at 266 mμ is 15.9×10^3), 92.6%. The ratio of the base to total P=0.87:1.00. Rf 0.51 (solvent A), 0.20 (solvent C).

6-Dimethylamino-9-β-D-ribofuranosylpurine 5′-monophosphate (Xb)—All procedure was essentially analogous to that described in the previous section. From 1.8 g. of the above isopropylidene derivative (XIVb), 500 mg. (18.5%) of monophosphate Ba-salt was obtained. *Anal.* Calcd. for $C_{12}H_{16}O_7N_5BaP$: P, 6.08. Found : P, 6.42. Paper chromatography gave only one spot in two solvent systems at Rf 0.37 (solvent E) and 0.29 (Solvent A). Purity calculated on the basis of ultraviolet absorption (ε of dimethylaminopurine riboside at 268 mμ, 18.3×10^3), 89.7%. The ratio of the base to total P=0.85:1.00.

The authors express their thank to the Elementary Analysis Laboratory of Kowa Chemical Laboratories and of Faculty of Pharmaceutical Sciences, University of Tokyo, for elementary analyses. A part of the expense of this work was financed from Grant-in-Aid for Scientific Research from the Ministry of Education, to which authors' thanks are due.

Summary

The phosphorylation of isopropylidene derivatives of adenosine and guanosine using tetrakis(*p*-nitrophenyl) pyrophosphate and phenyl phosphorodichloridate was examined to establish a general method for monophosphorylation. With the aid of the latter reagent, 6-methylamino- and 6-dimethylamino-9-β-D-ribofuranosyl-β-purine 5′-monophosphates were synthesized.

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29. Takuo Okuda : Studies on the Components of *Coriaria japonica* A. Gray. XIV.1) Two New Compounds isolated from Old Stem and Seed.

(*Faculty of Pharmacy, Kyoto University*[*1])

In the course of studies on the components of *Coriaria japonica*, it sometimes happened that leaves of this plant did not produce the toxic principle by the regular method of extraction.1) This may partially be due to decomposition of the toxic principles which took place during drying of the leaves. However, it is also considered that leaves of *C. japonica* contain the toxic principles only in certain periods of the year.

In order to determine the amount of toxic principles in the plant at all seasons and also to determine if the toxic principles are contained in other parts of the plant, every part of the plant above the ground was collected every month from a colony,[*2] quickly dried, and extraction was carried out by the regular method. The plant of this colony carries flowers at the beginning of May and the leaves appear a little later. Leaves and young stems are fully grown by the end of August and wither by the beginning of October. In March and April, old stems covered by brown bark and small buds are only part of the plant seen on the ground. Although no compound which is considered to be any of the toxic principles was extracted from this part, a pale yellow crystalline component was newly isolated.

As it is probable that this compound is a derivative of ellagic acid (I), which was formerly isolated from leaves of this plant by Kariyone, *et al.*,2) properties of this new product

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[*1] Yoshida-konoe-cho, Sakyo-ku, Kyoto (奥田拓男).

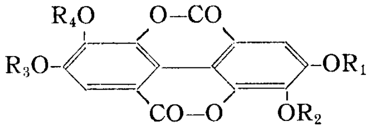
[*2] The plant was collected from a colony on Kitahira Pass, Mt. Hira, Shiga-ken.

1) Part XIII : This Bulletin, **2**, 185 (1954).

2) T. Kariyone, K. Kashiwagi, S. Mizutani : Yakugaku Zasshi, **57**, 800 (1937).

were compared with those of ellagic acid. The new compound decomposes at 315~320° turning to a black mass. It is sparingly soluble in organic solvents except acetic acid and pyridine, but readily dissolves in 5% sodium hydroxide giving a yellow solution. Infrared spectrum shows absorption peaks at 3.06, 6.21, and 6.34 μ, indicating presence of a hydroxyl group and aromatic ring. UV : $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (log ε 4.7). This range of the ultraviolet absorption peak is close to that of ellagic acid (Fig. 1). Molecular formula $(C_8H_5O_4)_n$ indicates that this compound could be an ellagic acid dimethyl ether (II), $C_{16}H_{10}O_8$.

