THE HISTORY OF HOW CATECHIN WAS DISCOVERED

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Summary

The discovery of catechin started in the research of catechu which is a kind of tannin. Catechu began to be used as a medicine about the17th century. At the same time we find the term 'tan', which is used the skin of animals from hide to leather, and also the term 'astringent'. The term 'astringent' was used for tannin on the studies of tea components. But it was in the early the19th century that the term 'tannin' was found to be principle of tan.

In the17th and 18th century, we can find a lot of discussion on the origin of catechu and its chemical nature. In 1679, Hagendornii said that catechu is produced from mineral source and called it the Japanese earth. But it was revealed later by many scientists that catechu was botanic origin.

Catechu was obtained from the two kind of plant. One is Acacia catechu and the other is Uncaria gambir. In 1832, T. F. L. Nees von Esenbeck succeeded in isolating crystalline substance which is thought to be the principle of gambir-catechu. And he named it catechin as the principle of catechu.

Keywords

Catechin, Tannin, Catechu, Astringents, Tan

Introduction

The discovery of "catechin" started in the research of "catechu" and it has a long history. Catechu was being used as a kind of medicine around the 17th century. At the same time the word "tan" has been used for "tanning" of the skin of animals from hide to leather for thousands of years. But it was not until the early 19th century that the term 'tannin' was found to be the principle of tan, and later still that catechin was identified as a kind of tannin. Both tannin and catechin are known to be astringents.

This brief description deals with the historical emergence of the terminology "catechin", "catechu, ,"astringent", "tan" "tannin" and their relationships.

The term 'astringent' was used for 'tannin'

In 1798, J. Frank, a court pharmacist carried out an analytical study of tea and reported the results in the Berlin Pharmaceutical Annual Report (Berlinisches Jharbuch fuer die Pharmacie) issued 1798. The title of the paper was 'Studies on Thea bohea and viridis'.

Frank was influenced greatly by C. von Linne, a famous botanist who claimed that there are two kinds of tea plants. One is 'Thea bohea' producing bohea tea, and the other is 'Thea viridis' producing green tea. This theory later turned out to be false.

Frank prepared infusions from two kinds of tea and tasted their flavor. He reported that both

infusions had strong astringency. Further, he observed that both infusions immediately turned black on the addition of drop of iron chloride solution. He declared that there must be many astringents in the tea solutions.

A similar theory was found in 'The Natural History of the Tea Tree', written by J. C. Lettsom in 1799. He observed that infusions of various kinds of tea turned deep purple when iron chloride was added. He concluded that tea infusion has astringent power. It is clear that what these two scientists called principle of astringent is the tannin of today.

The word 'Astringent' is found in N. de Blegney's essay in 1680 and T. Short's essay in 1730. Also it is found in 'Chambers Dictionary', a big encyclopedia of Arts and Science(Britain) in 1786. In this dictionary, we can find the word 'tan(the powder of oak tree bark ,used for tanning the skin)', 'tanner(workman for tanning)' and 'tanning(the skill of tanning the skin)', But we cannot find the word 'tannin'.

The discovery of tannin is attributed to A. Séguin in 1797. He contributed his work to a French chemical journal titled 'A New Method of Tanning' as an official report. He declared especially that he was a citizen. It was just after the French revolution. It may be showing the social atmosphere of those days.

When he mixed a solution of tan and glue, white precipitate was produced, which was insoluble both in cold and hot water. He explained that this is the mechanism for tanning the animal skin. He stated that the material combined with glue was the principle of tan. However the word tannin does not appear in this paper.

We can find the word tannin in C. H. Pfaff's annual report, 1811, and in the paper by Séguin, 1814. Accordingly, we can assume the word tannin began to be used from the end of the 18^{th} century or the beginning of the 19^{th} century.

In Japan, we can find the word 'tannin' and 'gallic acid' in the book of 'Shokubutu Keigen' by Y. Udagawa, 1833.

The discovery of catechin as the principle component of catechu

In the17^{th} and 18^{th} century, we can find a lot of discussion on the origin of catechu and its chemical nature.

In 1679, Hagendornii published his detailed (80 pages) thesis under the title, 'catechu or 'Japanese earth',officially reported by the academie of nature from the aspect of natural or medical point of view.

