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EDITORIAL

A tribute to Stanislao Cannizzaro, chemical informationist and photochemist

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Stanislao Cannizzaro is known widely for the Cannizzaro reaction, the "disproportionation" of benzaldehyde upon reaction with alkali, for his approach to teaching chemistry, "Sunto di un corso di filosofia chimica", which he presented at the Karlsruhe Congress of 1860, and for his work on the photochemistry of santonin. In Cannizzaro's laboratory two research associates, Giacomo Ciamician and Paul Silber, and a senior colleague, Emanuele Paternó, became acquainted with the basic methods of sunlight-inducd photochemistry.

The life and times of Stanislao Cannizzaro

"In the year 1826 Stanislao Cannizzaro opened his eyes to the resplendent light of July in Palermo." These words of an enthusiastic biographer describe the birth of an Italian patriot and scientist who was destined to play a key role in the development of chemistry in the nineteenth century.[1] After completing the study of medicine at the University of Palermo, Cannizzaro decided to study chemistry. He joined R. Piria, who first isolated salicylic acid, the pain-killing ingredient of willow bark. After two years he left to join Garibaldi's revolt; the failure forced Cannizzaro into exile. He spent three years (1848–1851) in Paris, furthering his chemical education in Chevreul's laboratory.

In 1851 Cannizzaro returned to Italy as professor at Collegio Nazionale di Alessandria (Piedmont). There he completed work on the dismutation of benzaldehyde with concentrated alkali, the Cannizzaro reaction. Four years later, Cannizzaro moved to Genoa where he had adequate teaching facilities, but very poor laboratory space. He used this setting to summarize his method of teaching chemistry ("Sunto di un Corso di Filosofia Chimica"), critically selecting the most consistent data available in the chemical literature. It was from Genoa that Cannizzaro traveled to the Karlsruhe Congress in 1860.

Five years later he resigned this post and joined Garibaldi's renewed Sicilian campaign. After a decisive victory Cannizzaro accepted a professorship in Palermo in 1861, where he had the opportunity to build good laboratory facilities and was able to attract gifted collaborators, including Körner and Paternò.

In 1871 Rome became part of the Italian state and became its capital. Cannizzaro was called to the newly reopened Universita degli studi di Roma, "La Sapienza", as professor of chemistry. He transformed an old convent into the first Italian Institute of Chemistry and worked as its director until his retirement.

On the occasion of his death, Senator Giacomo Ciamician, a former research associate, gave a memorial tribute before the Italian Senate on May 11, 1910, closing with the words: "*Invece Cannizzaro é morto! Ma non é morto per noi: la sua memoria rimarrá sempre scolpita nei nostri cuori. Nella scienza egli é giá immortale!*"[2] [Alas, Cannizzaro is dead! But he is not dead to us: his memory will always remain engraved in our hearts. And his chemistry surely is immortal!]

In 1926, the centenary of his birth, Cannizzaro's mortal remains were transferred to the Pantheon, where, according to our enthusiastic biographer, they "now repose near the remains of the other great with whom he had in common the flame of science and faith".[1] Alas, on a recent visit to the Pantheon (July 2006) the author's tour guide had no knowledge of the great Italian chemist.

Several universities whom Cannizzaro had served named chemistry departments or buildings in his honor: Genoa has an Istituto di Chimica "Stanislao Cannizzaro", and Palermo a Dipartimento di Chimica Inorganica e Analitica, Stanislao Cannizzaro. In 2006 the Chemistry Department of "La Sapienza" named a chemistry building in his honor. Finally, the Accademia Nazionale dei Lincei honors him by awarding biennially the Premio "Stanislao Cannizzaro".

