On Kakishibu, VI.
Potash Fusion of Methyl Shibuol

By

Shigeru Komatsu and **Masao Kurata**

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Shibuol shows quite different properties from the natural colouring matters such as myricetin and delphinidin in spite of its being built up of the same constituents—phloroglucin and gallic acid—due to the difference in the manner of the linking of the two constituents.[1]

Acetylation and methylation of shibuol, mentioned in the third and fifth reports, postulate that shibuol must contain at least four free hydroxyl groups in the molecule, while both myricetin and delphinidin contain six free hydroxyl groups.[2]

Potash fusion of the methylated compound will afford some evidence of the way in which the two components are combined, as we have often experienced in the determination of the chemical constitution of the natural colouring matters.[3]

1. Action of alcoholic potash on tetramethyl shibuol

10 gms. of tetramethyl shibuol (M.W.=1392 by Rast's method) were heated with 10 gms. coustic potash in 100 c.c. of 80% alcohol on a water bath for 5 hours; the reaction product was divided by means of water into soluble and insoluble parts, and the former on being acidified with sulphuric acid yielded 1.1 gms. of gallic acid trimethyl ether which melted at 168° and gave on analysis C=56.9;

1. These Memoirs, **8**, 231 (1925).
2. Ibid., **11**, 211 (1928).
3. A. G. Perkin & A. E. Everest: The natural organic colouring matters (1918).

H=5.41 ; CH_3O=43.5 (Theory C=56.6 ; H=5.6 ; CH_3O=43.9 for $C_6H_2(OCH_3)_3CO_2H$).

The insoluble residue was a light brown amorphous substance melting at 298°—299° with decomposition, called by writers destetramethyl shibuol. The yield was 8.4 gms.

C=62.1, 6.28 ; H=5.5, 6.0 ; OCH_3=33.1 ;
Ash=0.17 ; M.W.=1243 by Rast's method.

When tetramethyl shibuol was hydrolysed with alcoholic potash, gallic acid trimethyl ether (A) and destetramethyl shibuol (B) resulted as reaction products, with some acetic, butyric and formic acids, the yield of A and B being 1 : 1.4 in molecular proportion.

2. Alkali-fusion of destetramethyl shibuol

26 gms. of the substance were heated with 79 gms. caustic potash at 190°—200° for 4 minutes, and the product was treated with water and 10.5 gms. of an insoluble amorphous substance (A) were separated by filteration from the alkali solution. On being acidified with sulphuric acid, this yielded 8.9 gms. of an amorphous substance (B), about 1 gm. volatile acids and 1.6 gms. of gallic acid-3-methyl ether and phloroglucin.

Insoluble Amorphous Compound (A)

This shrinks at 280° and melts at 310° with decomposition. It was separated by means of acetone and ethyl alcohol into soluble and insoluble substances, which gave on analysis the following results, which agree fairly with those of destetramethyl shibuol :

	C	H	Ash	OCH_3	
Sol. subst.	62.9	5.5	0.3	32.5	melts at 340° with decomposition
Insol. subst.	61.1	5.1	1.2	31.1	does not melt at 340°

When these substances were combined together and again subjected to potash fusion, phloroglucin, gallic acid monomethyl ether and an amorphous substance were formed. The latter, being insoluble in an alkaline solution, was purified by precipitation from acetone solution with alcohol.

C	H	OCH_3	Ash
62.8	5 8	33.8	0.28
62.4	5.7	33 7	—

The volatile acids were found to consist of formic, acetic and butyric acids by converting them into the ethyl ester. Gallic acid monomethyl ether and phloroglucin were extracted with ether from the alkaline solution after being acidified, and separated by means of neutral lead acetate solution.

Gallic acid-3-methyl ether[1]

This gives a blue colour with ferric chloride and a cobalt blue colour with barium hydroxide; it melts at 212°—213°.

C=49.7, 49.7; H=4.8, 4 7; H_2O=2.4; OCH_3=16 7; M.W.=205 (by Rast's method) (Theory C=50.9; H=4 5; H_2O=2.4; OCH_3=16.5; M.W.=184 for $C_6H_2(OH)_2(OCH_3)CO_2H\frac{1}{4}H_2O$).

