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Research Article

Peter Griess (1829-1888) – Breweries, Diazonium Salts, Dyes

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Abstract. Peter Griess was probably the chemist who exercised both sides of his profession with equal effectiveness: the rigorous researcher, and the industrial chemist, carrying out his duties with absolute seriousness and efficiency. After a rather hectic period in life, Griess began a scientific activity of extreme importance in Organic Chemistry: the discovery and study of diazonium salts, and work with dyes, aromatic compounds, and other nitrogenous compounds, an activity carried out mostly outside the academic context. His practical activity in the brewing industry is less publicized, due to professional secrecy, but no less interesting and varied. This dual activity is presented in the historical context in which it occurred, whenever possible based on primary sources.

Keywords: Peter Griess, Diazonium salts, Dyes, Aromatic compounds, Breweries, Royal College of Chemistry

“And since then Griess’s reactions have become so commonplace that enumerating them might seem an unnecessary task.” (Emil Fischer)¹

INTRODUCTION.

Among the less remembered – but no less important – organic chemists of the second half of the 19th century, we recall, among others, Peter Griess, a combination of industrial chemist and researcher, known for the discovery of diazonium salts, of such importance in Organic Chemistry, both in the synthesis of dyes and substituted aromatic compounds. He successfully fulfilled his dual role as an industrial chemist in the brewing industry and as a researcher in Organic Chemistry. Like other German chemists, such as Ludwig Mond, Carl Schorlemmer, and Hugo Müller, he settled permanently in Great Britain (1858), where he started a family (1869) in Burton-on-Trent. He died prematurely in Bournemouth in 1888. In 1891, his colleagues and friends August Bopp (1833-1904), August Wilhelm von Hofmann (1818-1892), and Emil Fischer (1852-1919) published a lengthy article in *Berichte*, “Zur Erinnerung an Peter Griess” (Remembering Peter Griess).² F. A. Mason

published, in 1930, “Johann Peter Griess 1829-1888”³; There are several concise articles on the life and work of Griess, all drawing from the rich source that is the rather personal article by Bopp, Hofmann and Fischer, and of which we highlight those by V. Heines in the *Journal of Chemical Education* (1958)⁴, Robert Wizinger-Aust (1896-1973) in *Angewandte Chemie* (1958)⁵, and W. H. Cliffe in *Coloration Technology* (1959)⁶. Edwin Yates and Andrew Yates wrote about Griess and the brewing industry (2016)⁷. This article aims to include other sources and new connections between Griess and Chemistry.

ORIGIN, YOUTH, STUDIES.

Johann Peter Griess was born on September 6, 1829, in Kirchholzbach, a small village of 200 inhabitants near Kassel, the son of Johann Heinrich Griess (1799-1870) and Catherine Elisabeth Griess (1803-1860). His father was a small farmer and blacksmith in the village, and owned a small stretch of forest from which he extracted timber, including the wood to build his own house. After primary school in the village, his father, who wanted his son to one day take over his small property, sent him in 1844/1845 to a private agricultural school in Beberbeck (now part of the city of Hofgeismar), but Peter had no interest whatsoever in agricultural activities. He then attended the *Höhere Gewerbeschule* (Higher Trades School) in Kassel, a technical education center founded in 1831 by Friedrich Wöhler (1800-1882), where he had his first contact with science (he had learned the rudiments of botany from the teacher in his native village), with professors Heinrich Buff (1805-1878), a physicist, and Amandus Philippi (1808-1904), a zoologist, who after the liberal revolution of 1848 emigrated to Chile, where he became a professor of Zoology at the University of Santiago.

He later attended the universities of Jena (1850/1851), Marburg (1851), where he attended the Philosophy lectures of Eduard Zeller (1814-1908), a follower of Kant, Munich (1854), where he was allegedly a student of Liebig, without official enrollment, and again Marburg (1854), as a student of Hermann Kolbe (1818-1884). Initially, he did not take academic life very seriously, incurred debts paid by his father, was imprisoned in the university jail (*Karzer*, common at the time) for disturbing the public order, and ended up suspended from Marburg, but he used the time to improve his deficient humanistic education.



(Fig.1) Peter Griess (1829-1888). Photograph by an unknown author, c.1885. Illustration from R. Anderson, “The Brewing Connection in the Oxford Dictionary of Biography” (public domain).



(Fig.2) Hermann Kolbe (1818-1884), Griess's professor in Marburg. Photograph by August Brasch, Leipzig, 1879 (Wellcome Foundation, London).

In 1856, temporarily away from the university and without resources, he found employment in industry, through A. W. Hofmann, at *Teerfarbenwerk Oehler* in Offenbach, which manufactured dyes from tar and residues from the Frankfurt gasometer. Karl Gottlieb Oehler (1797-1874) had acquired the factory in 1850 from its founder, the chemist Ernst Sell (1808-1854), a student of Liebig and a pioneer in the industrialization of tar in Germany, with the factory he founded in 1842 in Offenbach⁸. (Sell sent the first samples from his factory to Liebig, in whose laboratory A. W. Hofmann redis-

covered aniline (*Kyanol*) and Friedlieb F. Runge's [1794-1867] quinoline in 1842). The factory was destroyed by a fire in 1857, and Griess returned to Marburg and his mentor Kolbe, somewhat against the latter's wishes, but now demonstrating a great interest in chemistry and an unusual desire to research. In Marburg, Kolbe suggested to Griess to carry out the reaction of nitrous acid with aromatic amines, since experiments by Wurtz (1851)⁹ and Hofmann (1855)¹⁰ had already shown that aliphatic amines decompose into alcohol and nitrogen when reacting with nitrous acid. The reaction of nitrous acid with aromatic amines led to the discovery of diazonium salts (1858) by Griess, who published a "provisional notice" about them in the *Annalen* (1858)¹¹. This fell into the hands of Hofmann at the *Royal College of Chemistry* in London, and Hofmann, the director of the *College*, knowing of Griess's unemployment and financial precariousness, and heeding a request from Kolbe, invited him to be his assistant. Hofmann had realized (due to his experiments with coal tar derivatives Hofmann had a wider view of the future of synthetic dyes), before Griess himself, the scope of the discovery, translated Griess's article, added new discoveries by Griess, and published it¹². The various biographers of Griess are more or less benevolent regarding his time as a student in Marburg, considering that Griess became a serious and tireless worker, always willing to help those in need, and an exemplary family man. In Wizinger-Aust's opinion, the life and work of Peter Griess was still not properly valued by historiography, even to his days. Emil Fischer's assertion from the epigraph has lost some of its relevance today.



(Fig.3) August Wilhelm Hofmann (1818-1892), from an article by Edward John Hallock, published in *Popular Science Monthly*, volume 24, edition from April 24, 1884.

