48. Studies on "Bios." Part V.

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The authors made public, in a previous paper, their views on the constitution of γ -acid, a name given, for the time being, to a substance obtained by the alkali treatment of crude bios¹⁾. From the mother liquor of the γ -acid, 4 more crystalline substances were obtained and identified, an account of which is given in the present paper.

To the mother liquor of γ -acid, sulfuric acid (1:5) was added until the solution became slightly alkaline to litmus. Alcohol was distilled off and the solution made acidic by passing with CO₂ gas. The acidic solution was well shaken with ether until the ether was colored yellowish no more. The aqueous solution was then made distinctly acidic by adding sulfuric acid, at which time a resinous matter separated out. The clear solution, obtained by removing the resinous matter by decantation, was thoroughly shaken with ether. By distilling off the ether from the ethereal solution, some oily matter to the amount of 10% of crude bios was obtained. On standing several days, a yellowish crystalline substance separated out from the oily matter, which proved to be β -acid²⁾.

The residue of β -acid was dissolved in water and the aqueous solution well shaken with ether, a part of the substance removing to the ether. This ether soluble fraction was treated, on the other hand, with chloroform after the ether was distilled off. Thus we obtained 3 fractions; i.e., the first, soluble in water but insoluble in ether, the second, soluble in ether but with difficulty soluble in chloroform and the third, easily soluble in chloroform. From each fraction a crystalline substance was obtained as follows:

Fraction	Substance	Constitution
Oily matter	β -acid

1) B. SUZUKI and T. TAIRA, J. Chem. Soc. Jap. **45** (1924), 302.

2) K. SAHASHI, J. Agr. Chem. Soc. Jap. **2** (1926), 268.

Water	Nicotinic acid
Ether	p-Oxy-benzoic acid
Chloroform	Ferularic acid

Be it stated, here, that we succeeded, finally, in isolating the active principle, though perhaps not in the original form in which it exists in rice bran as the crude material was treated pretty severely with chemicals, in the crystalline state as a brucine salt, the principle being a substance of acidic nature. The details of the chemical properties of the substance will be given in a succeeding paper.

EXPERIMENTAL

Nicotinic acid

Picrate of nicotinic acid :— m.p. 216–217°C., N : 15.54% (15.91 as $C_6H_5NO_2.C_6H_3N_3O_7$).

Nicotinic acid :— m.p. 231°C., N : 11.14% (11.38 as $C_6H_5NO_2$)

Copper nicotinate :— Cu : 20.48% (20.68 as $(C_6H_4NO_2)_2Cu$)

Ferularic acid

Ferularic acid :— m.p. 167°C., C : 61.50%, H : 5.26% (C : 61.85, H : 5.15 as $C_{10}H_{10}O_4$)

If the substance under question should really be ferularic acid it would be expected to yield protocatechuic acid on alkali fusion, and this was the case with our substance.

Protocatechuic acid :— m.p. 198°C. (decomposing), C : 54.67%, H : 3.93% (C : 54.54, H : 3.89 as $C_7H_6O_4$)

Potassium ferulate :— K : 28.09% (28.9 as $C_{10}H_8O_4K_2$)

p-Oxy-benzoic acid

p-Oxy-benzoic acid :— m.p. 207°C., C : 60.79%, H : 4.83% (C : 60.87, H : 4.34 as $C_7H_6O_3$)

p-Oxy-benzoic acid, above mentioned, was methylated, using methyl iodide, and analysed.

Anisic acid :— m.p. 182°C., C : 62.83%, H : 5.32% (C : 62.74, H : 5.26 as $C_7H_5O_3CH_3$)

To identify anisic acid it was further brominated.

Dibromo-anisic acid :— 209°C., Br : 51.88% (51.41 as $C_7H_3Br_2O_3CH_3$)

Picric acid :— p-Oxy-benzoic acid was nitrated as usual. M.p. 122°C., N : 18.35% (18.32 as $C_6H_3N_3O_7$).

One of the authors (S)¹⁾ stated previously that picric acid has been obtained by the nitration of crude bios. The mother substance of the picric acid seems, now, to be p-oxy-benzoic acid.

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1) B. SUZUKI and T. TAIRA, loc. cit.