

Department of Cellular Biology & Pharmacology, Herbert Wertheim College of Medicine, Florida International University, Miami, USA

History of arsenic ethers: who was Felix D'Arcet?

G. A. PETROIANU

Received February 28, 2012, accepted March 12, 2012

Prof. Dr. med. Georg A. Petroianu, Florida International University Herbert Wertheim College of Medicine, Department of Cellular Biology & Pharmacology, University Park, 11200 SW 8th Street, Miami-33199 FL, USA
georg.petroianu@fiu.edu

Pharmazie 67: 951–953 (2012)

doi: 10.1691/ph.2012.2052

Williamson serendipitously discovered (1851) a new and efficient way to produce esters using ethyl iodide and potassium salts and in doing so elucidated the molecular mechanism behind ether formation. Lassaigne (1820) made the analogy between sulphovinic and phosphovinic acids and demonstrated the existence of phosphovinic acid, while Pelouze (1833) synthesised monoethyl phosphovinic acid. Finally 1848 Voegeli produced diethyl phosphovinic acid and the first neutral ester of phosphoric acid, the triethyl phosphate (TEP). The successes of Lassaigne and Pelouze in producing phosphovinic acids and Mitscherlich's theory of isomorphism fuelled the search for the vinic acids of arsenic, phosphorus neighbor in the periodic system. This short report attempts to identify the (less known) pharmacists and chemists involved in the quest for both arsenovinic acids and the neutral esters of arsenic and pyroarsenic acids.

1. Introduction

In 1801 Jean-Pierre Boudet (1778–1849) generated traces of “ether” by directly reacting alcohol and phosphoric acid. Pierre François Guillaume Boullay (1777–1869) recognized that Boudet's “phosphoric ether” was identical with both the “sulphuric ether” and the “arsenic ether” (and none of them contained phosphor, sulfur or arsenic)¹ (Boullay 1815). Soon thereafter in 1820 Jean Louis Lassaigne (1800–1859) drew the analogy between sulphovinic and phosphovinic acids and demonstrated the existence of monoethyl phosphovinic acid, while 1833 Th  ophile-Jules Pelouze (1807–1867) synthesized it. Finally 1848 Frauz Anton Voegeli (1825–1874) produced both diethyl phosphovinic acid and the first neutral ester of phosphoric acid, the triethyl phosphate (TEP) (Petroianu 2009, 2010).

The successes of Lassaigne and Pelouze in producing phosphovinic acids and Eilhard Mitscherlich's (1794–1863) theory of isomorphism fuelled the quest for the vinic acids of arsenic, phosphorus neighbor in the periodic system. Arsenic acid was first prepared by Karl Wilhelm Scheele (1742–1786) in the year 1775. Felix d'Arcet [Darcet] (1807–1846) published 1835 in Comptes Rendus his “*Note sur l'acide arseno-vinique*” and a year later a german version in Liebig's Annalen “*Ueber Arsenikweins  ure*” (D'Arcet 1835, 1836) (Figs. 1, 2).

Ether chemistry made a quantum leap when Alexander Williamson (1824–1904) serendipitously discovered a new and efficient way to produce ethers using ethyl iodide and potassium salts (Williamson 1851). Indeed the neutral alkyl esters of arsenic acid were first synthesized 1870 by James Mason Crafts (1839–1917) using this approach (Crafts 1870).

With the introduction of the Williamson method attempts to generate ethers via the cumbersome vinic acid route were

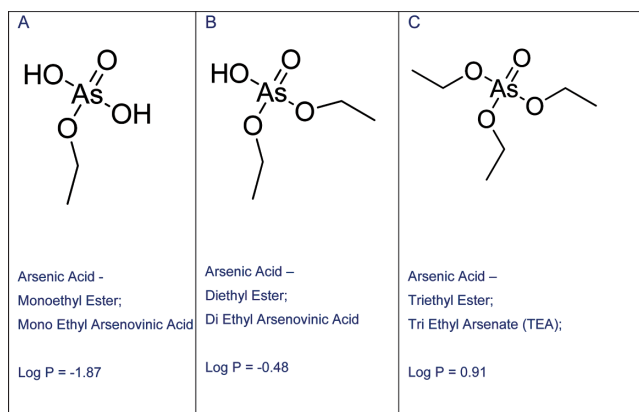


Fig. 1: D' Arcet described 1835 the isolation of diethyl arsenovinic acid (*acide arsenovinique*; *Arsenikweins  ure*; *Biaethylarsens  ure*) [1B]. The neutral esters (triethyl arsenate [1C] and trimethylarsenate, not shown) were synthesized by Crafts in 1870

abandoned. 1859 Hugo Schiff (1834–1915) confirmed earlier skepticism expressed by Christian Gottlob Gmelin (1792–1860) regarding the arseno-vinic acid by showing that D'Arcet's product was most likely a mixture of acetate and arsenate (Schiff 1859).

