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History of methyl phosphoric esters: Hall, Weger, and Lossen

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Received April 4, 2009, accepted June 25, 2009

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Pharmazie 64: 840–845 (2009) *doi: 10.1691/ph.2009.9113*

Williamson serendipitously discovered (1851) a new and efficient way to produce ethers using ethyl iodide and potassium salts and in doing so elucidated the molecular mechanism behind ether formation. Before Williamson, the direct reaction between alcohol and acids was the only method of generating the elusive "ethers". This tedious and low yield approach eventually led to Voegeli's synthesis of the first organophosphate ever, triethyl phosphate (TEP) in 1848. Based on the landmark work of Williamson, however, over the next thirty years or so numerous chemists managed to produce TEP and tetraethyl pyrophosphate (TEPP) using synthetic pathways of increasingly higher yield. With the "wood spirit" (methyl-alcohol) easily available attempts were also made during the same period to synthesize methyl ester analogues (TMP and TMPP). The synthesis of TMP was reported 1887 by Hall in a paper dealing with vanadium esters; he acknowledges his inability to synthesize methyl vanadate and states that "*methyl phosphate had not been described*" and goes on to briefly mention the synthesis of methyl phosphate by the Wiliamson method. Hall was however mistaken; the synthesis of TMP had previously been reported by Weger in 1883 and achieved even earlier by Lossen. Tetramethyl pyrophosphate (TMPP) was only recently (1949) synthesized by Toy. This report attempts to identify the pharmacists and chemists involved in the quest for phosphoric and pyrophosphoric acid methyl esters.

1. Introduction

The year 1801, when Boudet (1778–1849) generated traces of "ether" by directly reacting alcohol and phosphoric acid could be viewed as the beginning of organic phosphorus chemistry. Boullay (1777–1869) recognized 1807 that the Boudet's "phosphoric ether" was identical with the "sulfuric ether" (and none of them contained phosphor or sulfur). Soon thereafter in 1820 Lassaigne (1800–1859) draw the analogy between sulphovinic and phosphovinic acids and demonstrated the existence of phosphovinic acid, while 1833 Pelouze (1807–1867) synthesized it. Finally 1848 Franz Anton Voegeli (1825–1874) produced the first neutral ester of phosphoric acid, the triethyl phosphate (TEP), using salts of the phosphovinic acid (Petroianu 2008, 2009).

Shortly thereafter ether chemistry made a quantum leap when Alexander Williamson (1824–1904) elucidated the ether formula and described the intermediate reaction steps leading to ether formation (Priesner 1986). Based on the landmark work of Williamson and the availability of reactive compounds such as phosphorus pentacloride (Sir Humphry Davy, 1810), ethyl iodide (Gay-Lussac, 1815), and oxychloride of phosphorus (Charles Wurtz, 1846) numerous chemists managed to produce TEP using synthetic pathways of increasingly higher yield:

- Philippe de Clermont (1831–1921) and Wladimir Moschnin reacted ethyl iodide and potassium salts of the phosphoric acid (Williamson synthesis) (de Clermont 1854, 1855)
- Hugo Schiff (1834–1915) reacted oxychloride of phosphorus [$POCl_3$] with alcohol (Kopp and Will 1858).
- Heinrich Limpricht (1827–1909) and his assistant Emil Rubien reacted oxychloride of phosphorus ($POCl_{3)}$ with sodium ethylate (Et-O-Na, Limpricht 1865).
- Georg Ludwig Carius (1829–1875) reacted 1866 anhydrous phosphorus (P_2O_5) with alcohol (Carius 1866).

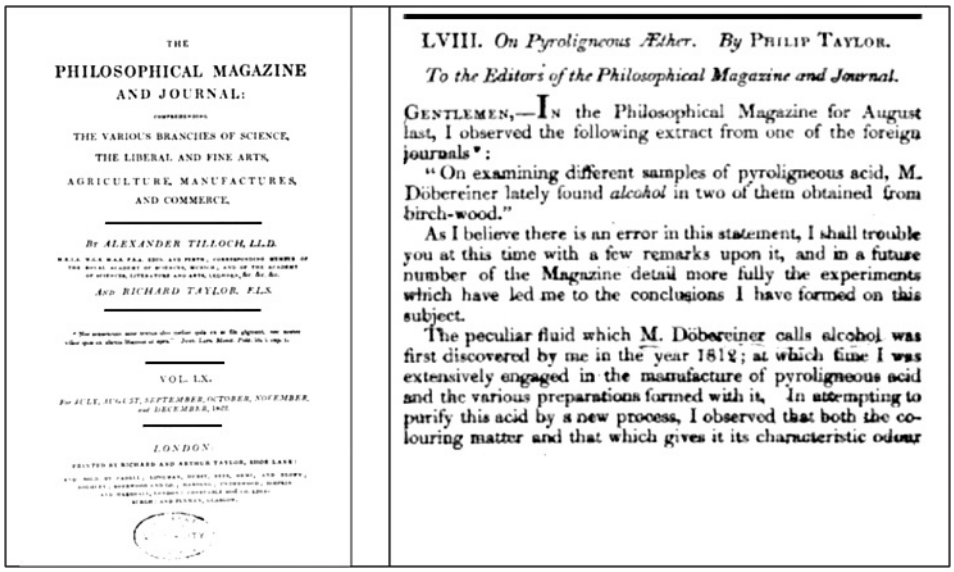
Pyrophosphoric acid was synthesized 1827 by Clarke[1] of Glasgow; Moschnin and de Clermont using the Wiliamson synthesis obtained tetraethyl pyrophosphate (TEPP) (Petroianu 2008; de Clermont 1854, 1855).