The Cannizzaro reaction

While in Alessandria Cannizzaro published his work on the dismutation of benzaldehyde with concentrated alkali, the Cannizzaro reaction (Scheme 1). In its simplest form, the reaction[3] can be explained by addition of hydroxide ion to benzaldehyde, **1**, followed by hydride transfer from the adduct ion, **A**, to benzaldehyde, yielding benzoate anion, **2**, and benzyl alcohol,

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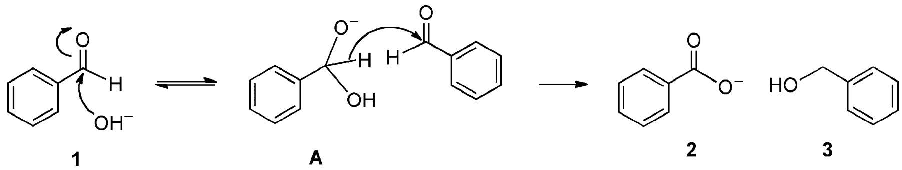


Scheme 1 The Cannizzaro reaction.

	Simboli delle molecole dei corpi semplici e formule dei loro composti fatte con questi simboli, ossia simb. e form. rappresentanti i pesi di volumi eguali allo stato gassoso		Simboli degli atomi de'corpi semplici, e formule dei composti fatte con questi simboli		Numeri esprimenti pesi corrispondent
Atomo dell'idrogeno . . .	𝔥1/2	=	H	=	1
Molecola dell'idrogeno . .	𝔥	=	H^2	=	2
Atomo del cloro	ℭ𝔩1/2	=	Cl	=	35,5
Molecola del cloro. . .	ℭ𝔩	=	Cl^2	=	71
Atomo del bromo	𝔅𝔯1/2	=	Ar	=	80
Molecola del bromo . . .	𝔅𝔯	=	Br^2	=	160
Atomo dell' iodo	𝔍1/2	=	I	=	127
Molecola dell'iodo. . . .	𝔍	=	I^2	=	254
Atomo del mercurio . . .	𝔥𝔤	=	Hg	=	200
Molecola del mercurio . .	𝔥𝔤	=	Hg	=	200
Molec. dell'acido cloridrico	𝔥1/2ℭ𝔩1/2	=	HCl	=	36,5
Mol. dell'acido bromidrico.	𝔥1/2𝔅𝔯1/2	=	HBr	=	81
Mol. dell'acido iodidrico .	𝔥1/2𝔍1/2	=	HI	=	128
Mol. del protocl. di merc.	𝔥𝔤ℭ𝔩1/2	=	HgCl	=	235,5
Mol. del protobr. di merc.	𝔥𝔤𝔅𝔯1/2	=	HgBr	=	280
Mol. del protoiod. di merc.	𝔥𝔤𝔍1/2	=	HgI	=	327
Mol. del deutoclor. di merc.	𝔥𝔤ℭ𝔩	=	$HgCl^2$	=	271
Mol. del deutobr. di merc.	𝔥𝔤𝔅𝔯	=	$HgBr^2$	=	360
Mol. del deutoiod. di merc.	𝔥𝔤𝔍	=	HgI^2	=	454

Fig. 1 Table of selected atoms and molecules in the notations of Avogadro (left) and Cannizzaro (right) with the corresponding weights (based on the weight of H = 1).[10]

Formule dei composti	Pesi delle loro molecole $=p$	Calorici specifici dell'unità di peso $=c$	Calorici specifici delle molecole $=p \times c$	Numeri di atomi nelle molecole $=n$	Calorici specifici di ciascun atomo $=\frac{p \times c}{n}$
$HgCl^2$	271	0,06889	18,66919	3	6,22306
$ZnCl^2$	134	0,13618	18,65666	3	6,21888
$SnCl^2$	188,6	0,10161	19,163646	3	6,387882
$MnCl^2$	126	0,14255	17,96130	3	5,98710
$PbCl^2$	278	0,06641	18,46198	3	6,15399
$MgCl^2$	95	0,1946	18,4870	3	6,1623
$CaCl^2$	111	0,1642	18,2262	3	6,0754
$BaCl^2$	208	0,08957	18,63056	3	6,21018
HgI^2	454	0,04197	19,05438	3	6,35146
PbI^2	461	0,04267	19,67087	3	6,55695

Fig. 2 Table of molar heat capacities of ten triatomic metal halides and heat capacities per atom compiled by Cannizzaro for Sunto di un Corso.[10] The molar heat capacities (18.7 ± 0.9 kcal mol^{-1}) and the heat capacities per atom (6.2 ± 0.3 kcal mol^{-1}) are essentially identical, indicating that the atomic weights of the ten metals and two halogens are consistent.

