

A historic perspective of Bordeaux mixture: the first commercial scale fungicide

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Fungicides are chemical formulations used to control or manage plant diseases caused by pathogenic fungi. Until 1940s, inorganic chemical preparations were used as fungicides for mainly protecting vegetable crops and cereals against fungal diseases. The most important inorganic fungicides is the copper-based Bordeaux mixture. Despite the negative impacts copper has on the plant and the environment, copper fungicides were popular due to their low cost and the inability of the pathogens to develop resistance against them. Modifications of Bordeaux mixture are used even today though with attendant precautions. The present note describes the invention of Bordeaux mixture, the first commercial fungicide.

Before the 1800s, it was believed that the sudden appearance of devastating blight and mildew diseases of crops were the act of gods and demons. Later, efforts were made by plant scientists to manage these diseases by using chemicals. For instance, though ineffective, during the mid-17th century, the method to control bunt disease of wheat (also called ‘covered smut’, ‘ball smut’ or ‘stinking smut’ and caused by the fungi *Tilletia laevis* (*Tilletia foetida*) and *Tilletia tritici* (*Tilletia caries*) (Exobasidiomycetes: Tilletiaceae) involved soaking the seeds in salt water and lime or cattle urine¹. This was in practice long before the French botanist Mathieu Tillet (1714–1791) showed with meticulous large scale controlled field experiments that wheat bunt was not the act of demons but a contagious disease² and that treating the wheat grains with cattle urine, lime and salt, and finally, with copper sulphate reduced the disease incidence^{3,4}. For these findings, Tillet⁵, who was an agronomist and metallurgist, received a prize awarded by the Academy of Bordeaux. The Tulasne brothers in 1847 honoured him by naming the wheat bunt fungus after him as *Tilletia caries*⁶. The first effective seed treatment fungicide was discovered by Isaac-Bénédict Prévost in 1807 (ref. 1). His observation that the spores of fungi of Tilletiales died when they were suspended in a weak solution of copper sulphate resulted in using this chemical for controlling bunt and smut diseases of cereals¹.

However, despite such reports, the first marketable fungicide which could be used as a foliar spray was discovered much later in 1885 by Pierre-Marie-Alexis-Millardet. He was born to his lawyer (*notaire*) father in Montmiery-la-Ville in France on 13 December 1838. During his medical course, Millardet did a small research project in botany under the supervision of Jean Pierre

François Camille Montagne (1784–1866), a retired army surgeon and a botanist and published his first research paper with him⁷. Montagne appreciated Millardet and expressed that he had found an intelligent collaborator in him⁷.

After graduation, despite having a medical degree, Millardet chose to specialize in botany instead of medicine and studied under the mycologist Heinrich Anton de Bary at the University of Freiburg. On returning to France, Millardet obtained Doctorate degree in both science and medicine. After working as Assistant Professor of botany in the University of Strasbourg he joined the University of Bordeaux (baw-dow) as Professor in 1876 and served until his retirement in 1899.

During the mid-1800s, France imported grapevine root stocks from the USA to produce hybrid grape varieties by grafting them to the local grapevines. With these imported grapevines arrived two exotic damaging organisms of grapes, viz. the tiny, sap sucking insect phylloxera (*Daktulosphaira vitifoliae* – Hemiptera: Phylloxeridae) and the downy mildew fungus, *Plasmopara viticola* (Peronosporales: Peronosporaceae)⁸. These two reduced the vine production of France⁸. *Phylloxera* infestation was an epidemic in France which led to a drastic decrease in wine production⁹. Millardet identified American rootstock which were resistant to *Phylloxera* to be grafted⁹.

The general version of Millardet’s discovery of Bordeaux mixture is as follows. Médoc, in the border of the city of Bordeaux had been cultivating grapes from 1760. Farmers of this region used to spray the vines grown along the margin of the plantation with a mixture of copper sulphate and lime in water to render the grapes unattractive for thieves¹⁰. In 1882, Millardet noticed that the vines sprayed with this

mixture were unaffected by downy mildew while the unsprayed ones were severely defoliated due to the infection by the fungus¹¹. Based on this observation, Millardet proceeded to experiment on the composition and concentration of this mixture which would be effective in controlling the fungal pathogen¹². He was helped by Ulysse Gayon, Professor of Chemistry in the University of Bordeaux in this process¹³ and by Ernest David who was the technical director of Château Dauzac vineyards where the initial trials were conducted. Millardet proved to the world that Bordeaux mixture (a mixture of copper sulphate (CuSO₄) and lime (CaO) in water) was an effective fungicide and could be sprayed on the aerial parts of the plant without affecting the leaves or fruits. The original composition tried by Millardet was 18 lbs : 33 lbs : 34 gallons – CuSO₄ : CaO : water¹³. Millardet and Gayon tried different concentrations of copper, lime and water from 25–5–50 to 4–1–50 and concluded that mixtures with lower concentrations of copper and lime were as effective as that with the higher concentrations of the compound¹⁴. This fungicide gained world attention as it was effective in controlling the potato blight fungus (*Phytophthora infestans*, Peronosporales, Peronosporaceae) which was responsible for the great Irish famine in 1880s. According Arthur Edmund Muskett (1900–1984)¹⁵, a distinguished British plant pathologist ‘the work of Millardet in the eighties, pioneering the use of Bordeaux mixture, must be regarded as outstanding and may be said to have laid the foundation for plant protection with the aid of chemicals’.