The history of pyroarsenates is less straight forward. The existence of pyroarsenic acid was to be expected according to the isomorphism theory and was first demonstrated, albeit indirectly, 1830 by Huenefeld² (Huenefeld 1830). While the synthesis of pyroarsenic acid was described 1856 by Kopp³,

¹ For a superb account of the history of ether discovery and of the phenomena involving etherification including the role of vinic acids intermediates, see Priesner (1986).

² Friedrich Ludwig **Huenefeld** (1799–1882), obtained his “*venia legendi*” in Chemistry and Pharmacy 1824 in Breslau and taught in Greifswald from 1826 to 1882 (since 1833 tenured Professor; Ordinarius).

³ Charles Emile **Kopp** (1817–1875), politician and scientist, taught at the Universities of Lausanne, Turin and Zuerich.

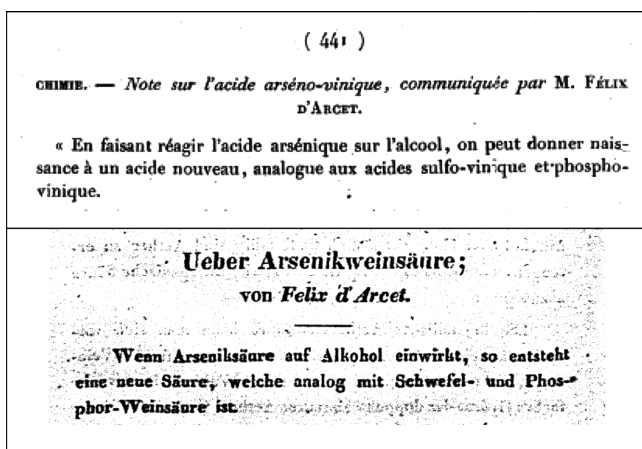


Fig. 2: The French (1835) and German (1836) publications of D'Arcet regarding the synthesis of arsenovinic acid by reacting arsenic acid with alcohol

its existence was questioned repeatedly over time, the issue being finally settled by Rosenheim⁴ about a century later (Kopp 1856; Rosenheim and Antelmann 1930). Neutral esters of the pyroarsenic acid have (to my knowledge) never been isolated. The purpose of this brief communication is to shed some light on the life and achievements of Felix D'Arcet.

2. Felix d'Arcet (1807–1846)

The Darcet or D'Arcet family can be traced back over many generations:

François (1695–1773), judge in Doazit, later became lieutenant general at the Gascogne bailiwick.

Jean (1724–1801) was the son of François and Marguerite d'Audignon. He was an important personality of his era: Physician, Professor of Chemistry at the College de France, Director of the Royal Porcelain Manufacture at Sevres and member of the Institute de France (Wisniak 2004). He married the daughter of Guillaume François Rouelle (1703–1770), the most famous French pharmacist of the time. Rouelle is the one who introduced the concept of a base into chemistry, as a substance which reacts with an acid to give it solid form as a salt (Jensen 2006).

Jean Pierre Joseph (1777–1844), son of Jean was a well-known chemist of his time best remembered for his “*soupes gélatineuses de Darcet*” or jelly-like gelatinous soups as mentioned by Balzac (1799–1850) in *The Magic Skin (La peaux de chagrin)*. These nutritious preparations of dubious taste were distributed in French hospitals to the poor. JPJ was a Member of the French Academy of Sciences. He married Claire Choron, and they had three surviving children: Félix, Louise and Pauline, Louise (1814–1885) being the most “*celebre*”. She married the sculptor James Pradier (1792–1852) and served as a real life inspiration for Emma in the novel “*Madame Bovary*” by Gustave Flaubert (1821–1880).

Felix (1807–1846) Fig. 3 obtained his bachelor's degree in science 1828 and subsequently participated as a chemist to the research expedition to Egypt (1828–1829) under Etienne Pariset (1770–1847), secretary to the “*Academie de Medecine*”. In Egypt D'Arcet studied the plague and introduced a method of

