterson function, can be introduced. The Patterson function represents the interatomic vector distribution by analyzing diffraction intensities alone) [12, 13].

This approach allowed researchers to determine the position of most atoms in the molecule; though stereochemistry, which is a particularly important characteristic of a biological molecule, was lost and could only be elucidated through laborious plotting three-dimensional maps. Without performing complex calculations, Dorothy, using innovative approaches, successfully identified all structural features, including the stereochemical configuration, of the sterol core [11].

William Henry Bragg, a British physicist, a pioneer in X-ray crystallography and Nobel laureate in Physics in 1915, noted that this work amply demonstrated how X-ray crystallography can be used to solve the structures of complex organic molecules.

This research was one of Dorothy's first brilliant results in crystallography, demonstrating the great potential of such methods in studying complex structures. D. Hodgkin did not stop there and extended her research to related compounds, solving the problem of the spatial features of calciferol, lumisterol, suprasterol II, and other substances with a similar structure.

It should be noted that Dorothy Crowfoot Hodgkin spent most of her career as a researcher and lecturer in Somerville, primarily teaching chemistry at women's colleges. In 1946, she became a university lecturer and demonstrator; in 1956 – a lecturer in X-ray crystallography; and in 1960, she was appointed a Wolfson Research Professor of the Royal Society. Initially, she worked at the Department of Mineralogy and Crystallography, where G. L. Bowman was a professor. In 1944, the department was divided, and Dr. Hodgkin continued to work in the Department of Chemical Crystallography [9]. Among Dorothy Hodgkin's students was Margaret Thatcher, who worked in her laboratory for a time, conducting X-ray crystallographic analysis of the antibiotic gramicidin C. Despite their opposing political views – Thatcher as a Conservative leader and Hodgkin as a supporter of the Labor Party – they were close and maintained a warm relationship. During her tenure as prime minister, Margaret Thatcher kept a photo of her former university professor on her desk [15].

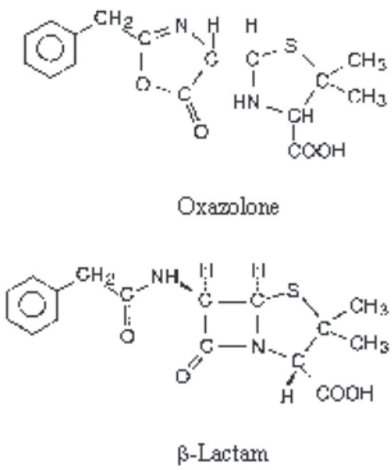
Let' us look now at Dorothy Hodgkin's groundbreaking discoveries that significantly impacted the

Professor Dorothy Crowfoot Hodgkin, 1964 [14]

development of the related fields of medical science and made her known worldwide: the discoveries of the structures of penicillin, vitamin B_{12}, and insulin.

The structure of penicillin

In 1942, during World War II, Dorothy Hodgkin began studying molecular structure of penicillin, supported by the Rockefeller Foundation. Oxford was one of the few places in the world where such



The differences in the proposed structures of penicillin. Structures containing oxazolone and β-lactam cycles [16] research was conducted during wartime. The penicillin research was highly demanded at the wartime.

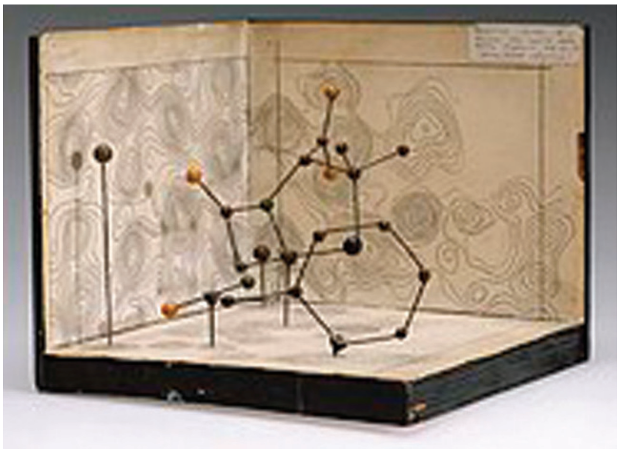
At the time, crystallizing penicillin had failed yet, likely due to impurities with barium, but after several attempts, Dorothy's team successfully crystallized sodium, potassium and rubidium salts of penicillin and obtained X-ray diffraction images. Two possible structures were suggested: one with an oxazolone ring and another with a β-lactam ring [16].

