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Studies on the Transforming Mechanism of Amino Acid Components in Ginseng in the Course of Ginseng Processing

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This talk is to give a conclusive review on my studying works on ginseng processing which had been carried out in our laboratory for years.

Panax ginseng had been known as the elixir of life in the orient ever since thousands of years before. It had been used long as a medicinal plant for the treatment of various pathological states and also as one of the tonic remedies. Recent studies on ginseng were concerned mainly with the chemistry and pharmacology of the components in ginseng. Summarizing these studying data, we could easily find the differences of chemical components and pharmacological effects among fresh, white and red ginseng. In our opinion, the differences of pharmacological effects was resulted from the differences of chemical components in various ginseng, it is processing that results in the changes of chemical components in ginseng. Red ginseng has its special bioacivity or stronger pharmacological effects than white ginseng only because it contains its special active components, such as ginsengside-Rh_2, 20(R)-ginsenoside-Rh_1, glycoside B, maltol, panaxydiol, panaxytriol and etc. What is the most interesting is that a large number of malonyl-ginsenosides contained in fresh ginseng, but after red ginseng is prepared, there is so little malonyl-ginsenosides remained that we just can detect a trace of them out.

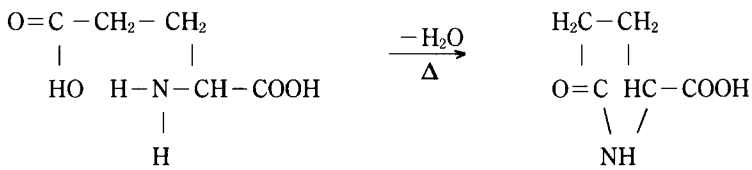
Through years of studying on ginseng, I could have a brief conclusion about the transformation of amino acid components in ginseng during red ginseng was processed by fresh ginseng as follows:

1. During fresh ginseng is heated, glutamic acid in ginseng was having as inner cyclodehydration to be pyro-glutamic acid.

2. In the course of ginseng being heated, dencichine was decarboxyl-grouped and degradated to be 2,3-diamino-propylaldehydecarboxylic acid.

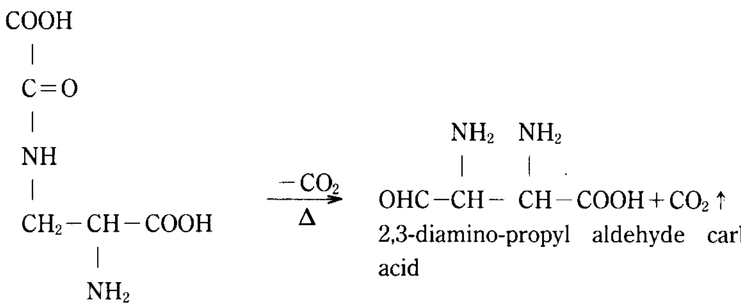
3. Some of the other amino acid compounds in ginseng take Maillard reaction with maltose and generate glycoside B and its relative compound-moltol.

The transformation of glutamic acid. : The amino acid contents of the fresh ginseng which was produced at the same place and its prepared red ginseng were analyzed in our lavoratory, from information we found the total amino acid content in red ginseng decreased from 10.4518 percent to 7.7423 percent, and glutamic acid decreased by 0.2058 percent. The result of Thin Layer Chromatography (GF254) with water extracts of red ginseng in butan-1-ol/acetic acid/water (6 : 2 : 2, v/v) appeared a blue-black spot similiar to standard pyro-glutamic acid (Rf=0.485) color reagented by the chloine-starch-iodide method (ninhydrin negative) and the chemical reaction of the water extracts had also confirmed the existing of pyro-glutamic acid in red ginseng. In order to research the origin of pyro-glutamic acid in red ginseng, we used glutamic acid as an experimental material to synthesize pyro-glutamic acid. A suspension of L-glutamic acid (30 g) in distilled water (120 ml) was heated under reflux at 100° for fifteen hrs. The resultant clear solution was cooled to room temperature and passed through a column of ion-exchange resion (H form : Φ 2.5 cm×70 cm) and washed through with distilled water until the eluate is no longer acidic. The combined aqueous eluates were evaporated on a rotary evaporator at 40~50°. A little ethanol was added to the residue and re-evaporated to remove trace of water and leave a crystal. The product was recrystallized by dissolving in boilling ethanol, after a few minutes cooling, adding light petroleum (bp. 60~80°), a crystal rapidly commences, and after five minutes a further quantity of light peterleum was added. The recrystallised material was collected after keeping overnight at room temperature; the yield of this procedure was fairly good. m.p. 156~158°. The crystalline material was identified with IR, ^{1}H-NMR, MS spectra, it was pyro-glutamic acid. Glutamic acid is a α-aminodiacarboxylic acid, when it is heated, it's very easy to take a reaction of inner dehydration and circulation to be γ-lactam. Therefore, we are assuming, in the course of red ginseng is prepared, that glutamic acid dehydrates and circulates into pyroglutamic acid.