2. Organophosphate synthesis

Although with the TEP synthesis by Voegeli the first organophosphate was created, this accomplishment is eclipsed by the Moschnin und de Clermont synthesis of TEPP five years later: while TEPP was not the first organophosphate ever to be synthesized it was however the first organophosphate cholinesterase inhibitor (Petroianu 2008).

Almost simultaneously the quest for the methyl ester analogues TMP and TMPP started. "Pyrolignaeus aether", later named by

[1] Thomas Clarke of Glasgow (1801-1867): The son of a captain in the merchant navy started as a chemist in Glasgow. After his paper on pyrophosphate he becomes a medical student and became an MD 1831. After some years as apothecary of the Glasgow infirmary he obtains by competition the Chair of Chemistry in Marischal College, Aberdeen. He contributed to water testing and softening hard (chalk) waters.



THE
PHILOSOPHICAL MAGAZINE
AND JOURNAL:
COMPREHENDING
THE VARIOUS BRANCHES OF SCIENCE,
THE LIBERAL AND FINE ARTS,
AGRICULTURE, MANUFACTURES,
AND COMMERCE.

By ALEXANDER TILLOCH, LL.D.
AND RICHARD TAYLOR, F.L.S.

VOL. LX.

LONDON:

LVIII. *On Pyroligneous Æther.* By PHILIP TAYLOR.

To the Editors of the Philosophical Magazine and Journal.

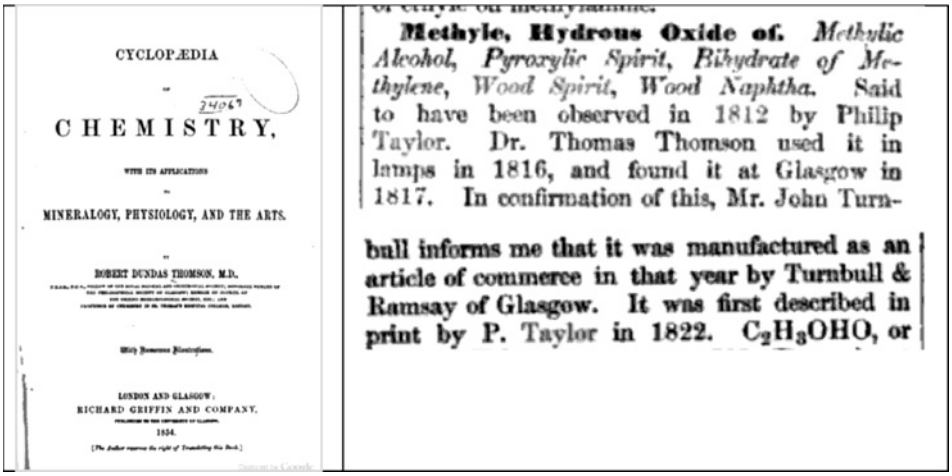
GENTLEMEN,—IN the Philosophical Magazine for August last, I observed the following extract from one of the foreign journals":

"On examining different samples of pyroligneous acid, M. Döbereiner lately found *alcohol* in two of them obtained from birch-wood."

As I believe there is an error in this statement, I shall trouble you at this time with a few remarks upon it, and in a future number of the Magazine detail more fully the experiments which have led me to the conclusions I have formed on this subject.

The peculiar fluid which M. Döbereiner calls alcohol was first discovered by me in the year 1812; at which time I was extensively engaged in the manufacture of pyroligneous acid and the various preparations formed with it. In attempting to purify this acid by a new process, I observed that both the colouring matter and that which gives it its characteristic odour

Fig. 1: Philip Taylor first observed and than manufactured "pyrolignaeus aether" (methyl alcohol) in 1812. His publication describing the product appeared ten years latter in the "Philosophical Magazine and Journal" edited by Richard Taylor (Philip's brother) and printed by Richard and Arthur Taylor (another brother)



CYCLOPÆDIA
OF
CHEMISTRY,
WITH ITS APPLICATIONS
TO
MINERALOGY, PHYSIOLOGY, AND THE ARTS.
BY
ROBERT DUNDAS THOMSON, M.D.
LONDON AND GLASGOW:
RICHARD GRIFFIN AND COMPANY.
1854.

Methyle, Hydrous Oxide of. *Methylic Alcohol, Pyroxylic Spirit, Bihydrate of Methylene, Wood Spirit, Wood Naphtha.* Said to have been observed in 1812 by Philip Taylor. Dr. Thomas Thomson used it in lamps in 1816, and found it at Glasgow in 1817. In confirmation of this, Mr. John Turnbull informs me that it was manufactured as an article of commerce in that year by Turnbull & Ramsay of Glasgow. It was first described in print by P. Taylor in 1822. C_2H_3OHO, or

Fig. 2: In the "Cyclopedia of Chemistry" from 1854 it is stated Philip Taylor observed methyl alcohol 1812 and that Dr. Thomas Thomson (M.D., F.R.S., Regius Professor of Chemistry in the University of Glasgow; 1773–1852) used it 1816 for lightning; "Turnbull & Ramsay" in Camlachie Street, Glasgow manufactured methyl alcohol as an article of commerce

Macaire[2] & Marcet[3] "pyroxylic spirit or "spirit of wood" was available since 1812, when Philip Taylor[4], first observed and than manufactured it (Taylor 1822, Figs. 1 and 2).

