76. The Colouring Matter of Eggplant (*Nasu*).

Part II.

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In the previous paper,¹⁾ the colouring matter, from the epidermis of the eggplant, (*Solanum Melongena*, L. var. *esculentum*, Ners.) was considered to be delphinidin glucoside combined with P-coumaric acid, in view of the analytical result of the chloride of its aglucon obtained in crystals (Fig. 1) and of its decomposition products by acid and alkali. Through further investigation of the pigment, two other glucosides [A] and [B] have been isolated in crystals, which are reported in the present communication.

The procedures of the isolation and of the confirmation of the above substance [A] which is considered to be diglucoside of delphinidin chloride are as follows.

When the amorphous chloride of the *Nasu* pigment in the previous report¹⁾ was left as solution in 20% HCl aq. at room temperature for a few days, dark purple crystalline precipitate slowly separated out. After washing with cold 5% HCl and recrystallizing with MeOH-HCl or dil. HCl several times, golden lustrous crystals [A] in fine needles [D.P. 197°] (Fig. 2) were obtained. The substance was difficultly soluble in cold CH₃OH and dil. HCl. It yielded delphinidin chloride and glucose (confirmed as glucosazone) on hydrolysis with boiling HCl. By above and following results, the glucoside was confirmed to be diglucoside of delphinidin chloride C₂₇H₃₁O₁₇Cl + 3H₂O. (Found C, 45.24; H, 5.30; Cl, 4.45%; calc. C, 45.25; H, 5.17; Cl, 4.6%). The estimation of the glucose was carried out by Pavy's method,²⁾ and the result was in agreement with two mols of glucose. (Found 50.2% calc. 50.28%).

Now one of the positions of glucose was proved to be "3" by Karrer's perhydrol method. Accordingly, the two formulae are possible as indicated below:—

[I]

[II]

[II] was obtained from Awobana.³⁾ Although the glucoside [A] in question corresponds well with the sample of [II] from Awobana in almost every respects (Absorption spectrum, appearance, and the results of analyses), however, there are some disagreements as follows:—

1) Kuroda and Wada: Proc. **9** (1933), 51.

2) Helv., 1212, 15 (1932).

3) Kuroda: Proc. **11** (1935), 238.

Fig. 1. Delphinidin chloride from Nasu.

Fig. 2. Diglucoside of Delphinidin chloride from Nasu.

1. Notwithstanding the fact that the glucose of Awobana is confirmed to be "3" "5" diglucoside by Karrer's perhydrol method, in the case of eggplant, there are some experimental evidences against the glucose linkage "5".

2. Comparing the two substances for reaction in Buffered solutions at 15 varieties of PH,¹⁾ Awobana gives very slightly more pink colouration than the other.

3. Solubilities of the two, in MeOH, H₂O, HCl are also somewhat different, Awobana being less soluble. D.P. was little different from that of Awobana.

1) R. Robinson and A. Robertson: Biochem. J., 1929, 23, 35.

With such experimental facts in consideration of the two proposed formulae, [I] seems more probable.

The isolation and the confirmation of the second crystalline substance [B] which was considered to be diglucoside* of delphinidin chloride combined with one mol. of P-coumaric acid was as follows:—

The amorphous chloride of the pigment was converted to the picrate in an aqueous solution. When recrystallized several times from hot water, the compound gave purplish red slender needles with copper-like lustre.

When treated with MeOH-HCl (2%), the picrate was reconverted into the chloride with the aid of ether. It was purified by successive recrystallization with MeOH-HCl or HCl aq. Fine needle crystals of reddish purple colour were obtained. The compound was then hydrolyzed with boiling HCl, yielding delphinidin chloride, glucose (confirmed as glucosazone), and P-coumaric acid.

The analytical results agreed remarkably with $C_{36}H_{37}O_{19}Cl + 10H_2O$.* (Found C, 43.97; H, 5.70; Cl, 3.33%; calc. C, 43.72; H, 5.77; Cl, 3.54). The quantities of P-coumaric acid was determined. (Found 15.0%; calc. 16.6%). The estimation of the glucose was carried out by Pavy's method.¹⁾ (Found 37.27%; calc. 36.44%).

Now as to the manner of combination of one mol. of P-coumaric acid, it may be linked as an ester to the biose at "3". Favorable as an example of such a view is violanin.²⁾ (Formula IV). In considering together the above examples and the previously mentioned substance [A] which seemed to be 3-biosid of delphinidin, the above conclusion (Formula III) may be much more probable.

Further studies will be made to confirm the present consideration.

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1) Helv., 1212, 15 (1932).

2) Karrer and Meuron: Helv., 292, 16 (1933).