Calculations revealed that the β-lactam ring was the most probable penicillin structure. Simultaneously, R. Woodward came to the same conclusion through thermochemical experiments [17].

As noted above, mathematical analysis of X-ray data was an arduous task. D. Hodgkin acknowledged that determination of the penicillin structure would of the Patterson have been achieved in the early 1940s if scientists had three-dimensional maps of Patterson function at their disposal, which were not available at the time.

Despite all the difficulties, and through sheer persistence, Dorothy and her team succeeded in deciphering the structure of penicillin in 1945, which made the mass production of this life-saving drug possible. Because wartime work on penicillin was secret, the findings on penicillin structure were not published until 1949.

Dorothy Hodgkin's next monumental achievement was the determination of the vitamin B_{12} structure (1948-1956) [7].



A molecular model of penicillin by Dorothy Crowfoot-Hodgkin [14]

The structure of vitamin B_{12}

In 1948, Hodgkin became intrigued by the structure of vitamin B_{12} – the most structurally complex vitamin among known at the time. Its complex molecular structure was a major puzzle for scientists at the time, even though as early as the 1920s, American doctors (future Nobel laureates) had demonstrated that B_{12} was synthesized in the liver and could treat pernicious anemia, that is, to be an antianemic agent [17]. However, isolating the antianemic factor in crystalline form remained unresolved for several decades until 1948, when two independent groups of researchers achieved this milestone. The teams from well-known pharmaceutical companies – Glaxo in England (Ernest Lester Smith with colleagues) and Merck in the United States (Karl August Folkers with colleagues) – succeeded in obtaining crystalline samples of the elusive and mystical yet vital substance from mammalian liver.

Further investigation of these red crystals revealed the presence of cyanide, cobalt and amino groups. As vitamins containing amino groups were categorized under the B group, Karl Folkers, head of the Merck laboratory, named the compound "*vitamin B_{12}*", or *cyanocobalamin*.

While research groups from the United States and England competed on an equal footing to isolate cyanocobalamin crystals, solving the molecular structure of vitamin B_{12} was ultimately a triumph of the British biochemical school. There were objective reasons for this. Thus, the leading experts in structural chemistry, who employed the advanced method of X-ray diffraction analysis, worked at the University of Oxford (UK). It should be noted that, at critical stages, the British researchers sought assistance from their American colleagues to tackle arch-complex challenge, later recognized with a Nobel Prize.

Ernest Lester Smith, head of the Glaxo research laboratory, once he had obtained vitamin B_{12} crystals and, recognizing that the next logical step would be to decipher the structure of the molecule, entrusted the crystals to Dorothy Hodgkin, a leading expert in X-ray crystallography at Oxford University.

By 1948, this remarkable woman-scientist had already accomplished outstanding tasks, including determining the structures of cholesterol, calciferol (vitamin D_3), penicillin, hemoglobin, and globulins of plant origin. Before World War II, she had begun analyzing the structure of insulin but paused this work to focus on the penicillin structure – an essential antibacterial agent that saved countless lives during the war.

Deciphering the molecule structures using X-ray diffraction analysis was an incredibly complex, multi-step and time-consuming process, but it was discovered that analyzing substances whose molecules contained metal atoms was comparatively easier. Metal atoms, being the heaviest in the molecule, produced more distinct signals, making their identification easier than interpreting spectral data from other elements. This crucial insight is credited to Dorothy Hodgkin. When it was determined that the vitamin B_{12} molecule contained cobalt, the work went forward.

Further research revealed that the cobalt atom was bonded to a carbon atom and a porphyrin ring, marking the first time discovery of a “carbon-metal” bond in organometallic compounds.