The only dimethyl ether of ellagic acid which has been isolated from a plant is the one from *Euphorbia formosana* (Euphorbiaceae)[3] *[3] and some difference is observed between this compound and the synthesized ellagic acid dimethyl ether, which was prepared by methylation of ellagic acid, although location of the methoxyl groups in these two compounds has not been determined yet.[4] The natural ether has been reported to be positive to Griessmayer reaction[5] and to give a dark color by addition of ferric chloride solution. The synthesized ether was reported to be negative to these color tests. The compound isolated from *C. japonica* is considered to be different from the one isolated from *E. formosana*, as the former is negative to these color tests.



(I) $R_1 \sim R_4 = H$

(II) $R_1 \sim R_4 = \times 2H,\ \times 2Me$

Bark and buds covered by a thin bark were separated from the old stem and extraction was carried out on each part. However, these two parts yielded the same pale yellow crystalline component.

Yield of crude crystals of the toxic components from the dried leaf collected at the beginning of June was 0.065% and the yield from the young stem collected at the same time was about one-half of the yield from the leaf. At the end of July, when about half of the fruit in the colony was ripe, dried leaves still yielded 0.055% of the toxic principles. However, no toxic principle was extracted from either the leaf or the stem collected at the end of August when all fruits had dropped.

The toxic principles from the fruit were obtained only from red fruit which is unripe but fully grown. No toxic component was extracted from juice of either green fruit or blackened ripe fruit. A small amount of the toxic principle was also extracted from the seed of red fruit and the yield from the seed of the black fruit was much lower.

Besides tutin and pseudotutin, another crystalline component of m.p. 259° was isolated from seeds of the fruit collected in July. This component is considered to be an analog of coriamyrtin because of its properties as will be described below and was named coriatin. Coriatin is a colorless crystalline compound and its molecular formula was found to be $C_{15}H_{20}O_6$ which corresponds to monohydrate of coriamyrtin. This relationship between coriatin and coriamyrtin is analogous to the relationship between picrotin and picrotoxinin as shown below :

Coriatin $C_{15}H_{20}O_6$	Picrotin $C_{15}H_{18}O_7$
Coriamyrtin $C_{15}H_{18}O_5$	Picrotoxinin $C_{15}H_{16}O_6$

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*[3] *E. formosana* grows in Formosa and is called "Kidachi-daigeki" in Japanese.

3) J. Shinoda, P. Chen : Yakugaku Zasshi, **51**, 502 (1931).

4) G. Goldschmidt : Monatsh., **26**, 1142 (1905).

5) V. Griessmayer : Ann., **160**, 54 (1871).

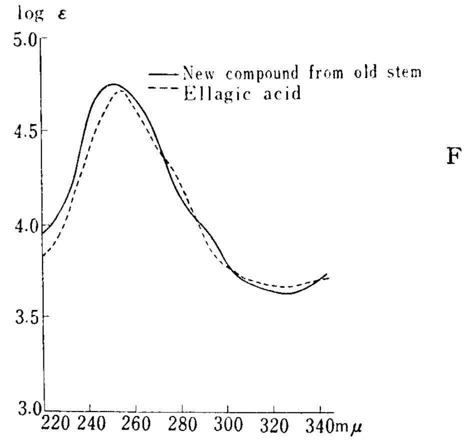


Fig. 1. Ultraviolet Spectra of the New Compound from Old Stem and Ellagic Acid (in EtOH)

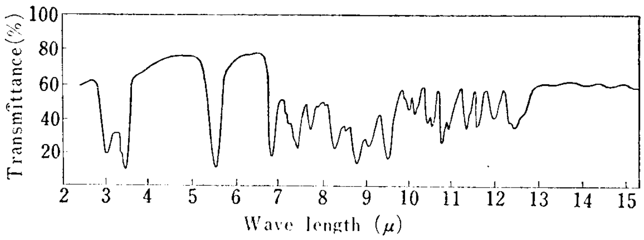
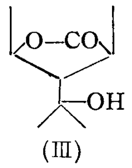


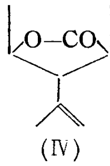
Fig. 2. Infrared Spectrum of Coriatin (in Nujol)

In infrared spectrum of coriatin (Fig. 2), absorptions of γ-lactone and hydroxyl group are observed respectively at 5.67 and at 3.05 μ. A broad absorption of hydrogen bond is observed at 3.0~3.5 μ and absorption of a double bond, which is found in the infrared spectra of coriamyrtin and picrotoxinin, is not seen in this compound. The infrared spectrum of coriatin is similar to those of the compounds of coriamyrtin and picrotoxin series. Absence of a double bond in coriatin was also confirmed by bromine water.

