William Garfield (Bill) Dauben, the son of architect Hyp J. Dauben and Leilah Dauben, was born in Columbus, Ohio. I know little about Bill’s boyhood—he didn’t talk much about his early years—but I did learn that he showed early promise even in high school. Bill participated in many activities and did well both in sports and the classroom, particularly in math and science. He loved chemistry even then, and came in first in the state in the Ohio Chemical Examinations.

Bill was the youngest of three boys. His middle brother, Jack, was a clothing salesman but Bill followed the footsteps of his eldest brother, Hyp J. Dauben, Jr. (1915–1968), who became an organic chemist and a professor of chemistry at the University of Washington. Hyp went to The Ohio State University, where he got his A.B. and M.Sc. degrees (1937), and did undergraduate research there with William Lloyd Evans in carbohydrate chemistry. Hyp then pursued graduate studies at Harvard University, where he did his Ph.D. research with Paul D. Bartlett in physical organic chemistry. Bill Dauben followed a few years behind. In 1937 he too entered The Ohio State (A.B. 1941) and did undergraduate research with Evans as well. Bill also went on to Harvard (M.A. 1942, Ph.D. 1944), where he was awarded an Edward Austin Fellowship for graduate studies, and parted company with his brother by concentrating on synthetic organic chemistry.

Bill worked first with Reginald Patrick Linstead but after a year switched to Louis Fieser in order to perform the synthesis of new antimalarial drugs. In this period he synthesized a naphthoquinone derivative known as M-1916, which at the time showed promise as an antimalarial. The story is told in Fieser’s book, *The Scientific Method*, which includes a wonderful picture of a very young Bill Dauben.
In 1945, Bill came to the University of California, Berkeley, as an instructor. He and James Cason, who arrived at the same time, were the first appointments in a postwar expansion of organic chemistry and chemical engineering planned by Wendell Latimer, dean of the College of Chemistry. Dauben and Cason initiated new courses and pursued further expansion that included the appointments of Henry Rapoport in 1946 and Donald S. Noyce in 1948. This group added modern organic chemistry to a department already exceptionally strong in physical and nuclear chemistry.

Bill Dauben was promoted to assistant professor in 1947, associate professor in 1952, and professor in 1957. During his long career at Berkeley he helped to train over 200 undergraduate, graduate, and postdoctoral researchers, together with many visiting scholars, in the course of carrying out investigations and publishing almost 400 papers. Bill was still doing active experimental research at the time of his sudden and unexpected death in his sleep during the early morning hours of January 2, 1997, at age 77.

Dauben was a chemical professional. He was rather formal in behavior and style, rarely seen without a white shirt and bow tie. He was always “Professor Dauben” to his students, very much mirroring the era of his professorship. For each of his students, as years passed from their time at Berkeley, his letters and Christmas cards would evolve to a more peer-like status, from his handwritten “WGD” to “Bill.” He always controlled his emotions and was never rude or intemperate. He was collegial to all, and built up associations with chemists around the world.
Dauben’s research interests covered a broad range. Indeed, the diversity of organic chemistry that he studied over his multi-decade career was one of his greatest strengths. This diversity included the use of C-14 as a tracer, the synthesis and chemistry of small-ring and strained compounds, organic photochemistry, and the use of high pressure in synthesis. Nevertheless, the core of all of these studies was his fascination with natural-products chemistry, reaction mechanisms, and structure determination, which were recurrent themes in virtually all of his research.

**C-14 tracer and steroid chemistry**

When he first came to Berkeley, Dauben was invited by Melvin Calvin to join his newly formed Bio-organic Group—with members such as James C. Reid, Bert M. Tolbert, and Peter E. Yankwich—which had been organized to develop the use of C-14 in organic chemistry and particularly in tracing the course of carbon in photosynthesis. Dauben collaborated actively with members of the group, contributing organic synthesis techniques in the preparation of labeled compounds and in turn learning about the handling and counting of C-14. Among the results of these collaborations was an early study on the Willgerodt reaction, a reaction that results in the movement of a carbonyl group to the end of a chain. The question is whether the carbonyl group with its carbon does the movement or whether the carbon chain remains intact and only the oxygen migrates. Labeling one carbon of acetophenone showed that the conversion to phenylacetamide occurs without skeletal rearrangement (Eq. 1).³