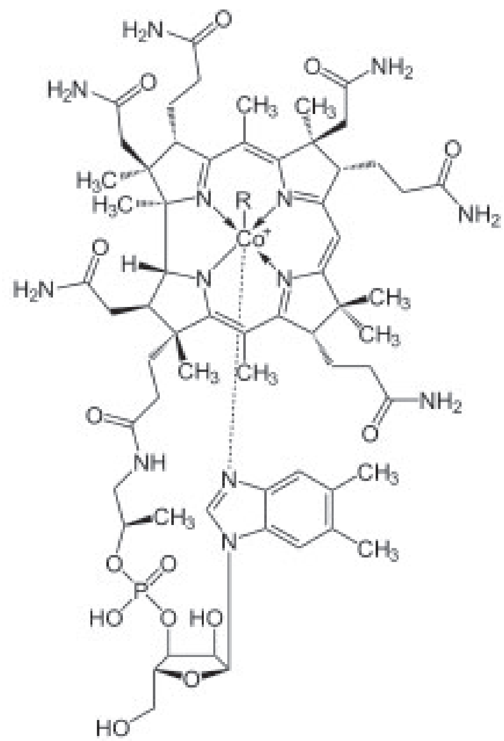
The main challenge of the X-ray diffraction method was the mathematical interpretation of the vast X-ray data. This involved complex calculations and plotting two-dimensional and later three-dimensional maps of molecular bonds – a rigorous and laborious task.

Dorothy Hodgkin was the only one who used the innovative approaches she developed, which streamlined these calculations, significantly reducing the time required without compromising accuracy in determining all components and bonds in the molecule. However, everything appeared to be much more intricated in the case with cyanocobalamin. The complexity of cyanocobalamin’s structure, containing approximately 100 atoms, necessitated extensive and precise calculations, which became easier to make since the mid-1950s when the first electronic computers were introduced. Dorothy Hodgkin sought assistance from American scientists who pioneered the development and use of computers to determine chemical structures – Dr. Kenneth Nyitray Trueblood and his colleagues from California.

Alexander Robertus Todd, an outstanding Scottish chemist and Nobel Laureate in Chemistry in 1957, also made a significant contribution to understanding cyanocobalamin composition. Using chemical methods, he identified its components and functional groups in 1955 [17].

Applying all the findings and discoveries, Dorothy Hodgkin succeeded in completing the analysis of vast crystallographic data and determined the precise structure of vitamin B_{12} in 1956 [18-20].

Thus, in 1956, the structure of vitamin B_{12} was deciphered, the molecule was found to contain 90 atoms. Dorothy Hodgkin’s exceptional merits were recognized with the Nobel Prize in Chemistry in 1964 “*for her determinations by X-ray techniques of the structures of important biochemical substances*” [1].



Structure of cobalamin (vitamin B_{12}) [14]

Lawrence Bragg, a renowned crystallographer and winner of the 1915 Nobel Prize in Physics, described the significance of these Dorothy Hodgkin’s discoveries as “*breaking the sound barrier*” for medicine [5].

At the ceremony of awarding Dorothy Hodgkin the Nobel Prize in Chemistry in 1964, Gunnar Hägg, a member of the Royal Academy of Sciences, said: “*Knowledge of a compound’s structure is absolutely essential in order to interpret its properties and reactions and to decide how it might be synthetized from simpler compounds… The determination of the structure of penicillin has been described as a magnificent start to a new era of crystallography... The determination of the structure of vitamin B_{12}, has been considered the crowning triumph of X-ray crystallographic analysis, both in respect of the chemical and biological importance of the results and the vast complexity of the structure*” [10].

The culmination of the meticulous research of vitamin B_{12} – essential for preventing pernicious anemia – was its chemical synthesis, enabling the mass production of this vital vitamin. This synthesis, based on the structure determined by Dorothy Hodgkin, was accomplished by Robert Woodward in the USA, the genius of organic synthesis in the 20th century and the Nobel Prize laureate in chemistry in 1965 [17].

After receiving the Nobel Prize, Dorothy Hodgkin continued to work hard, and in 1972, she determined the structure of Zn-insulin, a molecule nearly nine times larger than the molecule of vitamin B_{12}.