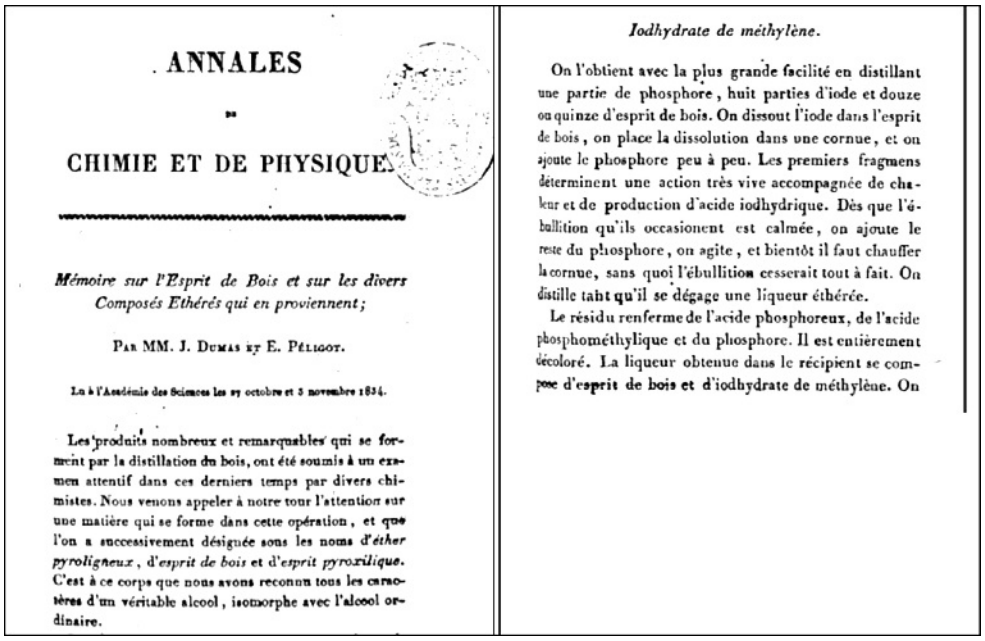
1835 Jean Baptiste Andre Dumas (1800–1884) and Eugène-Melchior Péligot (1811–1890) recognized the "spirit of wood" as being an alcohol and named it methyl alcohol. In the same publication they also described the synthesis of methyl iodide by mixing iodine, phosphorus and wood-spirit: the residue contained phosphorus, phosphoric acid and phosphomethylic acid. The phosphomethylic (phosphopyroxylic) acid was the analogue of the phosphovinic acid generated during ethyl ether production: this was the first step on the way to trimethyl phosphate (Fig. 3).

Some twenty years later Hugo Schiff (1834–1915) obtained both phosphomethylic and phospho-di-methylic acid by the interaction of oxychloride of phosphorus with methyl alcohol (Schiff 1857, Fig. 4). Having achieved the synthesis of phospho-di-methylic acid was the key to synthesis of trimethyl phosphate using the same method Voegeli used to generate triethyl

[2] Jean (Isaac) Francois Macaire [Prinsep] (1796–1869): honorary professor of medicinal chemistry, born in Geneva July 21st, 1796, son of Marc-Etienne Macaire (1765–1795) and Isaline-Françoise Pommier (1782–1861) ; first marriage Caroline Prinsep (1796–1827); second marriage (gives up the name Prinsep) with Agnès Catherine Blake the widow of George Alexandre Prinsep (1791–1839), a brother of the first wife.

[3] François Marcet (1803–1883): son of Alexandre Marcet, FRS (1770–1822) and Mary Jane Haldimand (1769 – 1858, born in Geneva to Anthony and Jane Haldimand). The father (Alexandre) fled Geneva 1794, become a physician in Edinburgh, practiced in London and taught chemistry at Guy's Hospital. In 1817 Jane's father died, leaving her a substantial legacy, and her husband gave up medical practice to devote himself full-time to chemistry. François was a professor of physics in Geneva and member of the city council; he published with Macaire. Best known is François mother Mary Jane Haldimand Marcet; she was a very successful author of popular science books.

[4] Philip Taylor (1786–1870): one of the five sons of John Taylor (1750–1826) of Norwich, affluent yarn manufacturer and apparently a talented hymn writer. Philip studies medicine and starts a surgical training in Tavistock. Realizing his lack of talent for surgery he returns to Norwich to work as a pharmacist, but he is not fulfilled by such "boring" activities. 1815 he joins his older brother John, a mining engineer, who just established a chemical factory in London. There he finds his true vocation: applied chemistry. After some success with street lightning and sugar refining he moves on to establish the "British Iron Company" producing steam operated machinery. After failure of this company he moves to France and then to Sardinia, running various businesses with mixed success. Best known is his sister Sarah Taylor Austin a successful editor and translator. For a detailed description of Philiip's entrepreneurial activities and of the historical context see the excellent review by Olivier Raveux (2000).



. ANNALES

DE

CHIMIE ET DE PHYSIQUE.