It therefore seems likely that the structural relationship between coriatin and coriamyrtin is the same as that between picrotin (III) and picrotoxinin (IV). As picrotin has been considered to possess a hydroxyisopropyl group in place of isopropenyl group of picrotoxinin,[6] coriatin may have a hydroxyisopropyl group in place of isopropenyl group of coriamyrtin.[7]



(III)



(IV)

Experimental

Extraction of Pale Yellow Crystals from Old Stem—Powdered stem of *C. japonica* (1 kg.) was extracted with three 4-L. portions of boiling 50% MeOH. Combined extract was distilled first at ordinary pressure and then *in vacuo*. The concentrated extract was heated on a boiling water bath and 80 g. of aluminum acetate was added. The mixture was heated for 1 hr. and the precipitate was filtered off with suction. The filtrate was further concentrated to 400 cc., cooled, and extracted with ten 100-cc. portions of $CHCl_3$. Combined $CHCl_3$ solution was dried over $CaCl_2$ and the solvent was removed by distillation to give a pale yellow crystalline residue. This residue was recrystallized three times from hot EtOH to pale yellow needles, m.p. 315~320° (decomp.). This compound is almost insoluble in water, but readily dissolves in NaOH and Na_2CO_3 solutions to give a yellow solution.

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[6] S. N. Slater, with an Appendix by M. Sutter, E. Schlittler: J. Chem. Soc., **1952**, 1597; S. N. Slater, A. T. Wilson: Nature, **167**, 324 (1951); J. S. E. Holker, *et al.*: J. Chem. Soc., **1958**, 2987.

[7] T. Kariyone, T. Okuda: Yakugaku Zasshi, **73**, 930 (1953).

It is sparingly soluble in EtOH. EtOH solution is negative to color test with $FeCl_3$ and to the Griessmayer reaction. The compound is insoluble in most of organic solvents except AcOH and pyridine. *Anal.* Calcd. for $C_{16}H_{10}O_8$: C, 58.19; H, 3.05. Found : C, 58.24; H, 2.98.

Isolation of Coriatin—To 2 kg. of the powdered seed (2 kg.), 3 L. of benzene was added and the mixture was kept at room temperature overnight. After filtration, the solid was extracted with three 3-L. portions of boiling 30% EtOH for 3 hr. each. The combined extract was concentrated to 100 cc. and extracted with Et_2O continuously for 24 hr. Et_2O solution was dried over $CaCl_2$ and Et_2O was distilled off to leave pale brown crude crystals. When these were recrystallized from hot water, a small amount of colorless crystals separated out which were recrystallized from EtOH, m.p. 259° (decomp.). *Anal.* Calcd. for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76. Found : C, 60.77; H, 6.88.

The aqueous mother liquor from the recrystallization of the crude crystals gave tutin on concentration, and then pseudotutin on further concentration.

The author wishes to express his sincere thanks to Dr. T. Kariyone, Chief of the National Institute of Hygienic Sciences, and to Prof. K. Kimura of Kyoto University for their guidance and encouragement. The author's thanks are also due to Dr. K. Takaishi and Messrs. T. Fujita and T. Miki of this Faculty for their kind help in collecting the plant material and in extraction of the components. The author is indebted to Dr. M. Yamaguchi of Osaka City University for taking infrared spectra, and to the members of the microanalytical center of this Faculty for microanalysis.

Summary

1) Each part of *Coriaria japonica* collected every month was extracted but the toxic principle was obtained only from the young leaf and stem collected in June and July.

2) A pale yellow crystalline component, which can be considered as a new kind of ellagic acid dimethyl ether, was isolated from the old stem of *C. japonica.*

3) Coriatin, $C_{15}H_{20}O_6$, was isolated from the fruit juice and it was considered to be an analog of coriamyrtin. The relationship between coriatin and coriamyrtin is considered to be analogous to that between picrotin and picrotoxinin.

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