## Note

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# **Takuo Okuda :** Coriamyrtin. IX.[1] Methanolysis of Coriamyrtin.

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Although lactone of coriamyrtin has been presumed[2] to be a γ-lactone bridged on six-membered ring, like the one of two lactones of picrotoxinin,[3] a product of simple saponification of the lactone of coriamyrtin has not been isolated. While picrotoxinin gives a monocarboxylic acid, picrotoxic acid,[4] when heated with dilute mineral acid and a dicarboxylic acid[4] under drastic conditions of hydrolysis, no carboxylic acid is obtained by hydrolysis of coriamyrtin, and an isomer, isocoriamyrtin,[5] which is considered to have an aldehyde group and to retain the γ-lactone, is obtained. By drastic hydrolysis both in acid and alkali, coriamyrtin gives only amorphous material which is considered to be produced by decomposition and polymerisation. Although determination of the number of lactones in coriamyrtin by hydrolysis with alkali indicates values corresponding to about one lactone, further proof of the presence of single lactone in coriamyrtin has been desirable since some of picrotoxinin analogs which have two lactones, one of which must be ana-

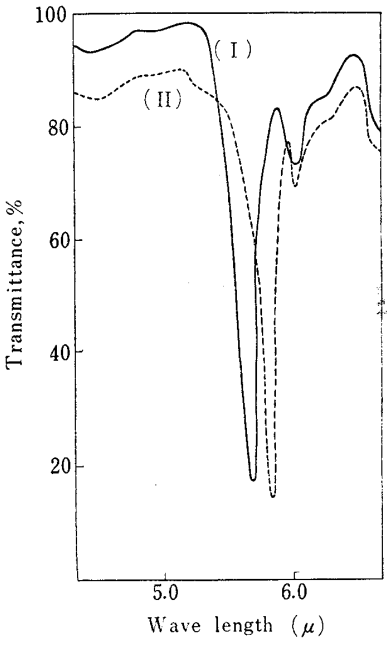

Fig. 1. Infrared Spectra of Coriamyrtin and Methyl coriamyrtate (in Nujol)
(I) Coriamyrtin
(II) Methyl coriamyrtate

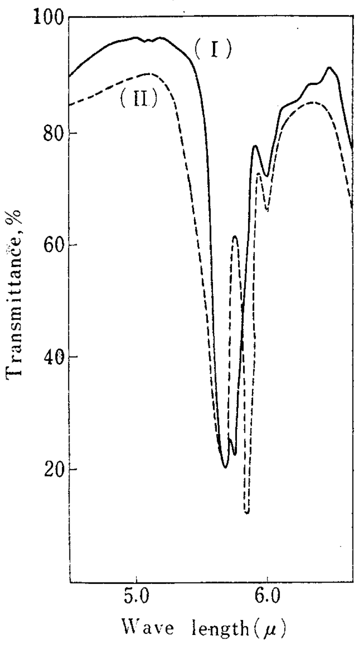

Fig. 2. Infrared Spectra of Picrotoxinin and Methyl picrotoxate (in Nujol)
(I) Picrotoxinin
(II) Methyl picrotoxate

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[1] This paper constitutes Part XVI of a series entitled "Studies on the Components of *Coriaria japonica* A. Gray." Part XV : This Bulletin, **9**, 379 (1961).

[2] T. Kariyone, T. Okuda : Yakugaku Zasshi, **73**, 930 (1953); Acta Scholae Medicinalis Universitatis in Kyoto, **23**, 45 (1955).

[3] H. Conroy : J. Am. Chem. Soc., **73**, 1889 (1951); **74**, 491, 3046 (1952).

[4] P. Horrmann, H. Wächter : Ann., **411**, 273 (1916).

[5] T. Kariyone, T. Sato : Yakugaku Zasshi, **51**, 988 (1931).

logous[2] to the lactone of coriamyrtin, have been reported[6] to behave as a monolactone on hydrolysis.

Methyl coriamyrtate, $C_{16}H_{22}O_6$, was obtained which is considered to be a methyl ester of an acid produced by opening of the lactone of coriamyrtin in the presence of sodium methoxide in methanolic solution at room temperature. As is shown in Fig. 1, absorption of γ-lactone (5.66 μ) in coriamyrtin disappeared after methanolysis and absorption of ester appeared at 5.81 μ. Since microanalysis indicates methanolysis of one lactone, the presence of single lactone in coriamyrtin is proved by this complete transition of the absorption of γ-lactone to ester.

Since coriamyrtin has been presumed[2] to have a hemiacetal group on the position which corresponds to the position of one of two lactones of picrotoxinin, a proof will be given to the presumed structure of coriamyrtin when the infrared spectrum of methyl coriamyrtate is compared with that of methyl picrotoxate (Fig. 2) which has an absorption of γ-lactone (5.67 μ) in addition to an absorption of ester (5.81 μ) in carbonyl region.

## Experimental

**Methyl Coriamyrtate**——To a solution of 0.5 g. of coriamyrtin in 60 cc. of dehyd. MeOH, 10 mg. of sodium was added. The solution was kept at room temperature (7~13°) for 30 hr., neutralized with AcOH, and then the solvent was removed by distillation *in vacuo*. White crystalline residue was dissolved in 100 cc. of $CHCl_3$, and the solution was washed with water and dried over $Na_2SO_4$. $Na_2SO_4$ was filtered and $CHCl_3$ was distilled to give white crystalline residue. The residue was recrystallized from water to give colorless needles, m.p. 210°. Very soluble in $CHCl_3$ and $Me_2CO$, soluble in $Et_2O$ and water. *Anal.* Calcd. for $C_{16}H_{22}O_6$ : C, 61.93; H, 7.09. Found : C, 62.19; H, 6.989.

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## Summary

Methyl coriamyrtate was prepared by methanolysis of coriamyrtin. Complete transition of γ-lactone to ester was confirmed by infrared spectra.

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[6] J.C. Benstead, *et al.* : J. Chem. Soc., **1952**, 1042.