Mémoire sur l'Esprit de Bois et sur les divers Composés Ethérés qui en proviennent;

PAR MM. J. DUMAS ET E. PÉLIGOT.

Lu à l'Académie des Sciences les 27 octobre et 3 novembre 1834.

Les produits nombreux et remarquables qui se forment par la distillation du bois, ont été soumis à un examen attentif dans ces derniers temps par divers chimistes. Nous venons appeler à notre tour l'attention sur une matière qui se forme dans cette opération, et que l'on a successivement désignée sous les noms d'*éther pyroligneux*, d'*esprit de bois* et d'*esprit pyroxilique*. C'est à ce corps que nous avons reconnu tous les caractères d'un véritable alcool, isomorphe avec l'alcool ordinaire.

Iodhydrate de méthylène.

On l'obtient avec la plus grande facilité en distillant une partie de phosphore, huit parties d'iode et douze ou quinze d'esprit de bois. On dissout l'iode dans l'esprit de bois, on place la dissolution dans une cornue, et on ajoute le phosphore peu à peu. Les premiers fragmens déterminent une action très vive accompagnée de chaleur et de production d'acide iodhydrique. Dès que l'ébullition qu'ils occasionent est calmée, on ajoute le reste du phosphore, on agite, et bientôt il faut chauffer la cornue, sans quoi l'ébullition cesserait tout à fait. On distille tant qu'il se dégage une liqueur éthérée.

Le résidu renferme de l'acide phosphoreux, de l'acide phosphométhylique et du phosphore. Il est entièrement décoloré. La liqueur obtenue dans le récipient se compose d'esprit de bois et d'iodhydrate de méthylène. On

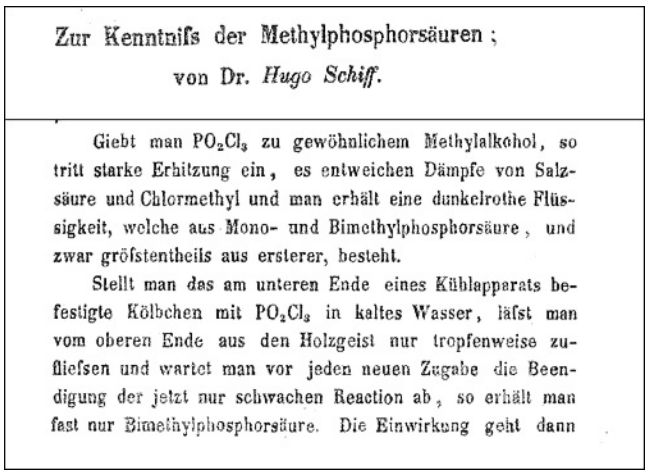
Fig. 3: 1835 Dumas & Peligot recognized the "spirit of wood" as being an alcohol and named it methyl alcohol. They wrote: "*C'est à ce corps que nous avons reconnu tous les caractères d'un véritable alcool, isomorphe avec l'alcool ordinaire*" or "This is a body displaying all the traits of a true alcohol, isomorphic with the common alcohol". In the same publication they described the synthesis of methyl iodide by mixing iodine, phosphorus and wood-spirit: the residue contained phosphorus, phosphoric acid and phosphomethylic acid. The phosphomethylic (phosphopyroxylic) acid was the analogue of the phosphovinic acid generated during ethyl ether production

phosphate from phospho-di-ethylic acid (Voegeli 1848). Whether Schiff took this step or not is unclear; he never published the synthesis of trimethyl phosphate. The 1866 edition of Henry Watts Dictionary of chemistry describes Schiff's synthesis of the mono- and di-methylic acids and goes on in stating that "*the trimethylic ether is not known*".

The synthesis of trimethylic phosphor ether is first mentioned in a Felix Weger publication from 1883 in Liebig's Annalen titled "*Untersuchung gesättigter und ungesättigter Ester und einiger verwandter Verbindungen*" (Weger 1883). The author acknowledges having received the substance (trimethyl phosphate) from Professor Lossen and goes on mentioning that it was obtained by reacting methyl iodide with a silver salt of phosphoric acid (Wiliamson method). He also acknowledges having received di-methyl-ethyl phosphate obtained by reacting ethyl iodide with a silver salt of di-methyl-phosphoric acid (Fig. 5). The publication was based on Weger's doctoral dissertation supervised by Lossen and defended on April 14th at noon in Koenigsberg, having as opponents Dr. Dumke and stud. chem. Behrend (Fig. 6).

3. Felix Viktor Heinrich Weger

Felix Viktor Heinrich Weger belonged to an old Eastern Prussian family where the men used to follow careers in administration and law. Grandfather Weger was law and finance commissioner (*Justiz- and Fiskalkommissar*) and Curator of a Bursary (*Roesenkirsch Stipendium*). Married with Aurora Hoepffner he had three sons; while the two elder ones followed the family tradition, Otto Carl Hermann became a practicing physician in Koenigsberg (*Dr. med. & Sanitaetsrath*). Hermann's youngest son (5th) was Felix Weger who studied chemistry at the Albertus University (documented for 1879 and 1880) in Koenigsberg in Prussia (now Kaliningrad). As a student he lived Steindamm No. 61 (now Leninprospekt), the main street in Koenigsberg. From fall (Michaelis) 1881 to 1882 he is listed as a "stipendiat"



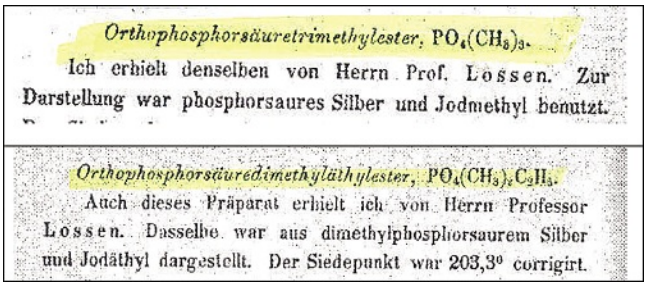
Zur Kenntnifs der Methylphosphorsäuren;

von Dr. *Hugo Schiff*.