3. Because the equilibrium precedes the hydride transfer step, the reaction proceeds with third-order kinetics.[4,5]

Sunto di un Corso di Filosofia Chimiche

Because of the extremely limited laboratory facilities at Genoa, Cannizzaro clarified his thoughts on the concepts and theories underlying the basic chemistry, which he presented in his lectures. He based his thoughts on four hypotheses or theories enunciated before, *viz*. John Dalton's atomic theory,[6] Joseph L. Gay-Lussac's law of combining volumes (1808),[7] Amedeo Avogadro's molecular hypothesis (1811),[8] and the hypothesis of atomic heat capacity advanced by Dulong and Petit (1819).[9]

These four contributions are now part of the foundation of modern chemistry. The problem at the time was the lack of a clear and generally accepted nomenclature: how were the *atoms* of Dalton, the *particles* of Gay-Lussac, and the *molecules* and *half-molecules* of Avogadro related? Particularly, Avogadro's nomenclature caused problems: how could *atoms* (Avogadro's *molecules*), indivisible by definition, be split?

Cannizzaro unified the essence of these hypotheses in his paper "Sunto di un corso di filosofia chimica".[10] He reformulated Avogadro's hypotheses using a clear differentiation between the terms *atoms* and *molecules*. In one table he listed atomic and molecular weights of simple elements and compounds: he showed Avogadro's symbols, *e.g.* 𝔥1/2 and 𝔥, and replaced them with H and H^2, in keeping with the proposed use of *atoms* and *molecules* (Fig. 1). In another table Cannizzaro compared the molar heat capacities of ten triatomic metal halides (Fig. 2). The nearly constant values, and the constant heat capacities per atom, show clearly that the atomic weights used are internally consistent. The Sunto is a remarkable document; it presented a unifying view of the science of chemistry and solved all major problems confronting chemists at the time.

Cannizzaro published the Sunto article in *Il Nuovo Cimento*[10] in 1858 and also had it printed as a pamphlet. Fortunately for Cannizzaro, and for the development of chemistry in the nineteenth century, he had the opportunity to present his ideas to an international assembly of his peers at the Karlsruhe Congress in 1860, the first international science congress.[11] The history of the congress and minutes of the proceedings were recorded by C.-A. Wurtz.[12] Wurtz listed 140 chemists from twelve countries, identifying 126 by name and affiliation. The majority of attendees came from Germany (56), France (21), and England (17).

Cannizzaro opposed a proposal "to adopt the principles of Berzelius again . . . " with "some modifications" He delineated flaws in Berzelius' teachings and presented the essence of the Sunto, arguing in favor of Avogadro's hypothesis in his rephrased version and emphasizing the merits of Avogadro, Dumas, and Gerhard. Wurtz must have considered Cannizzaro's presentation significant, for he reported it in great detail; however, it appears that Cannizzaro did not convince the audience:[11] the issue did not come to a vote.

Soon after the Karlsruhe Congress Cannizzaro received a call to Palermo as director of a chemistry laboratory in the planning stages. In 1870 Cannizzaro, with E. Paternò and others, founded a new periodical, *Gazzetta Chimica Italiana*, dedicated to chemistry. The *Gazzetta* played a significant role in the development of chemistry in Italy. It ceased publication 127 years later, in 1997, in order to merge with Belgian, Dutch, French, and German chemistry journals, forming the *European Journal of Inorganic Chemistry* and *European Journal of Organic Chemistry*.

Photochemistry of santonin

In Rome, Cannizzaro began to reap the rewards of his spreading reputation. In addition to numerous national honors, he was elected to honorary membership in chemical societies, including the Gesellschaft deutscher Chemiker; he was awarded the Faraday Medal of the Chemical Society in 1872[13] and the Copley Medal in 1891.