ENGLAND, THE ROYAL COLLEGE OF CHEMISTRY AND THE BREWERIES

For someone in Griess's difficult situation, Hofmann's invitation was irresistible. Griess accepted it, and by December 1858 he was already working at the *Royal College*. The *Royal College of Chemistry* had been founded in 1845 by a group of benefactors, with the aim of training the chemists needed for the growing Industrial Revolution; but the direct profits from research carried out there would also be welcome.... Among the members of the first board of directors were: Alexander Baring, Lord Ashburton (1774-1848), financier and politician, Sir James Clark (1782-1870), personal physician to Queen Victoria, Sir William Tite (1798-1873), architect, Warren De La Rue (1815-1889), chemist and industrialist. The cornerstone of the *College's* headquarters on Oxford Street, designed by James Lockyer (1796-1875), was laid on June 16, 1846, in the presence of Prince Albert (1819-1861), civil and religious authorities, and scientists (Graham, Brande, Hofmann, Wheatstone). The first director was August Wilhelm Hofmann, whose stay in England (he returned to Germany in 1865 to take up the chair of Chemistry at the University of Berlin) was supported by Prince Albert and the King of Prussia, Frederick William IV (1795-1861)¹³. Among the alumni of the *College* were Sir Frederick A. Abel (1837-1898), John Alexander R. Newlands (1837-1898), Sir William Perkin (1838-1907), Charles Mansfield (1819-1855), John Stenhouse (1809-1880), and Edward Divers (1837-1912), who was a professor in Japan from 1873 to 1899.



(Fig.4) The old laboratory building of the Royal College of Chemistry, by James Lockyer (1796-1875), begun in 1846, with the presence of Prince Albert. Lithograph by Day & Haghe (Wellcome Foundation, London).

Peter Griess remained at the *Royal College of Chemistry* from 1858 to 1861, continuing his research on diazonium salts, about which he published a new article in 1860¹⁴. But Griess's first scientific work produced there deals with the introduction of iodine into certain aromatic compounds¹⁵, also involving diazonium salts and in a way anticipating the future (1884) Sandmeyer reaction (Traugott Sandmeyer, 1854-1922), of the Zurich Polytechnic. Other work carried out at the *Royal College* addresses the nitrogenous derivatives of aniline and its homologues (1861)¹⁶, the action of nitrous acid on diamines (1862)¹⁷, and the production of non-nitrogenous acids from amines¹⁸. With Carl Adolph Leibius (1833-1893), Hofmann's assistant from 1857 to 1859 (when Leibius emigrated to Australia), he studied the action of HCN on methylamine, with the formation of methylurea¹⁹. This research was important for understanding cyanamides as fertilizers. In London, Griess met Heinrich Caro (1834-1910), one of the most important chemists involved in the synthesis of dyes, then working at *Roberts, Dale & Co.* in Manchester, and after his return to Germany (1866) technical director of *BASF* (where Griess would later patent his dyes). The friendship between Griess and Caro also resulted in a scientific partnership, which, however, was less productive than might have been expected.

GRIESS AND ALLSOPP & SONS

In 1861, at Hofmann's house, Griess met the German chemist Wilhelm Heinrich Böttinger (1820-1872), a student of Liebig, who from 1845 to 1865 (when he returned to Germany) was chief chemist of the large *Allsopp & Sons* brewery in Burton-on-Trent, a major brewing center near Nottingham. This meeting resulted in Griess being hired by Allsopp in 1862; Griess was a chemist and later chief chemist of the company until his death in 1888. Böttinger, a native of Heilbronn, was, on Liebig's recommendation, an assistant in Glasgow, then a chemist at *Allsopp*; returning to Germany, he turned his interests to research, in the laboratories of Lambert von Babo (1818-1899) in Freiburg, Emil Erlenmeyer (1825-1909) in Munich, and in Würzburg. He later founded a small brewery in Würzburg, where he died²⁰.

The friendship with Böttinger was beneficial to Griess, both when he moved to Burton (180 km from London), in the social contacts at his new workplace, and in the translation of his articles into English. After Böttinger left, Griess met the family of the physician Francis Albert Mason, whose daughter Louise Anna (1839-1886) he married in 1869. The couple had two sons and two daughters.

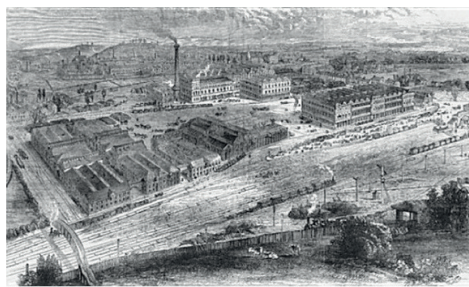
Upon joining *Allsopp*, Griess found other chemists working in the city: Horace Tabberer Brown (1848-1925), Adrian John Brown (1852-1919), both natives of Burton, and the Irishman Cornelius O'Sullivan (1841-1907), who worked at *Bass & Co.* (a company founded in 1777 by William Bass [1717-1787]). O'Sullivan had been a student of Hofmann at the *Royal College of Chemistry* and an assistant to Hofmann in Berlin). In 1876 Griess, the three other Burton chemists, two physicians and two brewers founded the "Bacterium Club", an informal gathering for the discussion of novelties in chemistry and biology.

The *Allsopp & Sons* brewery in Burton-upon-Trent traces its origins back to 1743 with the tavern owner and brewer Benjamin Wilson. In 1800, his nephew Samuel Allsopp (1780-1838) joined as a partner. In 1807, due to difficulties arising from Napoleon's Continental Blockade, Wilson sold the company to Allsopp. In the 1860s, it became the second largest brewery in Great Britain, operating as *Samuel Allsopp & Sons Limited* since 1887. In the 20th century, it faced significant financial difficulties and only returned to operating under its former name in 2020. When Griess joined the company, it was run by Sir Henry Allsopp (1811-1887), who was also active in politics.

The scientific study of the art of brewing began in the 19th century, during the time of Griess, not only from a chemical point of view, but also from a biological one (organisms and processes responsible for fermentation, a chemical reaction that was only then beginning to be clarified²¹, with the proposals of Pasteur, Liebig, Vicente Marcano [1848-1891] and finally Eduard Buchner [1850-1917] in 1897). The extensive research of the Carlsberg laboratory in Copenhagen also falls within this period. Quality control, which went hand in hand with potential for adulteration, also fell to the brewery chemists. For example, in 1852 Anselme Payen (1795-1871), professor at the *Conservatoire des Arts et Métiers* in Paris, recklessly accused English breweries of adding strychnine to the beverage to increase its bitterness. The "strychnine scandal" shook sales of Allsopp's famous *Pale Ale*, and it required the intervention not only of Böttinger, but also of Graham, Hofmann, and Liebig, who concluded in letters to the company that the accusation was false, but doubts about the case remain even today²². Graham and Hofmann published an extensive report in 1852 on their analyses of beers from many Burton breweries, concluding that "none of these varieties of beer, when tested with the greatest scrupulousness, gave the slightest evidence of the presence of strychnine"²³. According to the report, Payen apologized, claiming that similar suspicions had been raised in France, in a book by the pharmacist Jean-Baptiste Chevallier (1793-1870)²⁴. A year earlier, an investigation into food adulteration

and falsification had taken place. The investigation also included, among others, the company *Bass, Ratcliff and Gretton*, founded in 1777, also in Burton. The problem of adulteration and contamination not only of beverages but also of food was quite serious at the time, and the strychnine case caught the attention of Charles Dickens (1812-1870), who commented on it in “Household Works”, also mentioning the adulteration of beers with picrotoxin²⁵, a highly toxic substance extracted in 1812 by Pierre Boullay (1777-1869) from *Anamirta cocculus*, a plant from Southeast Asia, added to accentuate the bitter taste and increase the intoxicating effect of beer.

