

On Kakishibu, IV. Constitution of Shibuol, III.

By

Shigeru Komatsu and Naohiko Matsunami

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1. TINCTORIAL PROPERTIES OF SHIBUOL AND ITS AZODERIVATIVES.

It was shown, in the first communication on this subject, that shibuol $C_{14}H_{20}O_9$, on fusion with caustic potash, gave phloroglucinol and gallic acid as a principal reaction product¹.

The natural colouring matters such as myricetin and delphinidin give equal rise by alkali fusion to the identical decomposition units as shibuol. These colouring matters and the tannin-like substance, however, show quite different properties from each other, in spite of being built up of the same constituents, due to the differentiation of the chemical structure of the complex nuclei in their molecules or of the manner of the linking up of the two constituents.

The facts which were pointed out by Perkin² that gallotannin and myricetin, a catechol tannin and quercetin, cyanomaclurin and morin, and butin and butein respectively occurring together as glucosides, or in a free state in flowers and in bark, lead us to suppose that, though they possess complex nature in composition, a certain resemblance exists between these colouring matters, as regards the similarity of their decomposition products, and there is reason to suppose that they may be structurally related.

The tinctorial property of the natural colouring matters, flavons,

¹ These Memoirs A. 7. 15 (1923)

² A. G. Perkin and A. E. Everest. The natural organic colouring matters (1918) P. 17.

flavonols, and anthocyanins, and their azo-derivatives, according to the investigations by Buchner, Elsner and Kopp,¹ Willstaetter and Mallison² and Watson³ affords some evidence for the determination of the number of the free hydroxyl group in the phenyl residue of the molecule of the colouring matters.

In order to acquire some evidence for the constitution of shibuol, the tinctorial property of the compound was investigated with that of myricetin, quercetin and catechin, in comparison with their metallic salts and benzene-azo-derivatives.

Benzene-azo-Shibuol.

8.1 gm. of fresh shibu free from pectin, and containing 5.5 gm. of shibuol, dissolved in sodium carbonate solution (14.5 gm. of the carbonate in 1540 cc. of water) were mixed with a diazobenzene chloride solution (3.7 gm. of aniline diazotized at 0° with 2.8 gm. of sodium nitrite in 100 c.c. of cold water and 9.8 gm. of hydrochloric acid (1.19) in 40 c.c. of water) at 0°-5°. After the coupling of the shibuol with the diazo-compound was completed, the temperature of the solution 5-15° was kept for 6 hours and then raised gradually to 50°, and the brownish yellow disazo-compound was filtered, washed with hot water and dried on a plate. The yield was 8 gm. (85% of the theory)

It was a reddish brown powder, fairly soluble in boiling alcohol and in nitrobenzene, but insoluble in ether and chloroform.

On analysis C=61.20; 61.65; H=4.27; 4.40; N=11.02; theory for $C_{14}H_{10}O_7$ ($C_6H_5N_2$)₂ C=62.40; H=4.00; N=11.2.

1 gm. of benzene-azo-shibuol dissolved in hot alcohol was reduced with a saturated solution of sodium hydrosulphite. After the solution had become colourless, it was acidified with dilute hydrochloric acid, and concentrated to small volume under reduced pressure, whereas a light-brownish substance was deposited, which was filtered and recrystallized from an alcohol solution, the yield was 0.5 gm. It was analysed after being dried at 100° under reduced pressure.

C=55.80; H=4.75; N=4.57 :

theory required C=56.02; H=4.37; N=4.38 for $C_{15}H_{14}O_7N$.

The analytical results of the reduced substance $C_{15}H_{14}O_7N$ indicated that one of the azo group in the benzene-azo-derivative, in the course of

1 A. G. Perkin & A. E. Everest: The natural organic colouring matters p. 257.

2 Liebig, Ann., **408**, 29 (1915).

3 J. Chem Soc., **107**, 1477 (1915).

reduction, was removed in the form of NH_3 from the molecule.

Benzene-Azo-Catechin.

The crude catechu prepared from gambier catechu (*Uncaria gambier, Roscough*) was used for the preparation of pure catechin¹.

The pure substance prepared according to the directions suggested by A.G. Perkin and E. Yoshitake¹ was in colourless needles, melting at 96° and on drying in a desiccator melting at 176° - 177° .

Benzene-azo-catechin prepared by the method of Perkin and Yoshitake, and purified by recrystallization from a mixture of alcohol and nitrobenzene, was in salmon-red needles, melting at 194° - 196° . The yield was 75% of the theory.