Giebt man PO_2Cl_3 zu gewöhnlichem Methylalkohol, so tritt starke Erhitzung ein, es entweichen Dämpfe von Salzsäure und Chlormethyl und man erhält eine dunkelrothe Flüssigkeit, welche aus Mono- und Bimethylphosphorsäure, und zwar gröfstentheils aus ersterer, besteht.

Stellt man das am unteren Ende eines Kühlapparats befestigte Kölbchen mit PO_2Cl_3 in kaltes Wasser, läfst man vom oberen Ende aus den Holzgeist nur tropfenweise zufliefsen und wartet man vor jeden neuen Zugabe die Beendigung der jetzt nur schwachen Reaction ab, so erhält man fast nur Bimethylphosphorsäure. Die Einwirkung geht dann

Fig. 4: Hugo Schiff obtained both phosphomethylic and phospho-di-methylic acid by the interaction of oxychloride of phosphorus with methyl alcohol



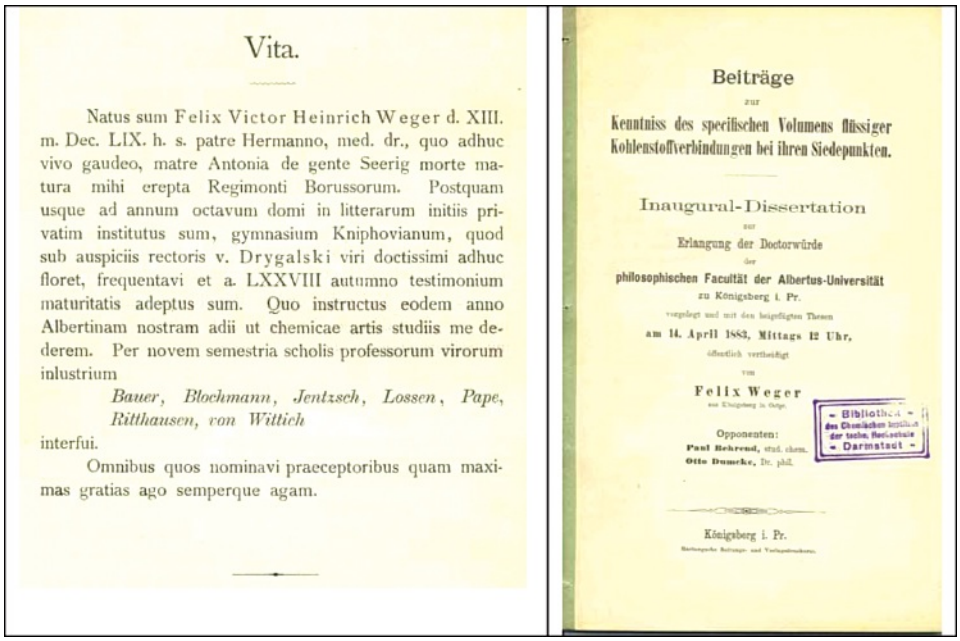
Orthophosphorsäuretrimethylester, $PO_4(CH_3)_3$.

Ich erhielt denselben von Herrn Prof. Lossen. Zur Darstellung war phosphorsaures Silber und Jodmethyl benutzt.

Orthophosphorsäuredimethyläthylester, $PO_4(CH_3)_2C_2H_5$.

Auch dieses Präparat erhielt ich von Herrn Professor Lossen. Dasselbe war aus dimethylphosphorsaurem Silber und Jodäthyl dargestellt. Der Siedepunkt war 203,3° corrigirt.

Fig. 5: The synthesis of trimethylic phosphor ether is first mentioned in a Felix Weger publication from 1883 in Liebig's Annalen titled "*Untersuchung gesättigter und ungesättigter Ester und einiger verwandter Verbindungen*". The author acknowledges having received the substance (trimethyl phosphate) from Professor Lossen and goes on mentioning that it was obtained by reacting methyl iodide with a silver salt of phosphoric acid (Wiliamson method). He also acknowledges having received di-methyl-ethyl phosphate obtained by reacting ethyl iodide with a silver salt of di-methyl-phosphoric acid



Vita.

Natus sum Felix Victor Heinrich Weger d. XIII. m. Dec. LIX. h. s. patre Hermanno, med. dr., quo adhuc vivo gaudeo, matre Antonia de gente Seerig morte matura mihi erepta Regimonti Borussorum. Postquam usque ad annum octavum domi in litterarum initiis privatim institutus sum, gymnasium Kniphovianum, quod sub auspiciis rectoris v. Drygalski viri doctissimi adhuc floret, frequentavi et a. LXXVIII autumno testimonium maturitatis adeptus sum. Quo instructus eodem anno Albertinam nostram adii ut chemicae artis studiis me dederem. Per novem semestria scholis professorum virorum inlustrium

Bauer, Blochmann, Jentzsch, Lossen, Pape, Ritthausen, von Wittich

interfui.