The major project Cannizzaro (Fig. 3) pursued in Rome concerned the photochemistry and structure of santonin.[14] This anthelmintic sesquiterpene had been isolated in 1830; its light-induced chemistry was studied by H. Trommsdorf[15] in 1834 and W. Heldt[16] in 1847 (Fig. 4). The interesting observation that santonin crystals burst upon irradiation may be the first

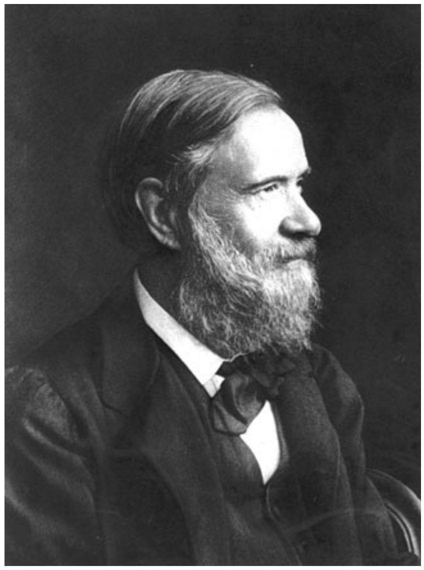
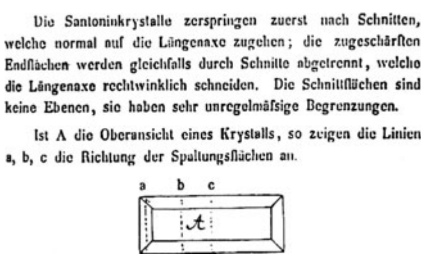


Fig. 3 Stanislao Cannizzaro during his tenure at Università degli studi di Roma, "La Sapienza". In his institute Ciamician, Silber, and Paternó were first introduced to preparative photochemistry induced by sunlight.



Die Santoninkrystalle zerspringen zuerst nach Schnitten, welche normal auf die Längenaxe zugehen; die zugeschärften Endflächen werden gleichfalls durch Schnitte abgetrennt, welche die Längenaxe rechtwinklich schneiden. Die Schnittflächen sind keine Ebenen, sie haben sehr unregelmäſsige Begrenzungen.

Ist A die Oberansicht eines Krystalls, so zeigen die Linien a, b, c die Richtung der Spaltungsflächen an.

Fig. 4 Description of the photo-induced break-up of santonin crystals.[16] ["The santonin crystals are cleaved first along cuts normal to the long axis; the inclined crystal faces are also separated along cuts perpendicular to the long axis. The newly created surfaces are not planar but have quite irregular boundaries. If A is the top view of the crystal, the lines a, b, c indicate the direction of cleavage."]

example of photochemistry in the solid state.

Cannizzaro learned about santonin photochemistry from Fausto Sestini who had been working on the isolation of photosantonic acid since 1865. In 1872 Sestini came to Rome as director of the agricultural station, where he met Cannizzaro. The following year, Cannizzaro and Sestini collaborated at the XI Riunione, a science congress in Rome; later that year Sestini and Cannizzaro jointly published the isolation of photosantonic acid.[17] Subsequently Sestini and Cannizzaro worked independently on various photoreactions of santonin. In our days, Sestini (Fig. 5)

Fig. 5 Fausto Sestini during his tenure at Università degli studi di Pisa. Sestini aroused Cannizzaro's curiosity for the photochemistry of santonin and, indirectly, the interest of Ciamician, Silber, and Paternó in photochemistry.

is best known for a 1863 paper about the balsamic vinegars of the Modena area.[18]

Cannizzaro and co-workers confirmed the formation of photosantonic acid and discovered an additional photoproduct, iso-photosantonic acid.[19] An 1886 publication with G. Fabris is remarkable for the enormous scale of the reaction: "*Ein Kilogramm Santonin, gelöst in 52 Litern Essigsäure (D = 1.054), wurde in mehreren Flaschen während einiger Monate dem Licht ausgesetzt*"[19] [one kilogram santonin, dissolved in 52 liters acetic acid (D = 1.054), was exposed in several bottles to (sun) light]. Based on these studies Cannizzaro recognized the correct composition of santonin, its relationship to naphthalene, major structural elements, even the presence of an unusual lactone function (Fig. 6). Marotta felt that Cannizzaro had essentially recognized the structure of santonin,[1] and none other than R. B. Woodward[20] acknowledged the "brilliant experimental results" of "the Italian school, led by Cannizzaro". Still, the intricate details of the structures of santonin and its photoproducts simply were not accessible to the limited analytical tools and structural insights of the 1880s or 1890s.[19,21] The structure of santonin was not elucidated until 1954,[20] that of