According to Chambers Dictionary published 1786 (100 years later for above thesis), catechu was explained as follows:

> "Catechu, a medical aromatic substance brought from East Indies ; called cachew, and japan-earth, and when prepared, ranked in the number of perfumes. It is of a dark purple colour, very austere upon the palate, seeming to melt in the mouth, and leaving somewhat of a sweetish taste behind it. It is the juice of a vegetable, not an earth, as its name imports.
>
> Notwithstanding the great use of catechu, before that of coffee and tea, and its being still frequently used by many people, especially in France, its nature and origin was long but little known, even among the ablest physicians. Some, from its being called Japan earth, ranked it

among medical earth, ----------"

According to the publication of Pfaff, 'System des Materia medica', 1811 version, a detailed and historical explanation on the studies of catechu is found. Hagendornii thought that catechu is produced from mineral source, but its theory turned out to be proven false by many scientists. Later, it was revealed that catechu was botanic origin.

There are two kinds of catechu-producing plant. One is Acacia catechu. Mimosaceae, which is grown around the Bengal region of East India. The other is Uncaria gambir, Rubiaceae, grown in the region around the strait of Malacca. In the document of 18th century, we can find catechu was also obtained from the sap of Areca catechu, a kind of palm, but later it turned out that the fruits were used as Betel nut, and it did not produce catechu. When Sprit cave, in North West of Thailand, was excavated, we found the remains of Betel nut, which is assumed to be used from B.C. 5000 to 7000. This is said to be possibly the first stimulant that human beings ever used.

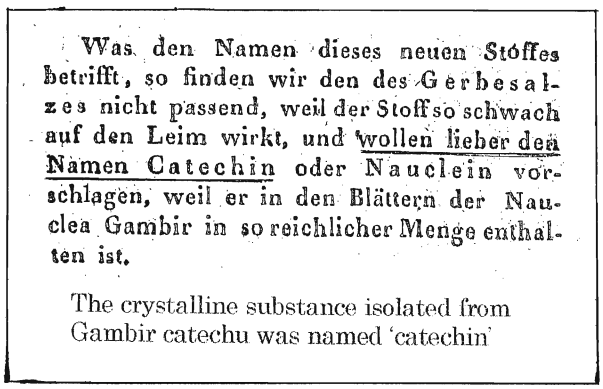
In 1821, F. F. Runge, reported in his book that he had succeeded in isolating tannin salt from Acacia catechu and gave it the name 'catechu tannin salt'. He obtained it by dissolving the ether extract in the hot water and by cooling as precipitate. He repeated dissolving and cooling several times, and finally obtained white crystal. Later research showed that it may have been (-)-epicatechin.

In 1830, T. F. L. Nees von Esenbeck carried out an experiment of comparing Gambir-catechu with other catechus produced in Bombay and Bengal. The results showed that both catechus had very similar chemical nature. Then he wondered if it was possible to gain an almost same product out of entirely different kind of plant, i.e. Nauclea gambir(Uncaria gambir nowadays) and Acacia catechu respectively.

Later in 1924, K. Freudenberg elucidated the existence of streoisomer among catechins. And he reported that the catechin prepared from Acacia catechu is mainly (-)-epicatechin while the catechin prepared from Uncaria gambir is (+)-catechin. Both catechins are isomers of each other and so have many similarities.

In 1831, J. W. Doebereiner carried out a chemical study on a crystalline substance that resembled Runge's tannin salt and named it catechutannin.

After reading Doebereiner's report, Nees von Esenbeck carried out further research of gambir-catechu and succeeded in isolating a crystalline substance, which is thought to be the principle component of catechu. He named it catechin. He reported the discovery of catechin in the 1832 version of 'Repertorium fuer Phamacie', Periodical for pharmacy as shown in the photograph.



Was den Namen dieses neuen Stoffes betrifft, so finden wir den des Gerbesalzes nicht passend, weil der Stoff so schwach auf den Leim wirkt, und wollen lieber den Namen Catechin oder Nauclein vorschlagen, weil er in den Blättern der Nauclea Gambir in so reichlicher Menge enthalten ist.

The crystalline substance isolated from Gambir catechu was named 'catechin'