Glutamic acid Pyro-glutamic acid

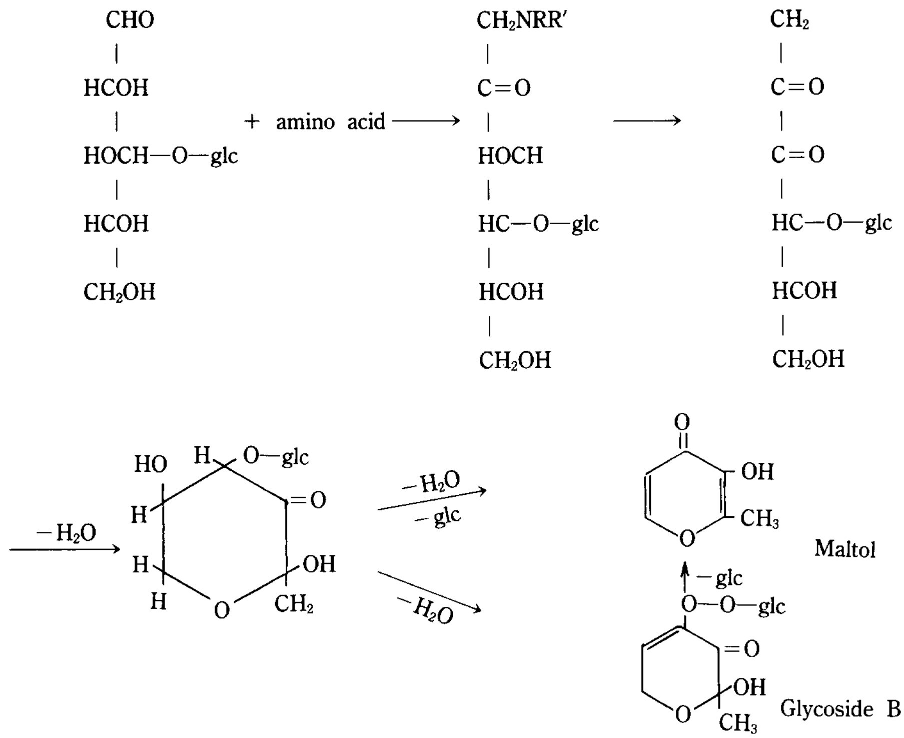
The change of dencichine : In our laboratory, the water soluble part of red ginseng had been obtained, passed through a column of Sephadex LH-20 with distilled water washing and obtained fraction A. Fraction A through the column of CM-Sephadex C-25, finally we obtained an active fraction B. The final product was dissolved in a refining water and kept for a little time, a crystal commenced immediately. The crystal was recrystallised by water. m. p. 208°, colorless plates. This substance is soluble in water, but not soluble in methanol, ethanol, acetone, and other organic solvent. Identifing with UV, IR, MS and ^{1}H-NMR spectra. Paper chromatography with standard dencichine, both of Rf value is the same. By amino acid analysis, there is a retention value in ginseng sample similiar to the result of standard dencichine. We determined the crystal was dencichine itself, e.g., β-N-oxalyl-L-α, β-diaminopropionic acid. From the result of quantitative analysis to the dencichine content of various ginseng products, we found that white ginseng contained much higher dencichine than red ginseng did. The content of decichine in white ginseng is 0.4906 %, but that in red ginseng is 0.2605%. In my opinion, dencichine is a dicarboxylic acid, not stable to heating, when fresh ginseng was prepared for red ginseng, dencichine is heated and degradated into 2,3-diamino-propyl aldehyde carboxylic acid, white ginseng is not prepared by the procedures of red ginseng, thus white ginseng contains higher dencichine.



2,3-diamino-propyl aldehyde carboxylic acid

Dencichine

The transforming mechanism of some other amino acid in ginseng in the course of ginseng processing : Except the above changes of that two amino acids in the course of ginseng processing, parts of some other amino acid compounds take Maillard reaction with maltose. After producing Amadori compound, 4-O-2-D-glucosyl-1-deoxidatyl-2,3-diketosaccharide was formed. Since this compound is unstable, 2-ketone group and C-6-hydroxyl dehydrate and condensate to circulate to be glycoside B. Glycoside B take a further hydrolytic deglycose and rearrange to be maltol. The reaction is taken as folllows.



Glycose B and its relative compound-maltol all are special anti-oxidant components of red ginseng. They have an anti-aging effect. In 1956, D. Harman's free radical theory reported that too much producing of free radicals in livings would cause the oxidation to peroxides from unsturated fatty acids, leading to the production of lipofuscin pigment. This would also cause the changes and damages of living cells and their important fraction such as DNA, protein and enzyme and resulting in the increasing of cellular aging. It is reported that maltol efficiently inhibits the lipid peroxide responses caused by ethanol in mice, decreases the accumulation of lipofuscin and aging pigment, it also decrease the inhibitions of lipid peroxides to enzyme, and plays the effect of prologing life. In our laboratory we have not only extracted, isolated and identified maltol by Bremman method of Pfizer Co. in U.S.A.

Maltol : white needles (recrystallised in nonwater ethanol), it has a delicious taste of fruit (low concentration) and caramel (high concentration). m.p. 159~160°, sublime at 93℃, soluble in water, methanol, ethanol, chloroform, diethyl ether and other organic solvents, soluble a little in benzene, but insoluble in petroleum. In our recent experiment, we have measured the content of maltol in different ginseng products prepared by different processing with the fresh ginseng produced at the same place, and we also have determined the producing of maltol in the different processing period during red ginseng being prepared. We found that maltol was produced mainly at the first drying stage, that is to say, at the period of ginseng was dried at high temperature to get a good color for red ginseng, maltol was producing. Before this stage, such as a ginseng being heated and parched, maltol had still not produced, but may middle productions had already formed for the producing reaction of maltol when ginseng was drying at high temperature. It is very interesting that the second drying to ginseng is not important for maltol's generation.

Conclusion

After years of works on the processing mechanism of ginseng, the difference of efficacies between white and red ginseng can be clear in modern scientific explanation. In aspect of chemistry, we have made a clear expression on ginseng processing mechanism and developed the traditional processing skills. In my opinion, the differences of pharmacological effects was resulted from the differences of chemical components in various ginseng, and it is processing that results in the changes of chemical components in ginseng.