Griess's activity at Allsopp is quite strange. He was not very involved with the chemistry related to beer production, but he carried out research of personal interest in the company's laboratory, such as the reactions of diazonium salts and the obtaining of dyes, which, when useful in the industry, were patented, not in Great Britain, but in Germany by German companies, such as *BASF*, and for Griess's own benefit. It is difficult to believe that Allsopp gave him so many privileges; explanations could be found in Griess's great prestige in the chemical field, as well as in the patent legislation in both countries (in Germany there was only unified legislation after 1871). When the demand for beer increased in the 1870s (*India Pale Ale*, a more bitter beer, richer in hops and with a high alcohol content, was exported worldwide), the company demanded greater involvement from Griess in the manufacturing aspects of the product, which did not please the chemist at all. However, Griess remained with the company until the end of his life. Few records exist about Griess's activity at Allsopp, but it must have been very fruitful, considering the quantitative and qualitative development of the company's production. The freedom he was granted in the laboratories also speaks positively about his activity in the brewing industry. The investigations and improvements he introduced to the brewing industry remained largely secret.



Allsopp's New Brewery from *The Illustrated London News*, 1 November 1862.



(Fig.5 - Left). Samuel Allsopp & Sons brewery, in Burton-on-Trent. From *The Illustrated London News*, November 1, 1862. (Right) Samuel Charles Allsopp, 2^o Baron Hindlip (1842-1897), caricature by Sir Leslie Ward (1851-1922), published in *Vanity Fair*, August 1885.

GRIESS, DIAZONIUM SALTS AND AZO COMPOUNDS.

Diazonium salts constitute one of the most important groups of organic compounds, as they are the basis of two important series of reactions: by coupling, the obtaining of a large number of azo compounds, among which are many dyes, a field of study of Griess himself; and a means of easily introducing substituents into aromatic rings, a method discovered in Zurich by Traugott Sandmeyer (1854-1922) in 1884 and known as the Sandmeyer Reaction (there are many variants of this reaction, such as the Balz-Schiemann Reaction [1927], for the introduction of fluorine)²⁶. Diazonium salts were discovered by Griess in 1858, while still at the University of Marburg, as already mentioned. Some authors cite as a distant inspiration a reaction discovered by Raffaele Piria (1814-1865), who obtained alcohols by treating primary amines with nitrous acid (1846)²⁷. Griess published his discovery in a “provisory note” in Liebig's *Annalen*. Diazonium salts are obtained by treating aromatic amines with nitrous acid (obtained in situ from nitrites and HCl), which precipitates yellowish crystals of diazonium salts that are purified by recrystallization. The salts are unstable at room temperature, are kept chilled, and used in situ, without being isolated from the mixture. The reaction became known as “diazotization.” But this simple diazotization method was only developed in 1873 by Victor Meyer (1848-1897). The path followed by Griess to arrive at diazonium salts was quite tortuous, and since the formula for benzene proposed by Kekulé, dating from 1865, was not yet known, it was also difficult to propose a structure for the salts. Only after the diazotization of aminonitrobenzoic acid and aminodinitrobenzoic acid did Griess perform the diazotization of aniline. Griess does not state in his publication why he did not begin his experiments with aniline. His articles are concise, without details regarding the experimental procedure. He initially obtained diazoaminobenzene, which he treated with bromine and nitrous acid in the presence of nitric acid:



According to Wizinger-Aust, these are the first true diazonium salts.

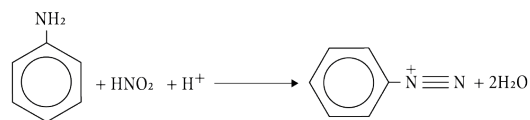


Fig. 6 Synthesis of diazonium salts

The structure of these compounds remained unknown for a long time, and several chemists proposed formulas for them, such as those in Figure 7 below, suggested by Griess himself, by Kekulé, and by Blomstrand. Elemental analyses of the compounds showed only the presence of two nitrogen atoms, but it was not possible to determine their position in the structure.

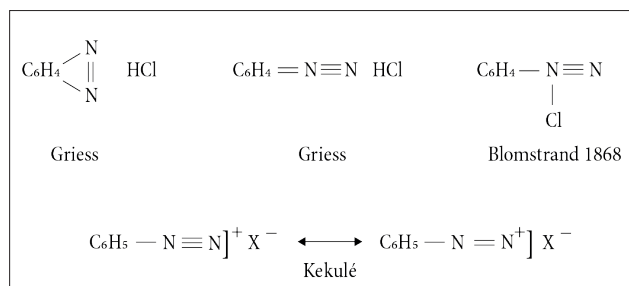


Fig. 7 Representations of diazonium salts

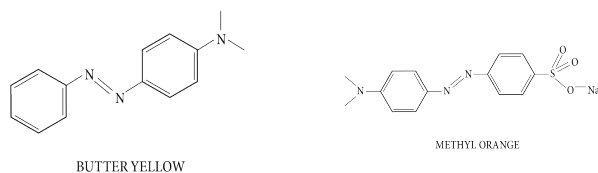
After diazotization of aminonitrobenzoic acids and aniline, Peter Griess wanted to determine the limits of his new reaction and studied the possible diazotization of naphthalene, naphthols (which both do not react), sulfanilic acid, benzidine, toluidine, etc., starting in 1858, communicating the results in 15 publications, and arriving at a general understanding of the “coupling” in 1864, concluding in 1875 with a summary in the *Berichte*.²⁸ In his papers, Griess defined “coupling” as the direct linkage of diazonium compounds with amines or phenols.

Griess dedicated his entire life to diazonium salts, working alone, and his study of these compounds was so thorough that for a long time, during Griess’s activity, there was little to add. Among future additions was the formation of azo compounds with an aromatic and an aliphatic chain²⁹, discovered in 1875 by Victor Meyer, who also determined the structure of these compounds³⁰. In 1882, Victor Meyer and Emil Constan (1858-1917), in Zurich (Constan’s doctoral thesis), believed they had obtained purely aliphatic azo compounds³¹. However, Heinrich Wieland (1877-1957) showed that it was nitrohydrazine. In 1910, Johannes Thiele (1865-1918) succeeded in obtaining purely aliphatic azo compounds³².