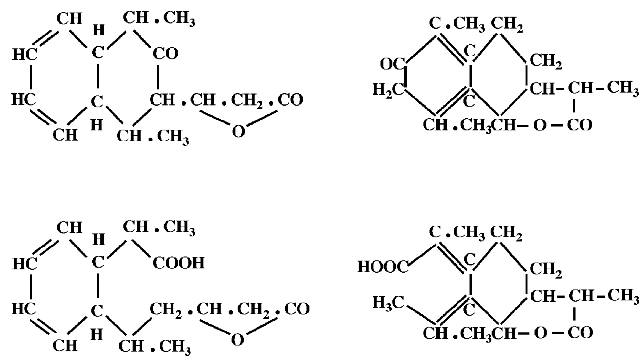


Fig. 6 Structures of santonin (top) and photosantonic acid (bottom), as formulated by Cannizzaro and Fabris, 1886 (left),[19] and Gucci and Grassi-Cristaldi, 1891 (right).[21]

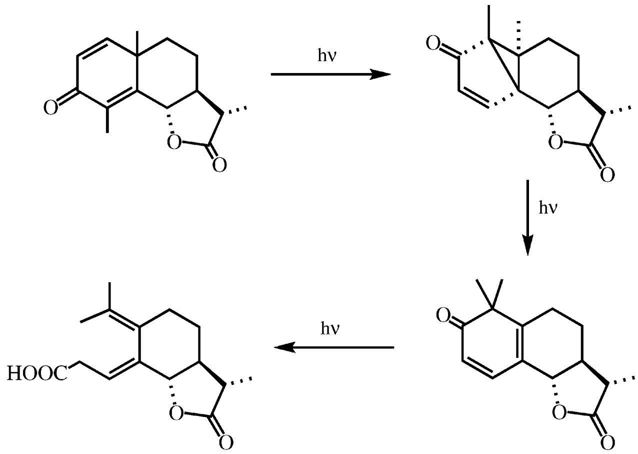
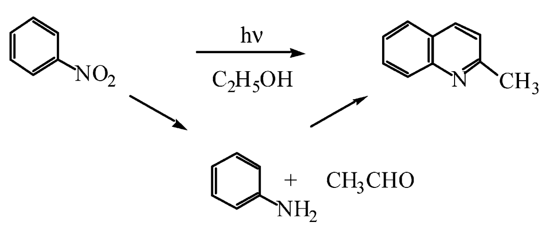


Fig. 7 Intermediates in the photo-conversion of santonin into photosantonic acid.[22,24]

photosantonic acid not until 1958;[22] one key intermediate in its formation was isolated and characterized only in 1963 (Fig. 7).[23]

Still, Cannizzaro's work on the photochemistry of santonin bore a significant benefit for Italian science and the entire discipline of photochemistry: he introduced Giacomo Ciamician, Paul Silber, and Emanuele Paternó to photochemistry. Ciamician joined Cannizzaro's group in 1881, working on natural products; Paternó joined La Sapienza as professor in 1882. They must have been amazed, perhaps awed, spectators of Cannizzaro's monumental santonin experiment.[19] In 1885/86 Ciamician carried out his first photoreactions,[24,25] soon joined by Paul Silber, another research associate of Cannizzaro.[26]

Ciamician exposed alcoholic benzoquinone solutions to sunlight and, after five month's exposure, observed the formation of hydroquinone and acetaldehyde.[24,25] The following year, Silber found an analogous redox reaction; exposure of alcoholic nitrobenzene solutions gave rise to aniline and acetaldehyde and, remarkably, 2-methylquinoline (Scheme 2).[26]



Scheme 2 Reaction of nitrobenzene in ethanol.[26]

Their work came to fruition in Bologna where Ciamician (Fig. 8) and Silber established a new center of gravity for the "photochemical map" of Europe (Fig. 9),[14,27] and where Ciamician conceived his vision of the Photochemistry of the Future.[28] The use of light as an inexhaustible "natural" energy source makes Ciamician an early proponent of "green chemistry".[29]

Fig. 8 Giacomo Ciamician during his early years in Bologna.