\[
\begin{align*}
\text{PhC}^*\text{OCH}_3 & \xrightarrow{\text{NH}_4\text{OH}} \text{PhC}^*\text{H}_2\text{CONNH}_2 \\
\text{PhC}^*\text{OCH}_3 & \xrightarrow{\text{Pyridine}} \text{PhC}^*\text{H}_2\text{CONNH}_2 \\
\text{PhC}^*\text{OCH}_3 & \xrightarrow{\Delta} \text{PhC}^*\text{H}_2\text{CONNH}_2
\end{align*}
\]

Equation 1

I don’t know why Dauben did not continue in the Calvin group, but I suspect it was to maintain his independence from Calvin—both of them were strong personalities. Instead, Dauben entered a long collaboration with physiology professor I. L. Chaikoff that resulted in some 50 papers dealing largely with the biological synthesis and metabolism of cholesterol and related steroids and triglycerides and also with the
formation, absorption, and lymphatic transport of fatty acids. The use of C-14 labeled compounds was key to these studies and this part was surely Dauben’s contribution to this collaboration.

H. Leon Bradlow came to Berkeley early in the Chaikoff/Dauben collaboration as a joint fellow with the two scientists. His project under Dauben’s direction was to synthesize cholesterol with a C-14 labeled side chain. At the same time, Jerome F. Eastham, another early coworker, synthesized ring-labeled cholesterol. One of their notable achievements was evidence using C-14 labeling that favored a proposed alternative to Sir Robert Robinson’s early mechanism for the biological conversion of squalene to cholesterol (Eq. 2). Bradlow and Eastham’s mechanism had also been proposed independently by R. B. Woodward and K. Bloch and published slightly earlier.

This early research involved Dauben in terpene and steroid chemistry—interests that lasted his entire career.

Organic photochemistry

In 1957, Dauben published, with G. J. Fonken, their work on “The Structure of Photoisopyrocalciferol,” marking the beginning of Dauben’s four decades of photochemical studies. His photochemistry research was pioneering, and he was at the forefront of the surge of activity in this area in the 1960s and 1970s. Dauben’s approach to organic photochemistry was to find pathways of reactivity leading to new reactions and syntheses, and then to explore the mechanistic significance of these observations.

His studies form the basis for the present understanding of polyene photochemistry, particularly with his mechanistic and synthetic investigations related to vitamin D. Although the photochemistry of vitamin D had been studied for many decades, few details had been worked out prior to Dauben’s research and that of others, including
the Havinga group in Leiden. In the early stages of organic photochemistry, unusual rearrangement products were being discovered, typically containing unique structures that required extensive ingenuity to unravel. Among Dauben’s earliest photochemical adventures was the determination of the structures of the over-irradiation products of the ergosterol-vitamin D series of compounds. The structure determinations of photopyrocalciferol, in addition to photoisopyrocalciferol, were among Dauben’s earliest successes.

Dauben also found that vitamin D$_2$ is photochemically transformed to suprasterol I and its stereoisomer suprasterol II. What is especially significant is that he was able to determine the structures of these compounds with primarily classical chemical methods.

Subsequent X-ray studies revealed that the stable form of vitamin D has the extended triene structure shown above, which corresponds to the 1-$s$-cis, 3-$s$-trans rotomer. Ring closure yields the suprasterols; the stereochemical differences in these two compounds arise only from the relative directions of the ring closures.

Thus began Dauben’s four decades of photochemical investigations, which resulted in the discovery of novel photochemical reactions and the determination of the structures of many remarkable photoproducts. He and others noted that 1,3-cyclohexadienes have
two primary routes of photoisomerization: to 1,3,5-hexatrienes (such as the ergosterol → previtamin D as shown above); and to bicycle[2.2.0]hexenes (such as the photopyro- and photoisopyrocalciferols) shown below. Dauben also was fascinated by the formation of the bicyclo[3.1.0]hexenes from the 1,3,5-hexatrienes, such as the suprasterols above.