With the discovery of diazonium salts, the study of these compounds led Griess to azo dyes, an important group of dyes containing one or more N=N= groups. Azo dyes are obtained by the coupling reaction of diazonium salts with aromatic amines, and the first azo dye was obtained by Griess himself in 1861: aniline yellow or butter yellow, by reacting a diazonium salt with dimethylaniline. (some historians mention a simultaneous discovery by the French chemist Charles Mène).

Butter yellow began to be produced commercially from 1864 by the company *Simpson, Maule & Nicholson*, in Locksfield, near London, and was used in the coloring of foods and pharmaceuticals, for example, to impart a yellowish color to margarine, to make it more similar to butter. This use was prohibited after the discovery of the carcinogenic activity of this dye in 1937 by Rioju Kinoshita (1893-1977) at Osaka University. The company *Simpson, Maule & Nicholson* was founded in 1853 by George Simpson (1819-1894), a merchant of scientific equipment, George Maule (1827-1890), a chemist, and Edward Chambers Nicholson (1827-1890), a student of Hofmann at the *Royal College of Chemistry*.

Another important azo dye in the history of Chemistry, developed in 1875 by Griess (independently and almost simultaneously by Nikolaus Otto Witt [1876] and Zacharie Roussin [1878]), is methyl orange (Goldorange, Orange III, Tropeolin). Georg Lunge (1839-1923), a professor in Zurich, introduced it into Analytical Chemistry as an indicator for the pH range of 3.1 to 4.4. Griess also developed other azo dyes, such as Chrysoidin (1876, also by Heinrich Caro), chrysoin (1875), Orange I and Orange II (1876).



Both at the *Royal College of Chemistry*, as Hofmann’s assistant, and in the Allsopp laboratories, Griess prepared a large number of azo dyes, which were sent to Dresden to be analyzed by his friend Rudolf Schmitt (1830-1898), professor of Organic Chemistry at the Dresden Polytechnic. Walther Hempel (1851-1916), Schmitt’s assistant and later professor of Technological Chemistry at the Dresden Polytechnic, recounts these discoveries: “The new compounds prepared by Griess were regularly sent, in small packages, from Burton-on-Trent to Dresden for analysis. At the same time, these shipments were accompanied by welcome barrels of the finest Pale Ale beer.”³³ As was customary at the time, the analyses were likely performed by Schmitt’s assistants, like Hempel, though Hempel also published analyses of his own³⁴. It is probable that Schmitt performed some analyses himself, given the close friendship between Griess and Schmitt. Since 1880, many dye industries regularly sent samples for analysis in Dresden, by Professor Rudolf Schmitt, and later by Professor Walter König (1878-1964). The Technical University of Dresden still holds a

large collection of dyes (samples of 12,000 synthetic dyes and 1,500 natural dyes), founded in 1926 by Professor Richard Möhlau (1857-1940).

Dyes developed by Griess

1875 Methyl Orange or Aniline Yellow

1875 Chrysoin

1876 Chrysoidin (also by H. Caro, 1875)

1876 Orange I

1876 Orange II

With these discoveries and syntheses, Peter Griess was an exponential figure in the development of synthetic dyes, although he himself had little advantage from these discoveries. Heinrich Caro (1834-1910), an undisputed leader of the nascent dye industry, said of him: "For the industry, he was a teacher and leader, but others reaped where he sowed; Griess was not a successful inventor."

Regarding a supposed isomer of alizarin.

Alizarin is a natural dye used since antiquity, obtained from the madder root (*Rubia tinctoria*), from which it was isolated by Colin and Robiquet in 1825. In 1868, Carl Graebe (1841-1927) and Carl Liebermann (1842-1914) succeeded in synthesizing alizarin from anthraquinone³⁵. For this reason, they determined its partial structure (dihydroxyanthraquinone). The definitive structure (1,2-dihydroxyanthraquinone) was clarified in 1874 by Adolf von Baeyer (1835-1917) and Heinrich Caro (1834-1910). This brief account shows that ignorance of a compound's structure leads to the formulation of hypothetical reactions, seemingly logical, but mistaken; we could say, in logical terms, that the premise is wrong. Thus, in 1850, Julius Wolff and Adolph Strecker (1822-1871) believed it would be possible to synthesize alizarin from naphthalene³⁶, based on the fact that alizarin and chloro-oxy-naphthalenecarboxylic acid, when heated with nitric acid, yield the same products: phthalic acid and oxalic acid. In practice, alizarin was not obtained. In 1865, Griess and Carl Alexander von Martius (1838-1920) revisited the subject³⁷, and starting from dinitronaphtyl alcohol and going through a reduction step (converting the groups $-\text{NO}_2$ in $-\text{NH}_2$) and successive decompositions, they obtained a compound with the formula $\text{C}_{10}\text{H}_6\text{O}_3$. Considered an isomer of alizarin (the molecular formula would be the same), this new compound does not exhibit the coloring properties of alizarin. The history of Chemistry shows that it was possible to synthetically reproduce a natural compound without knowing its structural formula (Graebe and

Liebermann synthesized alizarin knowing its structure partially), but these syntheses were exceptions. Griess's previous empirical work on azo compounds and picric acid simultaneously and gradually involved the structure of the participating compounds, and a careful interpretation of the empirical data allowed him to arrive at the structures in question. This is not the case with alizarin, which is discussed here.

OTHER EXPERIMENTAL WORKS BY GRIESS.

Peter Griess' experimental work focuses on the obtaining and investigation of azo compounds, with a high point in dyes, but there is also a great contribution to the chemical study of aromatic compounds. The research related to brewing is unprecedented because it was of industrial interest. There is only one publication by Griess (with G. Harrow) in this area, in the *Berichte* of the German Chemical Society, on the occurrence of choline in hops and beer, a publication of a more general scientific nature³⁸. His articles are scattered in many periodicals, mainly in the *Berichte* of the German Chemical Society and in Liebig's *Annalen*, but also in the *London Philosophical Transactions*, the *Journal für praktische Chemie*, and the *Zeitschrift für Chemie und Pharmacie* (edited by Emil Erlenmeyer). Let's look in detail at some of these investigations.

The Griess test and the Griess reagent.

The Griess test is used for the detection of nitrites in biological fluids and drinking water, and also for the detection of nitrates, properly reduced to nitrites, in explosives, a method used in forensics (detection of nitroglycerin). The Griess reagent consists of one part naphthylethylenediamine chloride in a 0.1% aqueous solution and 1% sulfanilamide in 25-50% acetic acid. The nitrite ion reacts with sulfanilamide, giving rise to a diazonium salt, which reacts with naphthylethylenediamine chloride in a coupling reaction, giving rise to a pink or red solution, the concentration of which is determined by spectrometry. The Griess test is based on a coupling reaction and was described in detail by Peter Griess in 1879. Instead of sulfanilamide, he used sulfanilic acid.