Omnibus quos nominavi praeceptoribus quam maximas gratias ago semperque agam.

Beiträge

zur

Kenntniss des specifischen Volumens flüssiger Kohlenstoffverbindungen bei ihren Siedepunkten.

Inaugural-Dissertation

zur

Erlangung der Doctorwürde

der

philosophischen Facultät der Albertus-Universität

zu Königsberg i. Pr.

vorgelegt und mit den beigefügten Thesen

am 14. April 1883, Mittags 12 Uhr,

öffentlich vertheidigt

von

Felix Weger

aus Königsberg in Ostpr.

Opponenten:

Paul Behrend, stud. chem.

Otto Dumcke, Dr. phil.

Königsberg i. Pr.

Fig. 6: Weger's doctoral dissertation supervised by Lossen and defended on April 14th at noon in Koenigsberg, having as opponents Dr. Dumke and stud. chem. Behrend

(bursary holder). In 1883 he received his doctoral degree from the same University; the thesis was entitled "*Beitrage zur Kenntnis des specifischen Volumens flüssiger Kohlenstoffverbindungen bei ihren Siedepunkten*"; 1884 he became an assistant at the University. Sometimes after 1884 (and before 1907) he enrolled as a graduate student at the Royal School of Weaving, Dyeing, and Finishing in Krefeld ("*Königliche Webe-, Färberei- und Appreturschule Krefeld-Uerdingen*"), probably indicating his desire to find a (better paid) position in the textile industry.

4. Wilhelm Clemens Lossen

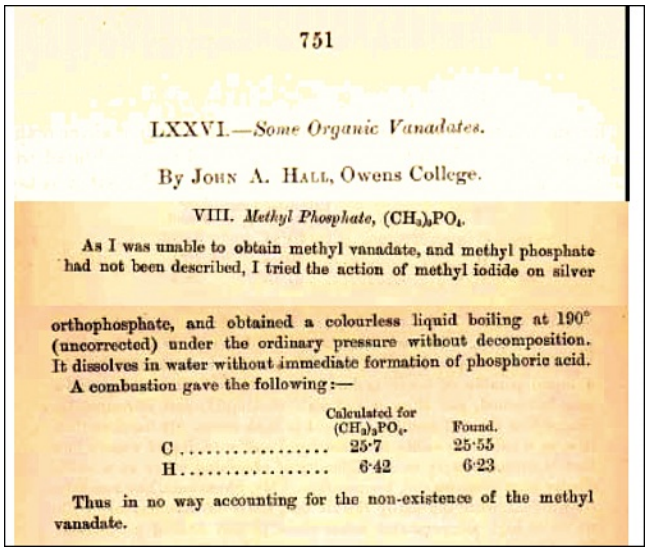
Professor Lossen who donated trimethyl phosphate to Weger was Wilhelm Clemens Lossen (1838–1906), since 1877 Chair of Chemistry at the Albertus University in Koenigsberg. Wilhelm was the first born son of Dr. med. Valentin Lossen (1803–1884), practicing physician in Kreuznach. Wilhelm studied first in Gießen (winter 1857 to summer 1859), than in Göttingen with Friedrich Wöhler (1800–1882) where he received his Ph.D. in 1862. After working as an assistant to Karl Weltzien (1813–1870) in Karlsruhe he went on to become an assistant to Wilhelm Heinrich Heintz (1817–1880) in Halle only to move on to Heidelberg where he received his Habilitation in 1877. After being appointed extraordinary Professor in Heidelberg 1877 he became the same year "*Ordinarius*" [Chair] in Koenigsberg, succeding Professor Carl Graebe. He chaired the Department until 1903 when he retired, being succeded by Heinrich Klinger. Professor Lossen was a secret government advisor (Geheimer Regierungs-Rath) and a member of the Imperial Leopoldine Carolinian German Academy of Nature Researchers (*Kaiserlich Leopoldinisch-Carolinische deutsche Akademie der Naturforscher*). Lossen is best remembered for elucidating the exact molecular formula of cocaine (1863) and the synthesis of hydroxylamine NH_2OH (1865), a substance which will turn out to be of great importance for those interested in the treatment of organophosphate cholinesterase inhibitor exposure.

Wilhelm's younger brother Karl August (1841–1893) was not less renowned; he was professor and state geologist (*Landesgeolog*) at the Royal Geological State Institution and Mining Academy (*koeniglichen geologischen Landesanstalt und Bergakademie*) in Berlin.

Four years later (1887) John A Hall, from Owens College, Manchester, published a paper dealing with vanadium esters; the final section (VIII) is dedicated to methyl vanadate. He acknowledges his inability to synthesize methyl vanadate and (erroneously) states that "*methyl phosphate had not been described*" and goes on to briefly mention the synthesis of methyl phosphate by the Wiliamson method (identical to Lossen approach mentioned by Weger) (Fig. 7).

5. John A. Hall

John A. Hall FCS (1868–1932), was born August 24th, 1868, at Manchester (Fig. 8). His father was Robert Hall, agent, and his



751

LXXVI.—*Some Organic Vanadates.*

By John A. Hall, Owens College.