$\text{N} = 11.12$ theory requires $\text{N} = 11.24$ for $\text{C}_{27}\text{H}_{22}\text{O}_6\text{N}_4$

Benzene-Azo-Myricetin²

Myricetin which was prepared from the bark of the myrica rubra, was combined with diazo benzene chloride in the usual manner to form the benzene-azo-myricetin which, thus obtained was recrystallized from a mixture of alcohol and nitrobenzene. The yield was 83% of the theory.

It melts above 270° , and is soluble in nitrobenzene and in glacial acetic acid.

$\text{C} = 56.25$; $\text{H} = 3.42$; $\text{N} = 10.43$; theory requires

$\text{C} = 56.60$; $\text{H} = 3.10$; $\text{N} = 10.64$, for $\text{C}_{27}\text{H}_{18}\text{O}_8\text{N}_4$.

Benzene-Azo-Quercetin³

Quercetin from Merk was coupled with diazobenzene chloride in the usual manner. The yield was 70% of the theory. It was purified from the alcohol solution, and was found to melt at 235° - 237° .

$\text{N} = 10.67$; theory requires

$\text{N} = 10.98$ for $\text{C}_{27}\text{H}_{18}\text{O}_7\text{N}_4$

In comparing the dyeing properties of these colouring matters, a quantity of shibuol or of flavones, corresponding to 5% by weight of the dyeing material-wools, was dissolved in a 5% acetic acid solution. Into this bath wools were dipped and left to soak for 50 minutes at a temperature of about 80°C . and the shades on the wools were shown

¹ A. G. Perkin & E. Yoshitake; J. Chem. Soc., **81**, 1163 (1902). and also refer Clauser: Ber. D. Chem. Ges., **36**, 101 (1903),

² S. Sato: J. Chem. Ind., (Japan) **17**, (1914)

³ A. G. perkin and Allison. J. Chem. Soc., **81**, 471 (1902).

in the following table :

Table I

Substance	Shade	Shade on wool after coupling with diazobenzene chloride
Shibuol	reddish brown	light brown
Catechin	yellow	pure orange
Myricetin	brownish yellow	brownish yellow
Quercetin	yellow	yellow

The shade given by shibuol was slightly darker than that by myricetin, but differs considerably from that given by catechin or quercetin.

Employing mordanted wool with chromium, aluminium, tin and iron, the following distinction of shade was observed, and these may be

Table II.

Substance	Chromium	Aluminium	Tin	Iron
Shibuol	yellowish brown	pale pink	pale violet	bluish violet
Catechin	dark olive brown	" orange	---	yellow
Myricetin	reddish brown	brown orange	reddish orange	olive black
Quercetin	" "	" "	orange	" "

due to different combinations of the two phenolic nucleus in the molecules of shibuol, catechin and myricetin.

Wool was dipped in a bath in which 5% of a benzene-azo-derivative of the above colouring substances was dissolved in 50% alcohol solution, and then acidified with 5% acetic acid. The shades on the wools were compared and the results are in the following table :

Table III.

Substance	shade	after treatment with iron mordant
Benzene-azo-shibuol	brown	greenish brown
"-catechin	orange	orange "
"-myricetin	yellowish brown	yellowish brown
"-quercetin	brownish orange	brownish yellow

In dyeing property, shibuol and benzene-azo-shibuol greatly resemble myricetin and its benzene-azo-compound, but differ from catechin and quercetin and their azo derivatives in this respect. It was thus probable that the number of the free hydroxyl group in the phenyl-residue of a shibuol molecule closely resembles that of myricetin.

Definite evidence, however, of the constitution of shibuol is still lacking.

2. REDUCTION OF SHIBUOL.

The reduction of shibuol was, attempted in the following manner :

10 gm. of shibuol was dissolved in 200 c.c. of a 15% caustic soda solution and treated with 100 gm. of zinc dust for 3 hours at a temperature of 50°, the solution being acidified with sulphuric acid and the brown precipitate was separated, filtered and the solution evaporated to dryness under reduced pressure. The residue was extracted with alcohol and from the solution 0.1 gm. of gallic acid (m.p. 238°-234°) and 0.5 gm. of phloroglucinol (m.p. 210°) were isolated. The reduction of shibuol in an acetic acid solution with zinc dust at 50°, was tried, the result however, was a failure, no reduced substance being produced.

By the action of magnesium powder and acetic acid, shibuol was converted into a reddish-coloured substance soluble in the solution, and the behavior of shibuol was similar to flavones in this respect.

When, however, tetramethylshibuol was reduced with hydroiodic acid (1.18) at 130°, a violet brown powder was obtained as a reaction product, which is easily soluble in alcohol, acetic ether and acetone, but not soluble in ether. It resembled in composition a substance resulting from kakigoma by potash fusion, giving, on analysis, C=63.28% and H=3.97%.