There are commercially available variants of the Griess reagent. In 1889, Casimir Wurster (1854 Weidenthal/Rhineland – 1913 Dresden), a student and assistant of Victor Meyer in Zurich and of Rudolph Fittig in Strasbourg (1877/1878), developed a very practical method for performing the Griess test, using "indicator

papers”: a yellow reagent paper impregnated with alpha-sulfanilamide and a red reagent paper impregnated with sulfanilic acid. Using both together detects nitrite. Wurster extended the method to detect the nitrogen oxide formed in the determination of HNO_3 with iron sulfate, FeSO_4 in the presence of ammonium acetate, which was once important for water quality control³⁹. Wurster also developed several other analytical reagents, such as redox indicators (Wurster blue) and reagents for use in industrial analyses.

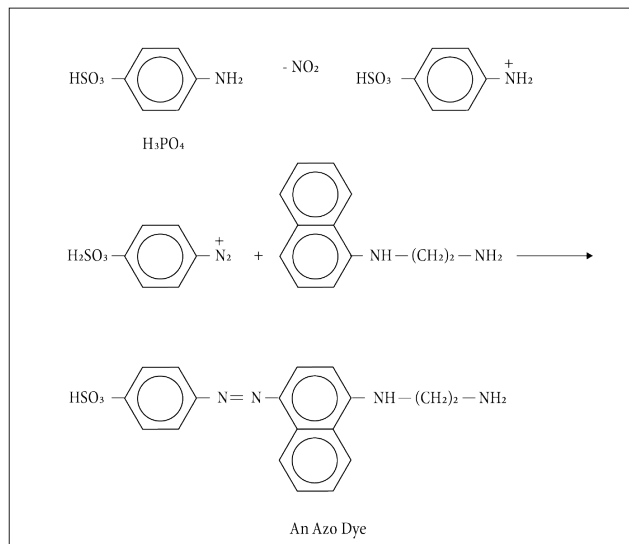


Fig. 8 Reaction of the Griess test

The structure of disubstituted benzene derivatives.

Wilhelm Körner or Guglielmo Koerner (1839-1925), professor at the Higher School of Agronomy of the University of Milan, is generally credited with elucidating the structures of the three disubstituted derivatives of benzene, in this case the structure of the three dibromobenzenes (1874). To do this, he performed the nitration of these compounds: the nitration of 1,2-dibromobenzene yields two nitrodibromobenzenes, the nitration of 1,3-dibromobenzene yields three derivatives, and the nitration of 1,4-dibromobenzene yields only one nitrated derivative. The careful separation of the isomers obtained thus allows the determination of the structure of ortho-, meta-, and para-dibromobenzene. The prefixes ortho-, meta-, and para- were proposed by Körner. Partington, in volume IV of his “History of Chemistry”, attributes this proposed nomenclature to both Koerner and Carl Graebe (1841-1927)⁴⁰.

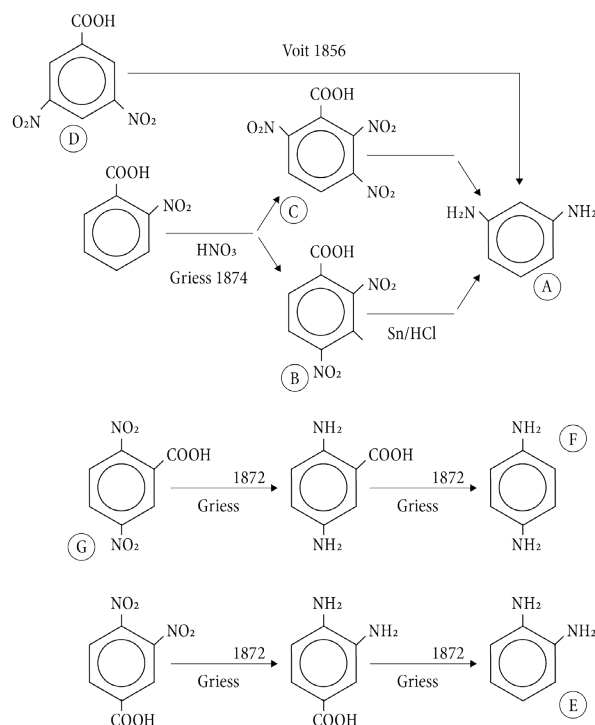


Fig. 9 Reactions involving dinitrobenzoic acids

In fact, Peter Griess had already clarified the structure of the three disubstituted benzene derivatives in 1872, but through reverse reasoning: he decarboxylated and reduced the six dinitrobenzoic acids, obtaining the three phenylenediamines (melting points 63°C, 99°C [current value 103°C] and 140°C). The sequence of experiments performed by Griess and the reasoning that followed to arrive at the structures of the three disubstituted benzene derivatives are more complex and involve previous experiments by other researchers. In 1849, Auguste Cahours (1813-1893) obtained a dinitrobenzoic acid⁴¹ (we know today that it was 3,5-dinitrobenzoic acid), which Carl von Voit (1831-1908), a student of Liebig and Pettenkofer in Munich and later of great importance in the evolution of Biochemistry, reduced to a diaminobenzoic acid⁴². In 1872, Griess observed that two of the dinitrobenzoic acids, upon decarboxylation and reduction, yield the same phenylenediamine with a boiling point of 99°C (compound A), and another dinitrobenzoic acid, by the same procedure, yields a phenylenediamine with a boiling point of 140°C (compound F). However, the dinitrobenzoic acid obtained by Cahours could not be decarboxylated and reduced using Griess's procedure⁴³, but in 1874 Casimir Wurster (1854-1913), a student of Victor Meyer, managed to obtain from a barium salt of this acid a phenylenediamine identical to that obtained from the compound pre-

pared by Voit⁴⁴ in 1856, with P.E. 63°C, in 1874, by nitration of (ortho)nitrobenzoic acid. In 1874 Griess obtained two of the dinitrobenzoic acids, B and C (one of which was still unknown, our 2,4-dinitrobenzoic acid, B), which also give rise to decarboxylation and reduction to phenylenediamine⁴⁵ of P. E. 63° C. In 1872, Griess treated 3,4-dinitrobenzoic acid in the same way and obtained ortho-diaminobenzene (compound E). Combining all this data, Griess was able to arrive at the structure of the three diaminobenzenes. Figure 9 illustrates these transformations that lead to the three diaminobenzenes. Manning A. Smith (1915-2012) and William Gower compiled a very enlightening table containing all this information⁴⁶.

The nitration of ortho-nitrobenzoic acid.