VIII. *Methyl Phosphate*, $(CH_3)_3PO_4$.

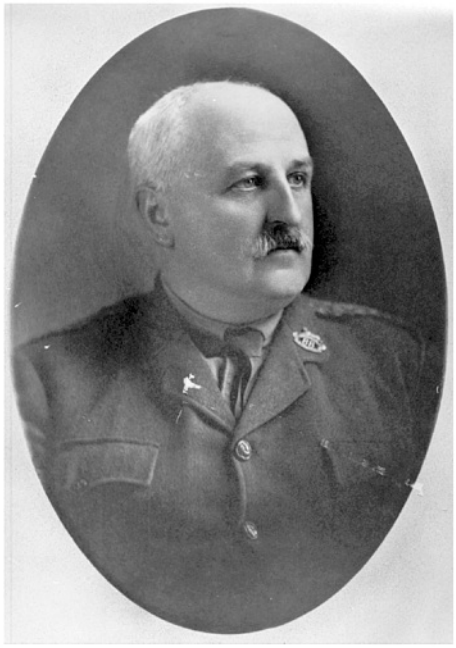
As I was unable to obtain methyl vanadate, and methyl phosphate had not been described, I tried the action of methyl iodide on silver orthophosphate, and obtained a colourless liquid boiling at 190° (uncorrected) under the ordinary pressure without decomposition. It dissolves in water without immediate formation of phosphoric acid.

A combustion gave the following:—

	Calculated for $(CH_3)_3PO_4$.	Found.
C	25·7	25·55
H	6·42	6·23

Thus in no way accounting for the non-existence of the methyl vanadate.

Fig. 7: John A Hall, from Owens College, Manchester, published a paper dealing with vanadium esters; the final section (VIII) is dedicated to methyl vanadate. He acknowledges his inability to synthesize methyl vanadate and (erroneously) states that "*methyl phosphate had not been described*" and goes on to briefly mention the synthesis of methyl phosphate by the Wiliamson method (identical to Lossen approach mentioned by Weger)



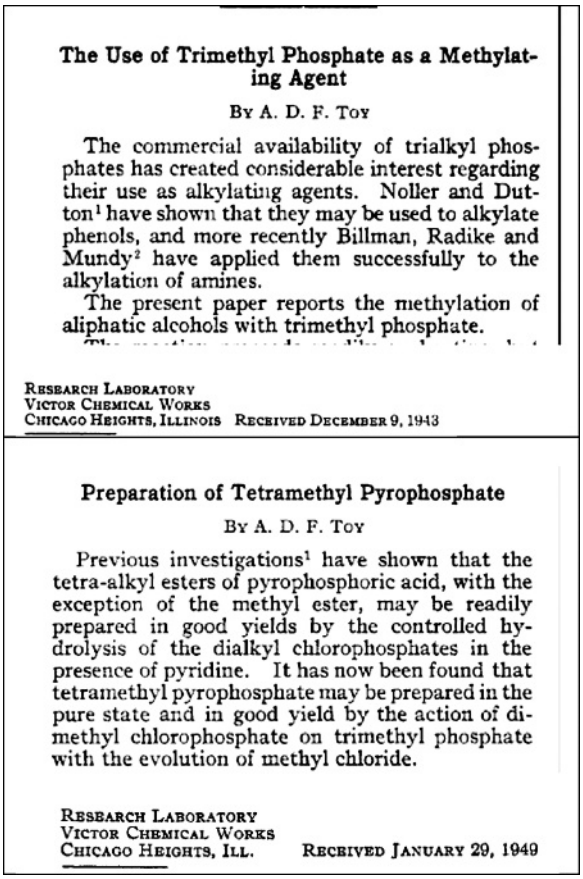
"Image G-03821 courtesy of Royal BC Museum, BC Archives" Kelly-Ann Turkington, Permissions Officer, BC Archives, Canada

Fig. 8: Lieutenant-Colonel John Albert Hall

address 128, Lloyd Street in Greenheys, Manchester, location which is very close to the University site. In 1885, he entered October Owens College (established 1851), the predecessor institution of the University of Manchester (named after a textile merchant who financially supported it); 1880 it became part of the Victoria University of Manchester. Henry Enfield Roscoe (1833–1915) was Chair of the Chemistry Department at Owens College until 1887, so Hall was a Roscoe student. Roscoe is best known for having discovered the element 23, Vanadium, in 1865. Hall earned his B.Sc. in Chemistry with distinction (1st class) in 1888. The same year he received the prestigious Mercer Scholarship: the scholarship was founded under the will of the late Robert Clayton Mercer (1828–1881) for the encouragement of the study of chemistry. Robert Clayton Mercer was the son of John Mercer (1791–1866) one of Britain's great textile chemists and the inventor of a process which was named after him, the "mercerisation".

After graduation he became a Fellow of the Chemical Society (1889) and while continuing to work towards a master's degree he joined the Clayton Aniline Co. in Manchester (1888–1893). The Clayton Aniline Company was founded in 1876 by a chemist from Alsace, Charles Dreyfus (1848–1935), to manufacture intermediates and dyestuffs. During Hall's time at Clayton Aniline his name appears in patents for improvements in dye manufacture.

