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Review

Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: A tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial

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ABSTRACT

Two hundred years ago, Henri Braconnot described a polysaccharide containing a substantial percent of nitrogen, later to be called chitin: that discovery stemmed from investigations on the composition of edible mushrooms and their nutritional value. The present interdisciplinary article reviews the major research topics explored by Braconnot, and assesses their importance in the light of our most advanced knowledge. Thus, the value of fungi, seafoods and insects is described in connection with the significance of the presence of chitin itself in foods, and chitinases in the human digestive system. The capacity of chitin/chitosan to depress the development of microbial pathogens, is discussed in terms of crop protection and food preservation. Other topics cherished by Braconnot, such as the isolation of pectin from a large number of plants, and inulin from the *Helianthus* tubers, are presented in up-to-date terms. Acids isolated from plants at that early time, led to enormous scientific advancements, in particular the glyoxylic acid and levulinic acid used for the preparation of soluble chitosan derivatives that paved the way to a number of applications. An opportunity to trace the origins of the carbohydrate polymers science, and to appreciate the European scientific heritage.

Contents

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1. Introduction

This review article intends to revisit the major research topics to which Henri Braconnot devoted his scientific life, on the occasion of the bicentennial of his discovery of chitin in edible fungi. He was always attracted by the alimentary aspects of botany, and his research was most often aimed at alleviating food shortages, not to say famine, that the majority of the French population had to face. Concisely, we present here the current views on the title points to underline the durable validity of Braconnot's interests, experimental approaches and results. The problems faced 200 years ago still persist for the majority of the exceedingly large world's population, notwithstanding the technological advances made. A glimpse back to 1811 would give us an opportunity to appreciate the immense spiritual resources of the western Countries that, in the context of the American and French revolutions, elaborated new scientific interests, methodologies and communication ways. For this Journal, the chitin bicentennial is also an opportunity for tracing the roots of the carbohydrate polymers science.

2. The precursor of the carbohydrate polymer science

Henri Braconnot (1780–1855) laid the foundations of the carbohydrate polymer science: after the discovery of chitin, the first polysaccharide described 30 years earlier than cellulose, he continued with his idea of extracting sugars from edible fungi such as *Agaricus bisporus*, and remarkably extracted inulin from the tubers of *Heliantus tuberosus*. He also studied pectins of various origins, and isolated pure sugars after chemical hydrolysis of straw, wood and cotton; likewise, he isolated trehalose from edible fungi, and refined beet sugar to a white and crystalline substance. Among various biographies, those by Labrude and Becq (2003) and Prévost and D'Amat (1956) deserve mention.

Systematic sulfuric acid treatment of a large number of substances led him to isolate glycine, "glycocolle", from gelatine. Simultaneously with Proust, he described leucine. These discoveries brought him a certain acclaim. He also isolated several vegetable albumins.

Research activities of more chemical flavour were those on the nitration of cellulose, that yielded a hydrophobic and flammable product, "xiloidine", endowed with filmogenic properties: this was a precursor of Celluloid® that in the second half of that century led to "fulmicoton" and other explosive substances that replaced the black powder. From plant tissues, a series of acids of major importance were isolated by Braconnot: namely acetic, malic, maleic, sorbic, gallic, ellagic, pyrogallic, and lactic; the picric acid among others was synthesized.

In 1807 Henri Braconnot was appointed director of the Botanical Garden in Nancy with teaching duties of natural history. The four-century old University of Nancy, as well as the University of Strasbourg, had been suppressed by the Assemblée Générale, and in Nancy the Medical School and the Academy were the only structures for further education. Actually, the Garden was part of the Medical School because of the interest in officinal plants: there, Braconnot started a research programme on the chemistry of vegetal extracts, and his publications attracted the attention of learned societies and eminent chemists, so that King Louis XVIII appointed him as a member of the Royal Medical Academy (1820) to become "Chevalier de la Légion d'honneur" in 1828.

While taking care of the Garden, Braconnot started a large scale cultivation of sugar beet and extraction and purification of sugar with the intention of alleviating food shortage. He studied the cultivation of Italian rice and used starch in various experiments. Braconnot was interested in the definition of the nutritional value of mushrooms: he wrote that poor countrymen considered mushrooms a manna given free as a gift of providence, and eagerly waited for the mushroom seasons.

Management of the Garden and the relevant problems (risky use of gas for heating the hothouses, diatribes against military plans to build barracks inside the Garden) prevented Braconnot from exploiting his chemical discoveries. He was a precursor of Chevreul with his studies on fats, but he had no means of identifying the fatty acids; he brought forward the idea of plant alkali but he could not isolate the alkaloids. Braconnot published 112 papers in the form of memoirs of the Academy of Sciences, Letters and Arts of Nancy, also known as the Academy of Stanislas, the King of Polish origin who ruled the Lorraine region. Other publications are in the *Annales de Chimie et Physique* and the *Journal de Chimie Médicale*.

Braconnot certainly was an eminent chemist, as his successor wrote, but he dedicated most of his energy to botany (Godron, 1872). Actually his teaching followed Linnée's principles, in a period when novel theories on cellular structure, plant sexuality and alternate generations were being brought forward, as a consequence of the studies conducted on enormous collections of previously unknown plants. For instance the Flinders expedition (1801) made available 4000 unknown species of plants from Australia. The Empress Joséphine visited the Nancy Garden and sent a large number of plants to Braconnot, so that in 1852 the 14,100 m^2 Garden had 3452 plant species, including some from New Zealand and Reunion Island.

2.1. The discovery

The discovery of chitin was essentially based on some reactions carried out on raw material isolated from *Agaricus volvaceus*, *A. acris*, *A. cantarellus*, *A. piperatus*, *Hydnum repandum*, *H. hybridum* and *Boletus viscidus*. The fungal material was partially purified by boiling in dilute (potassium) hydroxide [that removed proteins and pigments, to yield the chitin–glucan complex]. The resulting "fungine", when distilled in admixture with KOH, released ammonia, that demonstrated the presence of nitrogen as the fourth element. On the other hand, concentrated sulfuric acid liberated acetic acid