For example, Dauben discovered that palustric acid photolyzes only to the 1,3,5-hexatriene shown below, while its sibling, levopimaric acid, isomerizes to the bicyclo[2.2.0]hexane. Shortly thereafter, he discovered a cyclohexadiene which, upon photolysis, produces both the [2.2.0] product and the hexatriene simultaneously. By
examining the wavelength and temperature dependence of these and analogous photo-
reactions, he was able to conclude that ground state conformations are important
controlling factors in many photochemical reactions.

This fundamental principle was generalized with other examples based on the hexalins 1-4.

The triene 2 is first formed by a ring-opening reaction, followed by the buildup of the
two final photo-products, the bicyclo[3.1.0]hex-2-ene 3 and the cyclobutene 4. An
increase in the steric bulk of R results in an increase in 4 relative to 3. The initial triene 2
can either return to 1 or form the cyclobutene 4.

Rotation about the single bond gives the s-trans rotomer, which cannot give 1 or 4 but
only the bicyclic compound 3. The s-trans rotomer is disfavored by bulky R groups, such
as isopropyl or t-butyl; these substituents favor the formation of 4.
These examples show Dauben’s approach in a wide-ranging study that was especially important in establishing the role of the triplet state in the photochemistry of dienes and trienes. The resulting synthetic routes to cyclobutenes led to further studies on the stereochemistry of thermal ring-opening of these compounds and contributed importantly to the experimental basis for the Woodward-Hoffmann rules for photochemical electrocyclic processes. Dauben’s characterization of the role of ground state conformational control in organic photochemistry was a highly controversial concept when first proposed, but it is now the basis for understanding many photochemical mechanisms. His perception of the importance of conformations in reactions was demonstrated quite early by his 1956 chapter, coauthored with his colleague Kenneth Pitzer, on “Conformational Analysis” for Melvin S. Newman’s book on *Steric Effects in Organic Chemistry.*

Following Dauben’s work discussed above, many additional examples were reported by others. The presence of a triene in a ring restricts conformational mobility and further demonstrates the generality of Dauben’s findings. For example, irradiation of the diene 5 gives a strained cyclononatriene 6 containing a trans-double bond, which on further irradiation gives two products: 7, resulting from an electrocyclic reaction of the diene portion; and 8, resulting from a 1,3-suprafacial hydrogen sigmatropic rearrangement.

Dauben’s interest in Vitamin D lasted his entire life. And a continuation of these studies formed an important part of a National Institutes of Health (NIH) proposal put forward at the time of his death. Dauben’s final studies in this area made use of tunable dye lasers and the effect of wavelength dependency on the photochemical behavior, fluorescence spectra, and quantum yields of previtamin D. In a real sense, his photochemical research had transitioned from descriptive organic chemistry to photophysics and high-level quantum theory, as demonstrated by his important 1975 collaboratory paper, *A Classification of Photochemical Reactions.*
Strained rings

For many years, Dauben studied highly strained ring compounds. For example, in 1961, he and R. L. Cargill observed the photoinduced valence-bond isomerization of norbornadiene to quadricyclane.

\[
\text{Norbornadiene} \xrightarrow{\text{hv}} \text{Quadricyclane}
\]

In 1970, Dauben published on the metal-catalyzed and thermal isomerizations of cubane derivatives and on the related chemistry of such strained ring compounds.

Natural products

In the natural products area, Dauben developed the structure and chemistry of ψ-san-tonin—the first eudesmane sesquiterpene lactone, a class now found to be widely distributed in nature. His study of the acid-catalyzed rearrangement of this compound not only extended the scope of the well-known dienol-phenol rearrangement but also led to the correction of the structure of the lactone terpene artemesinin. Dauben’s studies of thujopsene—a tricyclic sesquiterpene that is a constituent of the wood oils and heartwood of many genera belonging to the natural order Cupressales—included its synthesis and various rearrangements, some of which were followed by deuterium labeling.
Different conditions give rise to a number of rearrangements (probably the most extensive of any known sesquiterpene), which he summarized as in the figure below.