After receiving his M.Sc. degree in 1892, Hall emigrated (1893) to British Columbia and settled in Victoria. The subsequent month were rich in events for Hall both personally and professionally. He married Annie Gatenby (1868–1937) who also moved from Britain to Canada the same year and together with two friends he co-established the Victoria Chemical Works located at 7 Dallas Road in Esquimalt (incorporated on November 29, 1893). The company manufactured acids, fertilizers and tree sprays. After merging with other Companies in 1912 Victoria Chemical Works became part of Canadian Explosives Company. Hall served over the years as chief chemist of the enterprise.



The Use of Trimethyl Phosphate as a Methylating Agent

By A. D. F. Toy

The commercial availability of trialkyl phosphates has created considerable interest regarding their use as alkylating agents. Noller and Dutton[1] have shown that they may be used to alkylate phenols, and more recently Billman, Radike and Mundy[2] have applied them successfully to the alkylation of amines.

The present paper reports the methylation of aliphatic alcohols with trimethyl phosphate.

Research Laboratory
Victor Chemical Works
Chicago Heights, Illinois Received December 9, 1943

Preparation of Tetramethyl Pyrophosphate

By A. D. F. Toy

Previous investigations[1] have shown that the tetra-alkyl esters of pyrophosphoric acid, with the exception of the methyl ester, may be readily prepared in good yields by the controlled hydrolysis of the dialkyl chlorophosphates in the presence of pyridine. It has now been found that tetramethyl pyrophosphate may be prepared in the pure state and in good yield by the action of dimethyl chlorophosphate on trimethyl phosphate with the evolution of methyl chloride.

Research Laboratory
Victor Chemical Works
Chicago Heights, Ill. Received January 29, 1949

Fig. 9: Tetramethyl pyrophosphate[TMPP] was only recently (1949) synthesized by Toy using TMP as a methylating agent

After a successful scientific and business career Hall's interest turned towards the military and he joined the 1899 the Canadian Artillery Militia (5th British Columbia Regiment) where he quickly rose to the top. He served as a commanding officer of the regiment for some years before moving on to the 88th Victoria Fusiliers, and than to command the Civil Aid Forces raised to quell miners rioting at Nanaimo.

At the onset of the Great War Lieutenant-Colonel John A. Hall joined the Canadian Over-Seas Expeditionary Force: The 30th Battalion formed in Victoria, BC in the fall of 1914 sailed for England February 23rd 1915, with 980 other ranks and 35 officers under his command. Apparently after a short period in France Hall returned to Britain for special duty related to the manufacturing of explosives.

After the War he received a *honoris causa* D.Sc. degree from his alma mater. He did not attend the degree ceremony. He returned to British Columbia where he died May 18th, 1932 at Castlewood (1211 Old Esquimalt Rd).

6. Arthur Dock Fon Toy

Tetramethyl pyrophosphate (TMPP) was quite recently (1949) synthesized by Toy using TMP as a methylating agent (Fig. 9). Arthur Dock Fon Toy (1916–1996) (Fig. 10), while best known for his best-seller "*Phosphorus Chemistry in Everyday Living*", a superbly written chemistry book for the masses, his research in phosphorus chemistry earned him more than 80 patents. Dr. Toy, a native of China, came to the US as a child. He received his doctorate in chemistry from the University of Illinois. He originally worked at Victor Chemical Works in Illinois. After its merger with the Stauffer Chemical Company in Westport, Conn., he assumed increasingly higher positions, retiring from

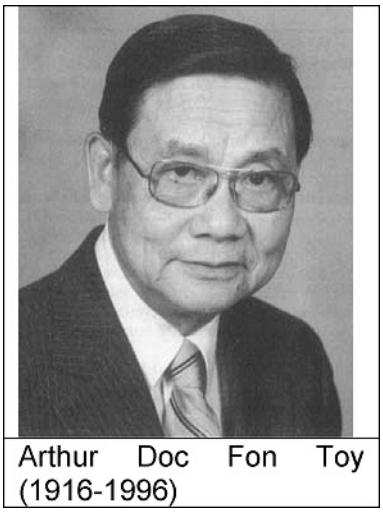


Fig. 10: Arthur Dock Fon Toy**,** while best known for his best-seller "*Phosphorus Chemistry in Everyday Living*", a superbly written chemistry book for the masses, was an expert in phosphorus chemistry with more than 80 patents

Stauffer in 1981 as the company's director of research. Victor Chemical Works, was started by the German-born August Kochs (1871–1960) in 1902. While working for Victor, Toy improved the synthesis of TEPP and TMPP.

7. Conclusion

In conclusion, Lossen is the father of trimethyl phosphate (TMP) while Toy can claim paternity of tetramethyl pyrophosphate (TMPP). While this short communication does not exhaustively answer the questions "who was Lossen or Weger or Hall?" it should satisfy the idle curiosity of most researchers. For those wishing to know more, it gives some direction for future investigations.

Acknowledgements: My gratitude to all those who helped gather the information and/or write the manuscript: Guido Dresbach (Mainz, Germany), Wilfried Melchior (Antiquariat & Verlag, Spreewaldheide, Germany), James Peters (University Archivist, John Rylands University Library, University of Manchester), C. Schummer (Universität Heidelberg, Mannheim), Larry Toy (United States), Kelly-Ann Turkington (Permissions Officer, BC Archives, Canada) - and to the miracle of Internet connectivity and Google Books, who made these and many other things possible.

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