According to Peter Ayres (Plant Pathologist, University of Lancaster)⁷, if Millardet could have named the fungicide after him, he would have been as famous as Bunsen or Petri. Millardet published three research papers on the discovery of

Bordeaux mixture titled: (i) treatment of mildew and rot, (ii) treatment of mildew with copper sulphate and lime mixture and (iii) concerning the history of the treatment of mildew with copper sulphate. These were translated by Felix John Schneiderhan (1891–1974, plant pathologist, Agricultural Experiment Station, West Virginia University) and published in 1933 by the American Phytopathological Society¹³.

Although Millardet is celebrated for his discovery of Bordeaux mixture, it is possible that his discovery may not be absolutely original. As highlighted by Nicholas P. Money¹⁶, several years before Millardet and just 200 km from Médoc, Benedict Prevost had observed that treating wheat seeds with a mixture of lime and copper sulphate controlled the smut disease in them. Money raises a valid question when he asks will not the farmers of Médoc noticed that the plants sprayed with the mixture to discourage theft also remained uninfected by the disease? The French farmers had likely used the mixture for seed treatment and as foliar spray to manage fungal disease long before the Bordeaux mixture appeared. In 1940s, James Gordon Horsfall (1905–1995, American plant pathologist) noted that Bordeaux mixture was deleterious to tomato and wondered about its proclaimed stimulatory effect on its close relative, the potato. So, along with his collaborators Albert Eugene Dimond (Connecticut Agricultural Experiment Station) and John William Heuberger (University of Delaware), he discovered ethylene bis-di-thiocarbamate (nabam) which controlled the potato blight better than Bordeaux mixture and also it did not dwarf the crop as Bordeaux mixture did¹⁷. This ended the monopoly of Bordeaux mixture as ‘the’ fungicide.

To Millardet’s credit, it should be underscored that though people like Benedict Prevost knew about the fungicidal property of copper¹⁸, it was he who proved its efficacy experimentally. It is in honour of him that the period between 1883 and 1906 is termed as ‘The Millardetian Period’ and a statue has been erected in Bordeaux in his honour. He could have contributed more to plant pathology but his work demanded him to be involved in teaching and administration. Yet, Millardet worked and published till his retirement in 1901. He was made an honorary member of the Linnean Society before he died in 1902. Millardet was a man of ethics and he acknowledged in his publications all those who helped

him on the discovery of the first effective foliar fungicide⁷. Ayers⁷ notes,

‘given Millardet’s first-hand experience of the Franco-Prussian war – the second-hand experience which turned Pasteur into a bitter Germanophobe – and the ill-will towards Germany still felt by many Frenchman at the time, it is Millardet’s great credit that it was in a German journal in which in 1883 he first gave notice of his discovery.’

Despite his contributions to plant pathology of his time, Millardet did not receive the national recognition he deserved perhaps because of Edouard Prillieux, the then Director of the French laboratory for phytopathology did not support him⁷. Dixon¹⁹, in his article, in *Lancet* laments,

‘What a pity that today Millardet’s statue, covered in verdigris, stands in a run-down part of his adopted city, and is not even mentioned in the local guidebook.’

Copper fungicides such as Bordeaux mixture kill plant pathogenic fungi and bacteria by releasing positively charged copper ions (Cu⁺ and Cu²⁺) which affect the nucleic acids, energy transport, enzyme activity and membrane integrity of the pathogens. The copper ion concentrations of the fungicides are toxic to the pathogens but are not enough to damage the host plants. The disadvantage with copper fungicides is that they are effective in killing the pathogens when they are present near or on the plant surface but are not effective once the pathogen has entered the plant host. Higher concentrations of copper ions could kill the pathogen after its entry into the host but that would be harmful to the plant.

Bordeaux mixture (both prepared on the field and instant formulation), despite its poisonous nature, is still widely used as protectant fungicide in plant disease control¹⁹. However, due to its alkaline nature, it is incompatible with other fungicides and insecticides and hence other copper fungicides like copper oxy chloride, cuprous oxide and copper hydroxide are more popular.

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