In 1962, Dauben reported the structure of the diterpene cembrene, the first naturally occurring 14-membered ring compound, and in 1974 he reported its first synthesis. This nucleus has since been found to be the most widely distributed diterpene in nature, being a constituent of trees, other plants, insects, and soft coral; and many cembrene derivatives possess interesting biological activity. Dauben also studied the rearrangements and photochemistry of this important diterpene.
Dauben’s total syntheses of natural products also included all of the naturally occurring spirotetivanes—α- and β-vetispirenes, β-vetivone, and hinesol—as well as the fusidic acid. A potent steroidal antibiotic, fusidic acid is structurally unusual because of its unnatural ring fusions between rings B and C and between rings C and D. These structural features, plus the multiplicity of substituents, pose a significant synthetic challenge for any laboratory.

**New synthetic methods**

Dauben developed a variety of new synthetic processes for different types of compounds. These processes included, for example, the stereospecific synthesis of cyclopropanols and their utilization in the preparation of β-substituted lactones. He showed that the intramolecular Wittig reaction is an efficient process for the preparation of cyclic olefins. And
he developed one of the most useful methods for the attachment of the side chain to a steroidal nucleus.

A special interest late in Dauben’s career was the use of super-high pressure in synthetic organic chemistry—a method that has since been widely used by others. He showed in particular that the method is useful in reactions that are sterically hindered or sensitive to acid- or base-catalysis. Such reactions include a variety of cycloadditions, 1,4-conjugate additions, ketalizations, etherification and esterification, phosphonium salt formation, and the Wittig reaction itself.

He was especially proud of this method’s efficient synthesis of cantharidin—an active agent of *Cantharis vesicatoria* and the putative aphrodisiac in “Spanish fly.” The compound has other commercial applications in medicine. Its structure suggested availability by straightforward Diels-Alder reactions, but synthesis via this route was accomplished only with great difficulty. The Dauben group discovered, however, that a useful Diels-Alder approach from readily available starting materials resulted by reaction under 15 kbars pressure. The major product, converted by one step to cantharidin, represented the first total synthesis feasible on a large scale.

![Diels-Alder reaction](image)

**Awards and service**

Bill Dauben received such a large number of awards for his research discoveries and skills that I’ll mention only a few. He was honored with two Guggenheim Fellowships, in 1951 and in 1966. He was a recipient of the California Section Award of the American Chemical Society (ACS), the Ernest Guenther Award in the Chemistry of Essential Oils and Related Products, and the Senior Scientist Award of the Humboldt Foundation. He was a Miller Professor at UC Berkeley and on becoming emeritus he was awarded a
Berkeley Citation. Bill was a fellow of the American Academy of Arts and Sciences and in 1970 was elected to the National Academy of Sciences, where he served as chair of the chemistry division from 1977 to 1980. In 1980, he was awarded the honorary degree of Doctor Honoris Causa from the University of Bordeaux, France.

Bill served his profession in many ways, including as a participant in an NIH study section and as a member of the chemistry panel of the National Science Foundation. He served on the editorial board of the *Journal of Organic Chemistry*, as chair of the organic division of the ACS, as editor of *Organic Syntheses*, and as president and editor-in-chief of *Organic Reactions*. In Bill’s 51-year career at UC Berkeley he served the campus in many ways, including a term as chair of the Academic Senate Committee on Academic Planning, membership in several administrative committees related to hazardous materials and waste management, and a five-year tenure on the Campus Discipline Committee. He was an inspiring teacher. Bill served national and international organizations as well. He was, for example, a member of the board of trustees of the International Photochemistry Foundation.