Investigation of the insulin structure

Insulin was one of Dorothy Hodgkin's most extraordinary research projects. It all began in 1934 when Robert Robinson provided her with a small sample of crystalline insulin. The hormone captivated her imagination due to its complex and wide-ranging effects on the human body [33]. However, at that time, X-ray crystallography was not yet advanced enough to handle the complex insulin molecule. Dorothy and other researchers spent years developing the technique to its full potential. Hodgkin's desire to decipher the structure of insulin was on hold until the end of the war when she became a professor and finally began working with her team of young scientists.

Focused on the research of insulin in 1935, D. Hodgkin faced serious challenges in producing sufficient quantities of this protein. After trying varying methods, she successfully grew crystals that provided usable diffraction patterns. To confirm that the signals came from the protein itself, she conducted a xanthoprotein reaction.

At the time, very few experts had experience in analyzing crystallographic data of proteins. There were several reasons for this: first of all, obtaining high-quality protein crystals. For some poorly structured proteins, this task was utterly irresolvable.

The situation remained unsolvable for compounds with complex structures, and even more so for biopolymers. The breakthrough came in the 1930s when A. L. Patterson developed a new approach to interpreting crystallographic data – the Patterson function (described at the beginning of this article).

Even with these advances, Hodgkin faced another major problem: the lack of computing algorithms to process crystallographic data. Electronic calculations became available only after 1950. A particular issue was also an accurate interpretation of the obtained and theoretically calculated data.

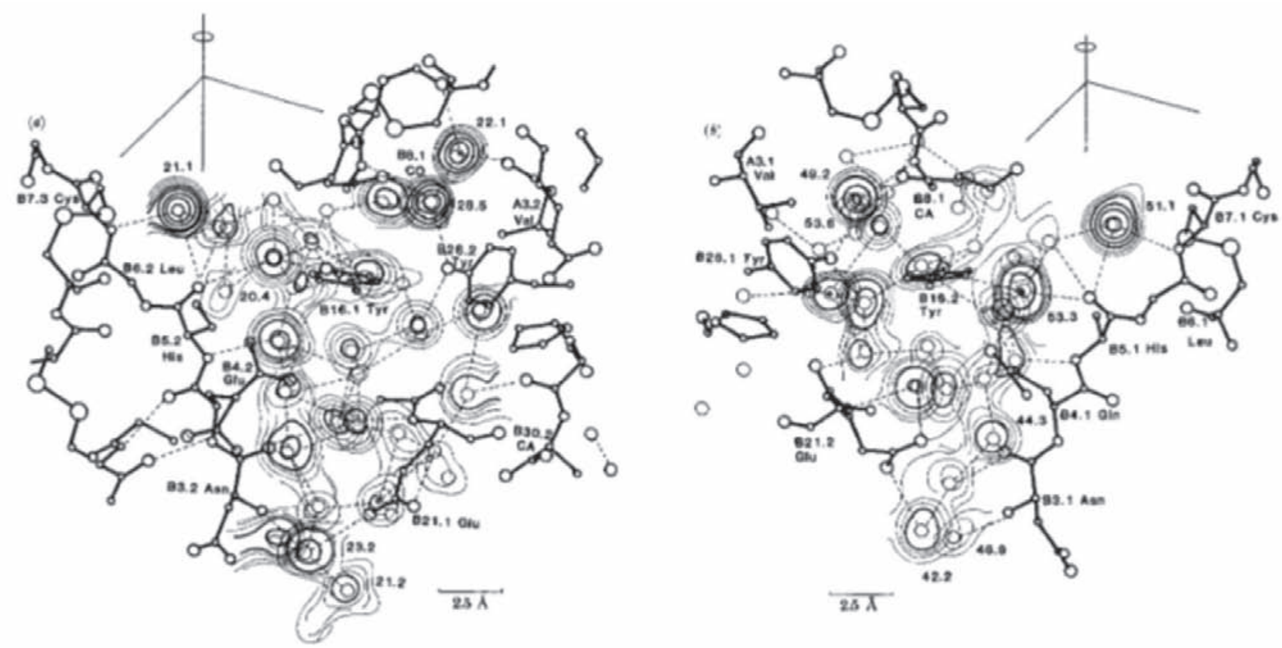
Dorothy Hodgkin in the laboratory, 1964 [21]

The study on insulin was delayed several times, not least because of the urgency of deciphering the structure of penicillin, which was desperately needed during World War II. The complete structure of insulin, a molecule comprising approximately 800 atoms, was therefore established by Dorothy Hodgkin only in 1969 [22].