This reaction has already been mentioned above, but we will present more detailed information about it here. The nitration of ortho-nitrobenzoic acid with nitric acid in the presence of sulfuric acid forms, according to Griess, four different compounds: styphnic acid (the trinitro-resorcinol of John Stenhouse [1809-1880] and Chevreul), the three isomeric dinitrobenzoic acids of formula $C_7H_4(NO_2)_2O_2$, which he named 1.2.4, 1.2.5 and 1.2.6 (compounds B, C, G in the figure), which are added to the already known compound D, obtained by Cahours in 1846. Compound C was obtained in 1870 by Ferdinand Tiemann (1848-1899) and his collaborator Judson, by oxidation of dinitrotoluene⁴⁷. Compounds A and B were then (1874) still unknown, although the corresponding diaminobenzoic acids were known. All these acids could only be efficiently purified in the form of their barium salts, obtained by reaction with barium carbonate. Griess's description of his experiments shows the empirical, experimental aspect of Organic Chemistry at the time, and since there were no theoretical, or even empirical, explanations for why the reactions occurred (considerations that only slowly began to emerge from that time onwards), Griess also does not explain how styphnic acid is formed from ortho-nitrobenzoic acid in this reaction.

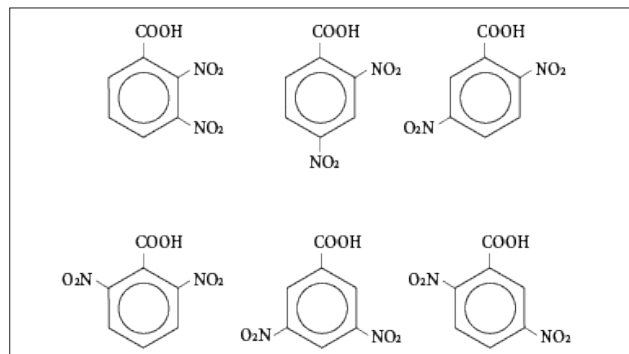


Fig. 10 The six dinitrobenzoic acids

A new derivative of picric acid. The series of picric acid derivatives.

Picric acid (2,4,6-trinitrophenol) was synthesized in 1771 by the Irish chemist Peter Woulfe (1717-1803), and was initially used as a yellow dye. The compound was immediately the subject of much research; for example, in 1848, in a still rudimentary study, Hermann Blumennau (1819-1899), in Trommsdorff's laboratory in Erfurt, observed the decomposition of picric acid into oxalic acid, nitrogen oxides, and carbon dioxide⁴⁸. John Stenhouse (1809-1880) treated picric acid with bromine⁴⁹ and obtained bromopicrin and bromoanil. In 1853, the French chemist Alfred Claude Aimé Girard (1831 Paris-1898 Paris), by selective reduction of picric acid with H_2S , obtained a derivative, picramic acid (2-amino-4,6-dinitrophenol)⁵⁰. It was initially believed that a further reduction of picric acid would not be possible. In 1870, Peter Griess, by modifying the reaction conditions, achieved a new reduction. Powdered picric acid is treated with an aqueous ammonia solution, rapidly introducing a stream of gaseous H_2S , which causes a new reduction, forming 2,4-diamino-6-nitrophenol⁵¹. Like other amino acids, this new compound also has both acidic and basic character, but as a base only with strong acids. As an acid, it forms, for example, barium and silver salts. Griess suggests that his new compound could have use as a dye. With the obtaining of diaminonitrophenol, the series of picric acid derivatives is completed. The first of these derivatives to be obtained was styphnic acid, first obtained in 1808 by Michel Eugène Chevreul (1786-1889), but by nitration of resorcinol, and not from picric acid.

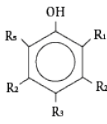
The other two picric acid derivatives were obtained even before Griess's compound, by different reduction processes. Eduard Lautemann (1836 Felsberg/Kassel – 1868 Biebrich/Rhine), a student of Hermann Kolbe in Marburg (1857/1861) and later assistant chemist at the Polytechnic School of Lisbon (1861/1864) and professor at the Medical School of Goa, in Portuguese India, discovered in 1863 the reducing activity of HI on picric acid (the reduction of organic compounds with HI was discovered by Lautemann⁵², and not by Berthelot – the “universal reducing agent of Berthelot” – as is generally read). Lautemann obtained a compound for which he determined the formula $C_6H_2(HO)(NO_2)_3 \cdot (HI)_3$, giving it the name picramine iodide (our picramine)⁵³. Picramine is not a phenolic compound, but it is now known that HI also reduces the OH group, an important fact for the study of carbohydrates. In 1865, Carl Heintzel (1841 Landshut – 1910 Lüneburg), a chemist at the *Gewerbeakademie* in Berlin, treated picric acid with tin and HCl as a reducing agent, and after further treatment with

H₂S, obtained the compound C₆H₂(HO)(NH₃)₃·(HCl)₂, our 2,4,6-triaminophenol, for Heintzel, triaminophenyl chloride⁵⁴. As early as 1867, Heintzel published an extensive article on the work of chemists with picric acid, primarily with its reduction⁵⁵. Thus, “nitrous acid” (HNO₂) or the group NO₂ can be successively replaced by the group NH₂, with the formation of three new compounds:

- aminodinitrophenol
- diaminonitrophenol
- triaminophenol.

The first of these compounds was obtained, as we have seen, by Girard in 1853, the third by Heintzel himself (1865), and the second by Griess in 1870.

Table 1. Picric acid derivatives

	R1	R2	R3	R4	R5	
	NO ₂	H	NO ₂	H	NO ₂	Picric Acid (Woulfe, 1771)
	NH ₂	H	NH ₂	H	NO ₂	Picramic Acid (Girard, 1853)
	NH ₂	H	NH ₂	H	NO ₂	Diaminonitrophenol (Griess, 1870)
	NH ₂	H	NH ₂	H	NH ₂	Triaminophenol (Heintzel, 1865)
	NO ₂	OH	NO ₂	H	NO ₂	Styphnic Acid (Chevreul, 1868)

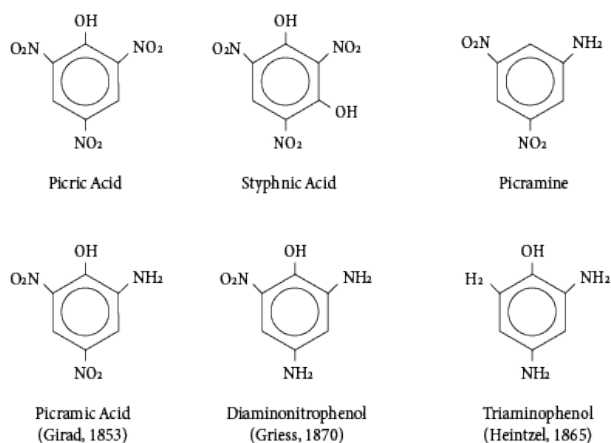


Fig. 11 Picric acid derivatives

Reactions of azo compounds and other nitrogen compounds.