Bill was a typical Berkeley professor in that he actively and effectively promoted his own research interests but gave highest priority to the welfare of the Chemistry Department’s organic group and of the department as a whole. I recall how he encouraged me to give a special-topics course during my second year at Berkeley. This course gave me the opportunity to present some new ideas in organic-reaction mechanisms. He also encouraged me to write my review on “Solvolytic Displacement Reactions,” a work that had a positive and important impact on my career. Ever interested in teaching, Bill pressed the organic group to continually develop and improve our course sequences and content in organic chemistry.
The man

Not long after he arrived in Berkeley, Bill met Carol Hyatt, who was then a graduate student in physics. Married in 1947, the Daubens enjoyed traveling through Bill’s sabbatical leaves and his frequent attendance at international meetings. As a result, they had friends around the world, especially in England, France, and Switzerland, and they frequently entertained international visitors at their house on Eagle Hill, just north of Berkeley, which they built in 1953.

A dinner party arranged one year for a visiting professor, Duilio Arigoni of the ETH, Zürich, was particularly memorable. Bill had asked me for advice on a suitable Italian wine for the occasion and I recommended a wine shop that specialized in Italian vintages. He researched these wines carefully and with the help of the proprietor finally picked one. Arigoni pronounced Bill’s choice of wine excellent, and he was even able to pinpoint the location of the vineyard. Bill was so proud of his wine choice that he alluded frequently to this fond event.

Bill’s favorite hobby was golf. He played it regularly, often with his wife, and organized an annual golf tournament with his research group. Bill was also one of the regulars at the chemistry luncheon table at the Faculty Club. He enjoyed a relaxing hour at lunch talking with colleagues about various topics (not only chemistry), after a busy morning and facing an equally busy afternoon.

Bill treated his students with warm respect, and this feeling was reciprocated. After his nominal retirement, many of his former research group members contributed to an endowment for an annual Dauben Lecture—the 20th was given in the spring semester of 2014. On August 31, 1976, to celebrate Bill’s “first 30 years at Berkeley,” 40 past and
present group members held a party at a San Francisco restaurant. There they presented
him with a *festschrift* of approximately 100 letters of tribute from his group and other
colleagues.

Some excerpts from these letters provide a measure of the man:

*There were many ways in which we felt that Professor Dauben was like a
father figure to us. He was certainly a central focus in our lives while [we
were] graduate students.*

*When I arrived in Berkeley [and went] to see Professor Dauben in his
office for the first time, around the middle of September 1955, I was
greatly impressed and encouraged by his heartfelt words.*

*Professor Dauben made three timely suggestions that saved the day and
raised my flagging spirits. [He] opened my eyes to new areas of research
ripe for exploitation, urged me to follow up on unexpected findings, and
imparted a sense of excitement and urgency to my research.*

*Bill Dauben is truly one of a rare breed: the gentleman and scholar that
the world always admires and approves.*

*I was especially impressed by your insistence on good experimental tech-
niques and complete and properly executed experiments. The spirit [that]
you gave to the research group gave us an excitement about chemistry
and a keen awareness of current research.*

*I’ve always admired The Man, as we affectionately knew him, because
he taught by example rather than by precept. His rigorous intellectual
honesty and his personal integrity were then, and remain, models worthy
of emulation. He set high professional standards for himself and for his
coworkers.*

*[W]hat I really learned was this: as important as science is, the all-im-
portant role of the individual is paramount.*
The annual evening dinners in [the Daubens’ home in] Kensington were always a delight. Carol Dauben’s flawless social sense and gracious entertaining were almost as much a part of my education at Cal as were WGD’s weekly discourses at group seminar.

Bill Dauben was a man of common-sense judgment, of warmth, and with a sense of humor. His opinions were valued by his friends and his chemistry colleagues. He highly valued basic research and was a staunch supporter of it. He took a phased retirement and became emeritus in 1990 but stayed active in his field, and at the time of his death he still had research grants and postdoctoral coworkers.

When Bill died on January 2, 1997, he was survived by his wife Carol (who died on January 10, 2010), two daughters—Barbara Baumer and Ann Klaus—and three grandchildren.

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NOTES


SELECTED BIBLIOGRAPHY


Published since 1877, *Biographical Memoirs* are brief biographies of deceased National Academy of Sciences members, written by those who knew them or their work. These biographies provide personal and scholarly views of America’s most distinguished researchers and a biographical history of U.S. science. *Biographical Memoirs* are freely available online at www.nasonline.org/memoirs.