Thus, it took 35 years from the first photograph of an insulin crystal for X-ray crystallography to gain the means to fully analyze such a large and complex molecule.

Dorothy Hodgkin's findings on insulin structure paved the way for insulin mass production and its widespread use in treating type 1 and type 2 diabetes. Her work also allowed scientists to modify insulin's structure to develop more effective treatments for patients. She continued collaborating with other laboratories engaged in insulin research. She traveled the world consulting and giving lectures about insulin and its importance to the future of diabetes treatment.

Hodgkin's breakthrough was also prompted by the discoveries of Frederick Sanger, who determined the amino acid sequence of the hormone insulin in 1955 (Nobel Prize in Chemistry 1958 [23, 24]. This foundation enabled the first synthesis of human insulin through genetic engineering in 1979. Three years later, the American company Genentech launched industrial production of human insulin using genetically modified *Escherichia coli* bacteria.



Electron density map of the zinc-binding fragment of insulin [8]

In addition to her major and landmark works, D. Hodgkin is known for her research on small molecules with biological activity. Dorothy Hodgkin had a solid reputation in the field, and many researchers turned to her laboratory in Oxford for authoritative advice. Thus, for example, the structures of morphine and some antibiotics were decoded under her guidance. She became the world's leading expert in the use of X-ray crystallography to determine the three-dimensional structure of complex organic molecules [13].

Her research on penicillin, insulin, and vitamin B_{12} earned her immense respect in the scientific community [25, 26]. In 1958, Dorothy Hodgkin's laboratory was transferred to the Oxford University Museum of Natural History. She held various prestigious positions: Research Professor at the Royal Society of London (1960-1977) and Member of the Council of Wolfson College, Oxford (1977-1982). Additionally, she served as Honorary Rector of the University of Bristol (1970-1988) and President of the International Union of Crystallographers (1972-1975) [27, 28].

Personality and Private Life

Dorothy Hodgkin's mild and modest demeanor concealed her steely determination to achieve her goals, no matter what obstacles stood in her way. She inspired deep loyalty among her students and colleagues, even the youngest of whom affectionately called her "Dorothy". She spent a significant portion of her Nobel Prize to support her university, students, and laboratory projects [4].

Dorothy Hodgkin was an engaged lifelong activist. Dorothy's uncles (Grace Mary's four brothers) were killed in World War I, and this heart-breaking loss profoundly impacted Dorothy, prompting her to be later a strong supporter of the League of Nations [4]. From 1962, she participated in Pugwash Conferences and served as President of the Pugwash Movement (1975-1988), opposing nuclear weapon proliferation). She also chaired the Medical Aid Foundation for Vietnam and was a member of a commission investigating U.S. war crime during the Vietnam War. In 1992, she signed the "World Scientists' Warning to Humanity".

In 1937, Dorothy Crowfoot married Thomas Lionel Hodgkin, a historian and activist who spent a long time in West Africa, where he was an ardent supporter and chronicler of the emerging post-colonial states. He was a member of the *Communist Party and later wrote several major works on African politics and history, and later became a distinguished lecturer at Balliol College, Oxford [29]. (*Because of the political activism and Communist Party membership, Thomas Hodgkin was banned from entering the United States from 1953).

Dorothy was happily married. The couple had three children: Luke (1938-2020), Elizabeth (born

1941), and Toby (born 1946). Their oldest son Luke became a mathematics lecturer at the new University of Warwick, England. Their daughter Elizabeth pursued her father's career as a historian, and their younger son Toby became a botanist and agriculture scientist.