Griess was not a chemist of high theoretical flights, and his range of empirical research was not very varied. His interest lay mainly in nitrogenous organic compounds, and the discovery of diazonium salts followed by that of aromatic azo compounds, among them many dyes, was the raw material for his entire life. Griess was quite jealous of his priority and primacy, as can be seen

in the following example. In 1879, Philipp Weselsky (1828-1889), a professor at the University of Vienna, and his student and collaborator Rudolf Benedikt (1852-1896) announced the discovery of a compound they named ‘azobenzenonaphthylamine’, obtained from the reaction of naphthylamine with diazobenzene⁵⁶. Griess, in an elegant and discreet manner, published another article⁵⁷, communicating that as early as 1864 he had carried out this and other similar reactions, with the publication of an article on the subject⁵⁸, the formation of the compound ‘diazobenzolaminonaphthol’, although it remains unclear whether it was an azo- or a diazo compound. The sulfonic derivative of this compound, with the formula C₁₆H₁₂N₂O₃SO₃, obtained by the reaction of naphthylamine with diazobenzenesulfonic acid, is a dye.

Other nitrogen compounds also sparked his interest. While at the *Royal College*, he studied with Carl Adolph Leibius (1833-1893), Hofmann’s assistant from 1857 to 1859, the action of HCN on methylamine, forming N-methylurea (Leibius was from Württemberg, received his doctorate in Heidelberg in 1857, and emigrated to Australia in 1859, where he was an analyst and, in 1870, chief analyst at the Sydney Mint, becoming a specialist in gold and silver)⁵⁹. Using the same method, Leibius obtained dicyanaminobenzoic acid (C₇H₅(H₂N)₂.2CN) from the reaction of HCN with one of the aminobenzoic acids⁶⁰. From this new derivative of benzoic acid, Griess obtained several products, of which he characterized two, “two new organic bases”⁶¹, to which he attributed the formulas C₇H₆N₂ and C₁₆H₁₈N₄O₆. At that time, the analytical resources available for the structural determination of these benzoic acid derivatives, Griess’s preferred field, were still insufficient: thus, from the first of these bases he concluded only that “it was not the cyanoaniline of [A.W.] Hofmann,” but he intended to obtain it in greater quantity to obtain cyanobenzene and cyanophenol. This analytical difficulty explains Griess’s interest in contributing to the clarification of the positions of the ortho-, meta-, and para- substituents. In 1859, Griess published an article on two new phenol derivatives, dinitrochlorophenol and aminonitrochlorophenol, the latter being obtained from the former⁶². It is difficult to say today what the position of the substituents is on the aromatic ring, since at the time of the synthesis there were no methods capable of determining the exact position, a matter to whose solution Griess himself collaborated, as we saw earlier. In Griess’s opinion, chlorophenol is formed initially, then converted into dinitrochlorophenol.

According to Emil Fischer, in the extensive obituary he wrote in partnership with Hofmann and Bopp⁶³, Griess arrived at his extensive work with azo com-

pounds, which he pursued from 1860 to 1866, in a somewhat convoluted manner, probably starting from Raffaele Piria's (1814-1865) discovery in 1848 of the possibility of replacing an NH_2 group with a hydroxyl group, OH , in the conversion of aspartic acid to malic acid⁶⁴. Along the same lines, A. W. Hofmann and Robert Hunt (1797-1887) obtained phenol from aniline by reaction with nitrous acid (1857). The reaction was repeated and analyzed in 1858 by Augustus Matthiessen (1831-1870), a student of Bunsen, with a reformulation of its representations⁶⁵ (Figure 12).

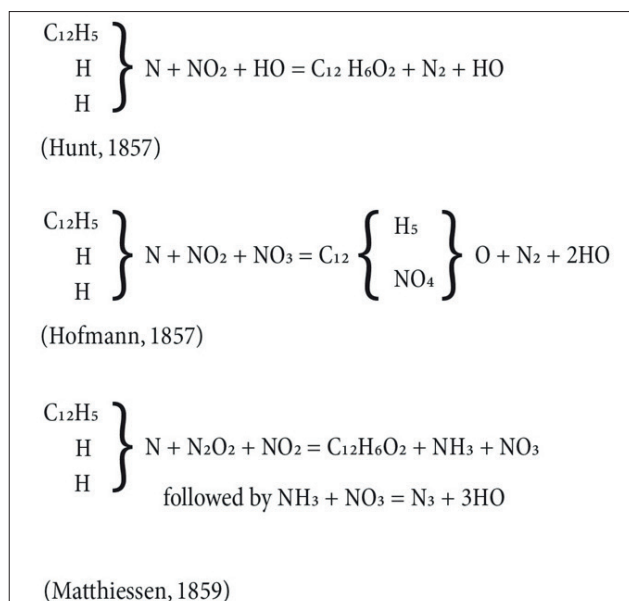
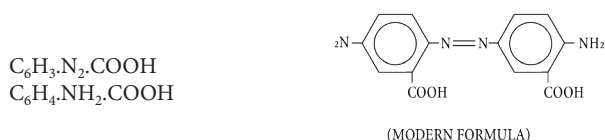


Fig. 12 Some reactions of nitrous acid and aniline

The investigation of the chemistry of azo compounds – their production and properties – did not occur in the systematic way we see it today, because Griess did not bother to explain theoretical aspects, motivation for studying a particular reaction, many details of the experimental part, or difficulties encountered in his articles. The systematization that we know is due to Kekulé, in his “Treatise on Organic Chemistry”⁶⁶.

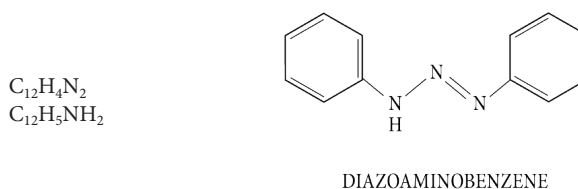
Having studied the nitro- and amino derivatives of phenols, and with aniline still difficult to access, Griess went on to study aminobenzoic acid⁶⁷ (1861), by treatment with nitrous acid he obtained a diazoamino compound to which he assigned the formula:



From anthranilic acid he obtained a more complex compound, to which he assigned the formula:



Only then did he begin to study the behavior of aniline under these conditions, obtaining diazoaminobenzene (1859, published 1862)⁶⁸, the first triazene:



Primarily, this last reaction was of great importance in obtaining azo dyes. The research on compounds grouped as ‘azo compounds’ occupied Griess until 1866, when he began to investigate other nitrogen compounds, generally isolated subjects unrelated to previous research, quite specific. Years later he would return to azo compounds, in articles generically titled “New observations on...”, now including substances such as naphthylamine (which led to Griess’s test for nitrites, discussed above), or benzidine (which led to new dyes, now considered carcinogenic). The most important dye derived from benzidine is Congo Red, developed by Paul Böttiger in 1884 while he was working at *Friedrich Bayer & Co.*, a company that showed no interest in the new dye. Böttiger used it at his father’s textile factory in Łódź and later offered it to *BASF*, which also showed no interest. He then sold the patent to *AGFA*, which made substantial profits from it. Almost nothing is known about Paul Böttiger. Congo Red is still used in biochemical analyses.