It gave on methylation with dimethyl sulphate, gallic acid trimethyl ether, M.p. 167°—168°, C=56 4; H=5.9 (Theory C=56.6; H=5.6 for $C_6H_3(OCH_3)_3CO_2H$).

Phloroglucin

This was isolated from the mother liquor separated from the lead salt of gallic acid methyl ether; it melts at 216°—217°.

C=44.3; H=6.4; H_2O=20.6; M.W.=125 (Theory C=44.4; H=6.2; H_2O=22.5; M.W.=126 for $C_6H_3(OH)_3.2H_2O$).

When destetramethyl shibuol was subjected to potash-fusion in a closed vessel and the aqueous extract of the reaction product was distilled in vacuo after being separated completely from phloroglucin and oxalic acid, an oily distillate was obtained, of which the CH_3O-group was determined. The presence of methylated compound of phloroglucin in the oily distillate was confirmed from its property of imparting a red colour to pine shavings moistened with hydrochloric acid and also a yellowish red colour to ferric chloride solution.

1. E. Fischer, Ber. D. Chem. Ges., **45**, 2715 (1912); **46**, 1116 (1913); W. Vogl, Monat. f. Chem., **20**, 397 (1899).

3 Potash fusion of tetramethyl shibuol

9 gms. of tetramethyl shibuol fused with 27 gms. caustic potash at 190°—200° for 3—4 minutes, yielded 10% gallic acid-mm-dimethyl ether, 4% volatile acids, 50% amorphous substances (A) and 17% of other amorphous substance (B) and a trace of a phenolic substance of unknown nature.

The volatile acids consisted of formic, acetic and butyric acids.

Gallic Acid-mm-dimethyl ether[1]

This substance precipitated from its aqueous solution with neutral lead acetate, was found to melt at 202°; it gave a pale pink colour to ferric chloride solution.

Analysis:	Calc. for $C_6H_2(OH)(OCH_3)_2CO_2H$
C = 53.6	54.5
H = 5.2	5.0
OCH_3 = 31.2	31.3

Amorphous substance (A)

This was obtained from the alkali solution as an amorphous precipitate on acidifying with sulphuric acid, it was purified from alcohol solution with ether; it melts at about 310°.

C = 61.1; H = 4.7; OCH_3 = 17.7.

Insoluble amorphous substance (B)

This compound was separated from its alkaline solution by filteration and gave on analysis, after being precipitated with alcohol from its acetone solution:

C = 61.2, 61.4; H = 5.0, 4.7; OCH_3 = 32.9; Ash = 0.90.

Tetramethyl shibuol by the hydrolysis of caustic potash at high temperature decomposed into gallic trimethyl ether and destetramethyl shibuol (OCH_3 = 33) and the latter by the further action of the reagent yields gallic acid monomethyl ether, phloroglucin and two amorphous

1. C. Graebe & E. Martz: Ber. D. Chem. Ges., **36**, 216 (1903); Ann. d. Chem., **340**, 220 (1905); A. G. Perkin: Jour. Chem. Soc., **99**, 1721 (1911).

substances, one of which is soluble in alkali and shows $CH_3O=22$, and the other is insoluble and shows $CH_3O=32$. These two substances are also obtained from tetramethyl shibuol by the direct action of caustic potash and show the same behavior towards caustic potash at high temperatures as the mother substance.

The insoluble amorphous substance generated from tetramethyl shibuol by potash-fusion is similar in its properties to tetramethyl shibuol and also destetramethyl shibuol but differs in its methoxy content and in its solubility in alkaline solution from the other degradation product which always occurs with the first compound in the reaction product.

Though the chemical nature of the main reaction products of tetramethyl shibuol is unknown, the manner in which the molecule of shibuol is decomposed by hydrolysis seems to be similar to that of a plant mucilage investigated by one of the writers and H. Ueda, and also to that of proteins.

Although unfortunately the present research could not accomplish the object of ascertaining the chemical structure of shibuol, the noteworthy fact was obserbed in this experiment that gallic acid trimethyl ether, in the course of potash-fusion yields gallic acid-m-m-dimethyl ether, the methyl group being split which combines with the oxygen attached in the para position to the carboxyl group of the ether.

A further communication from our laboratory on the decomposition of ethers such as phloroglucin methyl ether and gallic acid methyl ether by alkali fusion will appear in the near future in these memoirs.

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Laboratory of Organic- & Bio-Chemistry.