Last Years

Dorothy Thomas' husband, Lionel Hodgkin, retired from the service in 1970 and returned to his parents' home in Ilmington, Yorkshire and continued to work until his last days. He died in 1982 after a long illness now known as lymphogranulomatosis (Hodgkin's disease). His death deeply shocked Dorothy: the bouts of rheumatoid arthritis that had plagued her since her younger years became more frequent [28], but she continued her research and attended the International Conferences on Crystallography (IUCr International Union of Crystallography) in Bordeaux, 1990 and Beijing, 1993.

Dorothy Mary Crowfoot-Hodgkin died of a stroke on July 29, 1994, leaving behind an extraordinary scientific legacy. Her research on biomolecule structures established the standards for a field that developed largely throughout her working life - the crystallography of complex molecules of proteins, vitamins, antibiotics, and the like. She made fundamental contributions to understanding how these molecules function in living systems [30]. Dorothy remains the only British woman to receive the Nobel Prize in Natural Sciences. She was not only a fantastic scientist but also an icon for many women in science. She made breakthrough discoveries at a time when very few women were even studying chemistry, let alone contributing to the development of modern medicine.

Dorothy Crowfoot Hodgkin portrayed on the postage stamp [32]

Dorothy Hodgkin's Order of Meri exhibited at the Royal Society in London [14]

Recognition and awards

Dorothy Hodgkin was a member of numerous scientific academies worldwide, including the Royal Society of London (since 1947), the US National Academy of Sciences (1971), the Academies of Sciences of the Netherlands, Yugoslavia, Ghana, Puerto Rico, Australia, and the former USSR. She held honorary degrees from Cambridge, Harvard, and the Universities of Chicago, Leeds, Manchester, Sussex, and the University of the Republic of Ghana, among others.

She received many high scientific honors and state awards, including the Royal Medal of the Royal Society of London (1956) [2], the Nobel Prize in Chemistry for determining the structures of biologically active substances using X-rays (1964), Order of Merit (1965), Bunting Medal (1972), Copley Medal, (1976), to name but a few.

An asteroid (5422) discovered on December 23, 1982, was named in her honor [31]. Dorothy Crowfoot Hodgkin was honored with commemorative postage stamps issued in the United Kingdom in 1996 and 2010 [32].

The National Portrait Gallery in London has 17 portraits of Dorothy Hodgkin.

The Royal Society established the Dorothy Hodgkin Fellowship, which "*aims to support outstanding early career scientists who require a flexible working pattern due to personal circumstances, such as caring responsibilities and/or health-related conditions*" [34].

«ДОМОГОСПОДАРКА З ОКСФОРДУ» ЧИ ЄДИНА БРИТАНСЬКА ЖІНКА-НАУКОВИЦЯ, ЯКА НАГОРОДЖЕНА НОБЕЛІВСЬКОЮ ПРЕМІЄЮ З ПРИРОДНИЧИХ НАУК? – ДОРОТІ КРОУФУТ ХОДЖКІН

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Дороті Кроуфут Ходжкін – британська хімікиня, лауреатка Нобелівської премії, яка вдосконалила метод рентгенівської кристалографії для визначення структури біомолекул, що стало важливим кроком для розвитку структурної біології. В 1964 році Дороті Ходжкін отримала Нобелівську премію з хімії «за визначення за допомогою рентгенівських променів структур біологічно активних речовин», зокрема вітаміну B_{12} та антибіотика пеніциліну. Через п'ять років після отримання нагороди, Дороті Ходжкін також встановила структуру інсуліну. І хоча газета The Daily Mail у своєму заголовку назвала її «Домогосподарка з Оксфорду», Дороті Ходжкін подолала гендерну нерівність і стала третьою жінкою в історії, яка була нагороджена Нобелівською премією з хімії і залишається єдиною Британською жінкою-вченим, нагородженою цією найпрестижнішою премією в галузі наук.

Ключові слова: Нобелівська премія з хімії, Дороті Ходжкін, рентгенівська кристалографія, структури пеніциліну, вітаміну B_{12}, інсуліну.

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