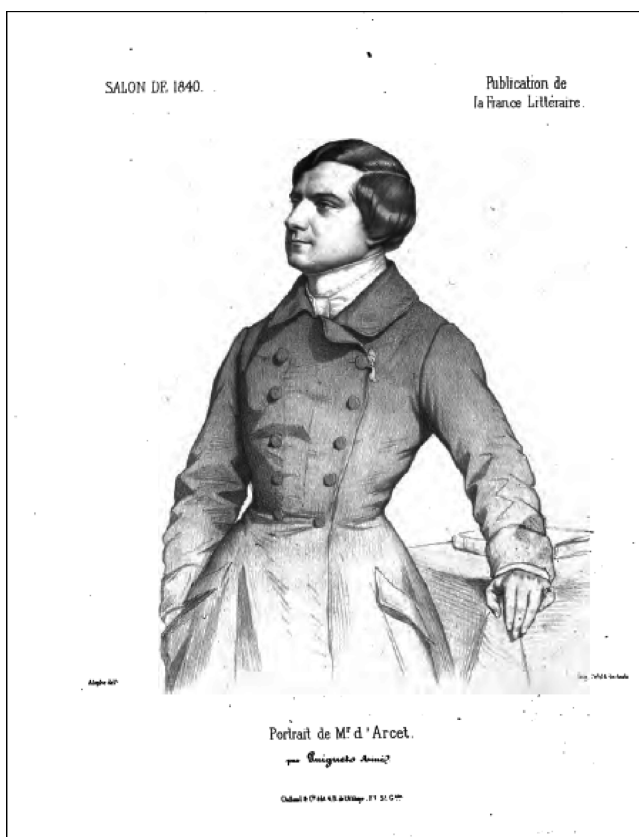


Fig. 3: Portrait of Felix d'Arcet by Jean Baptiste Guignet (1812–1857) from the “Album du Salon de 1840, Paris 1840”

water purification using alum (alumen *lat*; aluun *german*; alun *french*) (Fig. 4). For his services he was named *Chevalier de la Legion d'Honneur* at the early age of twenty-three.

Upon his return to France he continued work in chemistry leading to his “*discovery*” of the arsenovinic acid and of a number of salts and esters of succinic acid (D'Arcet 1835). Subsequently his interests shifted to medicine, received hospital privileges (*externe des hôpitaux*) and 1842 the Doctoral title from the Medical Faculty in Paris for work on pus and multiple abscesses (septicemia) (D'Arcet 1842). His subsequent application for a teaching position was however not successful (Thesis on eye infections) (D'Arcet 1844).

1845 he was sent on a mission to Brazil by the French Academy of Sciences; there 1846 he obtained a large contract from the Brazilian government to develop the local chemical industry and design a chemistry teaching curriculum; during his sojourn in Rio de Janeiro 1846 he lost his life during a fire, caused apparently by a servant attempting to fill a gas lamp.

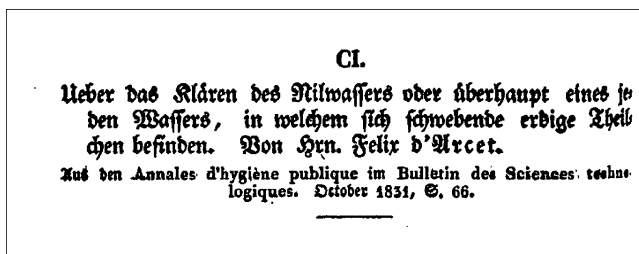


Fig. 4: “On purification of the Nile water or any water in which floating particles are contained”. Publication from 1831 by Felix D'Arcet

⁴ Arthur Rosenheim (1865–1942), 1906 non tenured (Extraordinarius) Professor and 1921 tenured Professor (Ordinarius) of Physical Chemistry at the Berlin University.

Acknowledgements: My gratitude to the miracle of Internet connectivity and Google Books, who made these and many other things possible.

References

- Arcet d', F (1835) Note sur l'acide arseno-vinique. *Comptes Rendus* I: 441.
- Arcet d', F (1835) Sur l'acide succinique. *Ann Mines* VII: 385–386.
- Arcet d', F (1836) Ueber Arsenikweinsäure. *Ann Pharm* 19: 202–203.
- Arcet d', F (1842) Recherches sur les absces multiples. These de Doctorat en Medecine, Paris.
- Arcet d', F (1844) Recherches sur les ophtalmies purulentes. Rignaud, Paris.
- Boullay PFG (1815) Premiere Dissertation sur les Ethers. *J Pharm Sci Access* 3: 7, 100–125.
- Crafts JM (1870) The ethers of arsenic acid and of arsenious acid. *Am J Science Arts* 50: 10–21.
- Huenefeld FL (1830) Zur Kenntniss der Pyrophosphorsäure und der Pyrophosphate. *Jahrbuch der Chemie und Physik*: 256–257.
- Jesnen WB (2006) The Origin of the Term "Base". *J Chem Ed* 83: 1130.
- Kopp E (1856) Note sur la preparation et les proprietes de l'acide arsenique. *Annales Chemie Physique* XLVIII: 106–109.
- Petroianu G (2009) The First Organophosphate: Who Was Voegeli? *Pharmazie* 64: 269–275.
- Petroianu GA (2010) History of organophosphate synthesis: the very early days. *Pharmazie* 65: 306–311.
- Priesner C (1986) Spiritus aethereus - formation of ether and theories of etherification from Valerius Cordus to Alexander Williamson. *Ambis* 33: 129–152.
- Rosenheim A, Antelmenn H (1930) Ueber Pyroarsensäure und Pyroarsenate. *Zschr Anorgan Allg Chem* 187: 385–397.
- Schiff H (1859) Einwirkung von Arsensäure auf Alkohol. *Ann Chem Pharm* CXI: 370–371.
- Williamson AW (1851) Ueber die Theorie der Aetherbildung. *Ann Chem Pharm* 77: 37–49.
- Wisniak J (2004) Jean Darcet. *Revista CENIC Ciencias Quimicas* 35: 105–110.