The photochemical research of Emanuele Paternó's had a somewhat longer "induction period", he began his studies only after Cannizzaro's retirement. Paternó started his photochemical research only in 1909, emphasizing preparatory aspects of photochemistry ("Sintesi per mezzo de la luce", "Syntheses by means of light").[30,31]

Conclusion

Aside from his work on the "disproportionation" of benzaldehyde upon reaction with alkali, the Cannizzaro reaction, Stanislao Cannizzaro played an important role in the development of chemistry in the nineteenth century. His "Sunto di un corso di filosofia chimica" used the best of theory and experiment available at the time and molded it into a homogeneous image of chemistry. The photochemical community

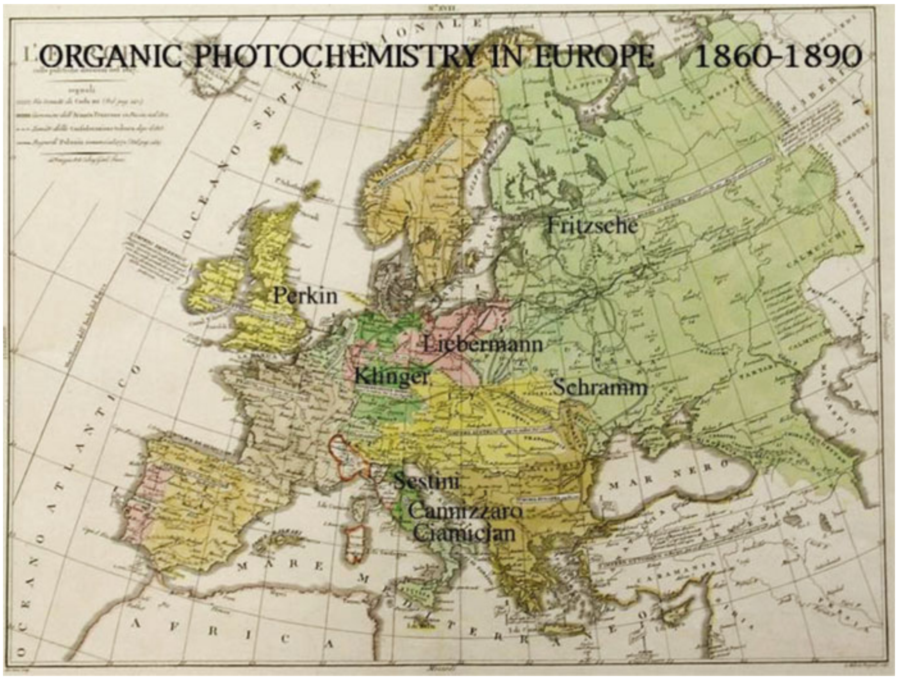


Fig. 9 Organic photochemistry in Europe during the time of Cannizzaro's santonin experiments in Rome. The names of principal investigators are inscribed on the "L'Europa colle politiche divisioni nel 1827" map (Venice, 1828, Calcog. Girol. Tasso; engraved by G. Valerio Pasquale) near the cities where they performed their work.[14]

appreciates Cannizzaro's work on the photochemistry of santonin and the fact that he introduced Giacomo Ciamician and Emanuele Paternó to photochemistry. The significance of Cannizzaro's work was acknowledged at the turn of the millennium when the Federation of European Chemical Societies (FECS) included him among 100 Distinguished European Chemists.[32,33] He shares this distinction with Avogadro, Dalton, Dumas, and Gay-Lussac, whose work he incorporated into his Sunto, and with Berzelius, against whose system he argued.

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