In the interval Griess occupied himself with other subjects, of which we will mention two. First, the obtaining of N-alkyl derivatives of aminobenzoic acids (1872), using alkyl iodides and potassium salts, which led to a method of alkylation of amino acids⁶⁹. Thus, starting from meta-aminobenzoic acid and with excess methyl iodide, Griess obtained a betaine, which he represented as [A]; from sulfanilic acid, he obtained the compound which he represented by [B], and from ortho-aminophenol, he obtained the compound represented by [C].

Today we say that we are dealing with a method for obtaining N-aminomethylbenzoic acid, N,N-dimethylaminobenzoic acid, etc. Figure 13 shows our representation of these reactions studied by Griess, who did not have the theoretical knowledge and chemical analysis skills that we have today.

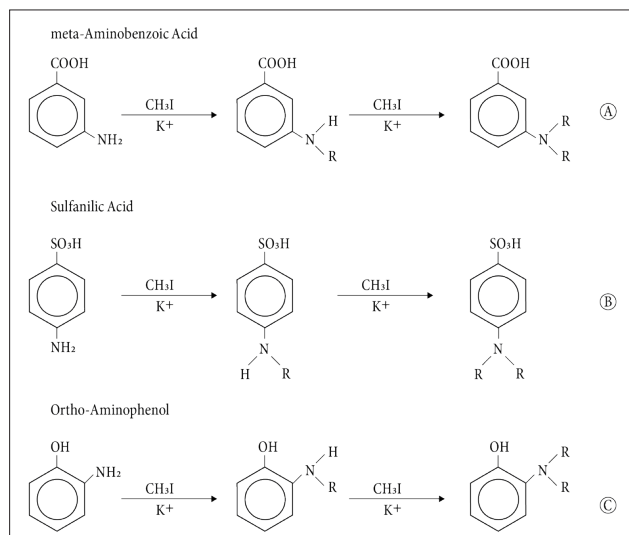


Fig. 13 N-alkyl - and N,N-dialkyl derivatives of aminoaromatic compounds

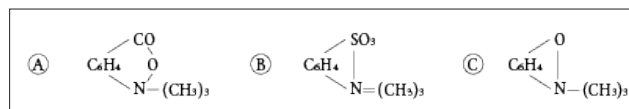
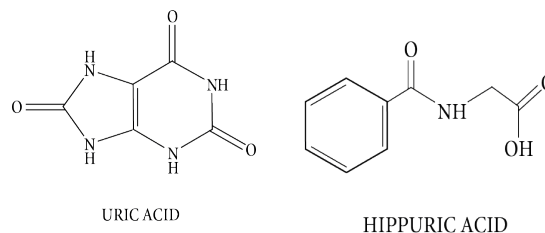


Fig. 14 Fischer's notation for the compounds in Fig. 13 (1894)

Emil Fischer observes that the complexity of the products obtained and the wide variety of possible transformations sometimes led an experienced and patient researcher like Griess down the wrong path, but in the end, the correct results were obtained⁷⁰. This situation is observed in the second group of experiments we wanted to mention, in which Griess worked from 1860 to 1885: the reactions of aminobenzoic acids with cyanide, cyanamide, and urea⁷¹. For example, the reaction of anthranilic acid with the cyano radical in alcoholic solution⁷² leads to a compound to which he assigned the formula $C_{10}H_{10}N_2O_2$, which with HCl forms $C_8H_6N_2O_2$, which would be an isomer of azodioxindole, obtained by Baeyer during the synthesis of indigo. To verify if the reaction also occurred with aliphatic amino acids, he reacted glycine with urea⁷³, obtaining a compound of the formula $C_3H_6N_2O_2$, whose structure he did not determine; had he done so, he would have discovered the synthesis of uric acid, which is now universally attributed to Ivan Horbaczewski (1854-1942)⁷⁴.

A third example (1880) of Griess's reactions involving aromatics is the reaction of isomeric aminophenols (ortho-, para-) with excess methyl iodide CH_3I . The reaction gives rise to betaines, which according to Griess undergo rearrangement to dimethylaminoanisoles⁷⁵. The variant with ethyl iodide does not occur.

Griess also worked with hippuric acid: starting from salts of diazohippuric acid, he obtained new derivatives such as hydroxyhippuric acid ($C_9H_9NO_4$) and iodohippuric acid⁷⁶ ($C_9H_8NIO_3$). Since many of the compounds studied by Griess had complicated structures, he often failed to determine them, identifying new compounds instead through comparison with other compounds and by their physical properties.



CONCLUSION.

Griess was averse to theoretical considerations, but some of his empirical results helped to define certain aspects of the theory, for example, his contribution to clarifying the positions of substituents on the benzene ring.

As an experimental chemist, his case is peculiar: as the head chemist of a large brewery, his experiments in this area, with few exceptions, remained unpublished, as industrial secrets: improvements in fermentation, detection of contaminants, quality control. One of the published works refers to the discovery of choline in hops⁷⁷.

As an experimenter, it could be said that Griess was a 'man of one instrument', but the results he obtained were of enormous importance, both from a scientific point of view (study of diazotization and azo compounds, of aromatic compounds) and from a practical and technological point of view: the use of diazonium salts in organic synthesis, both via azo compounds and through the possibilities of the Sandmeyer reaction. Rarely has a scientific topic been studied with such detail and so intensively as the formation of diazonium salts and azo compounds by Griess.

Interested in practical matters and needing employment, he went to England, as we have seen, at the invitation of A. W. Hofmann to conduct research at the *Royal College of Chemistry*, where he felt comfortable with his German colleagues. Leaving the *College*, he was unable to fully adapt to life in England, beginning with the language (he generally published in German, in journals like the *Berichte* and *Annalen*). He received several invitations to return to Germany, including one from Hein-

rich Caro to work at BASF. He refused them so that his English children would not feel ‘out of place’ in another country, as he himself felt ‘out of place’ in England. Social life intensified with his marriage to Louise Mason, who, however, fell ill and spent years unable to leave the house, eventually becoming bedridden under the care of her husband and housekeeper, until her death in 1886. Griess and his children continued to spend their summer holidays in Bournemouth, on the English Channel, which since 1810 had begun to emerge as a summer resort. During one of these stays in Bournemouth, Peter Griess died of a heart attack on August 30, 1888. He was buried in Burton, next to Louise, in the Mason family tomb.

Griess was a member of the *Royal Society* (1869), received a honorary *PhD* from the University of Munich (1877), and was vice-president of the Chemical Society and of the Society of Industrial Chemistry.



(FIG. 15) Bournemouth, resort where Peter Griess and his family spent their summer holidays. Postcard from 1895, showing the access to the pier (public domain).



(FIG.16) Peter Griess's house in Burton-on-Trent (courtesy Dr. Edwin Yates, University of Liverpool).

AKNOLEDGEMENT

The author expresses his gratitude to Prof.Dr. Edwin Yates, University of Liverpool, for the photograph of Peter Griess's house in Burton-on-Trent.

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