

**Studies on the Chemical Components of
Fruits of *Forsythia Koreana* NAKAI (II)
Occurrence of betaine in the fruits of *Forsythia Koreana***

by

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**Forsythia koreana NAKAI 씨 (토연교)의 성분에 관한 연구 (II)
(Betaine의 분리 및 확인)**

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요 약

Forsythia koreana NAKAI 씨(토연교)를 methanol로 추출 분리정제하여 얻은 quaternary base의 염산염을 mass spectra, ultraviolet spectra, Infrared spectra, 원소분석, 정성실험으로 확인한 결과 Betaine 염산염 임이 확인되었다.

ABSTRACT

The methanol extract of the fruits of *Forsythia Koreana* NAKAI was separated and purified. The quaternary base chloride was obtained. Through the mass spectrogram, ultraviolet spectra, infrared spectra, elemental analysis and qualitative tests it was identified as betaine hydrochloride.

The fruits of *Forsythia Koreana* has been used as a drug in the oriental medicine. There has been done some investigations upon the chemical constitution of the fruits of other *Forsythia* species and the presence of phytosterols and flavonoids was reported but no isolation of quaternary base has been made.^{1),2),3)} The Authors reported the isolation of a quaternary base

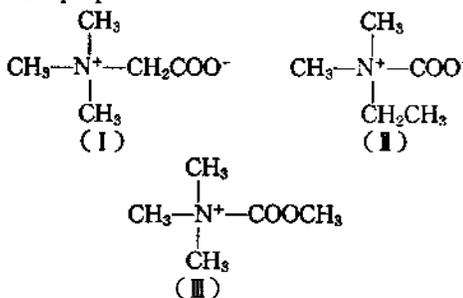
from the *Forsythia Koreana* previously.⁴⁾

The fruits were extracted with methanol in a continuous extractor. The methanol extract was evaporated in vacuo. The residue was dissolved in 5% sulfuric acid and filtered. The acidic solution was extracted with ether to remove any neutral or acidic components, the base was then separated as reineckate from the aqu-

eous solution. The base reineckate was converted into picrate and purified by recrystallization. The colorless crystals of the base chloride were obtained by the evaporation of the aqueous solution.

The molecular weight of this quaternary base was determined by the mass spectrographic method and found to be 152. The results agree well with the molecular formula of $C_5H_{11}NO_2Cl$ given by elementary analysis. The chromophoric group is absent as the ultraviolet spectra does not show a maximum peak. There is no unsaturation as the bromine test and the Baeyer test are negative. The infrared spectra shows an intensive absorption at 1740 and 1190cm^{-1} . This gives the assurance of the presence of the carbonyl group but the 2,4-dinitrophenylhydrazine test is negative; consequently, the substance is neither an aldehyde nor a ketone. These results narrow the structural possibilities considerably. The compound may be, then, an

ester or carboxylic acid. The following three structural formula (I) (II) (III) are proposed for a quaternary base which would satisfy all of the properties:



The infrared spectra (Fig. 1) is very similar to that of betaine, proposed structure(I), which often found as plant component.^{5),6),7)} In order to prove the identification, the infrared spectra of betaine hydrochloride(E. Merk reagent grade m. p., 228°C) was taken and compared with that of the compound identified. Two spectra match in every detail to prove the base is betaine itself.

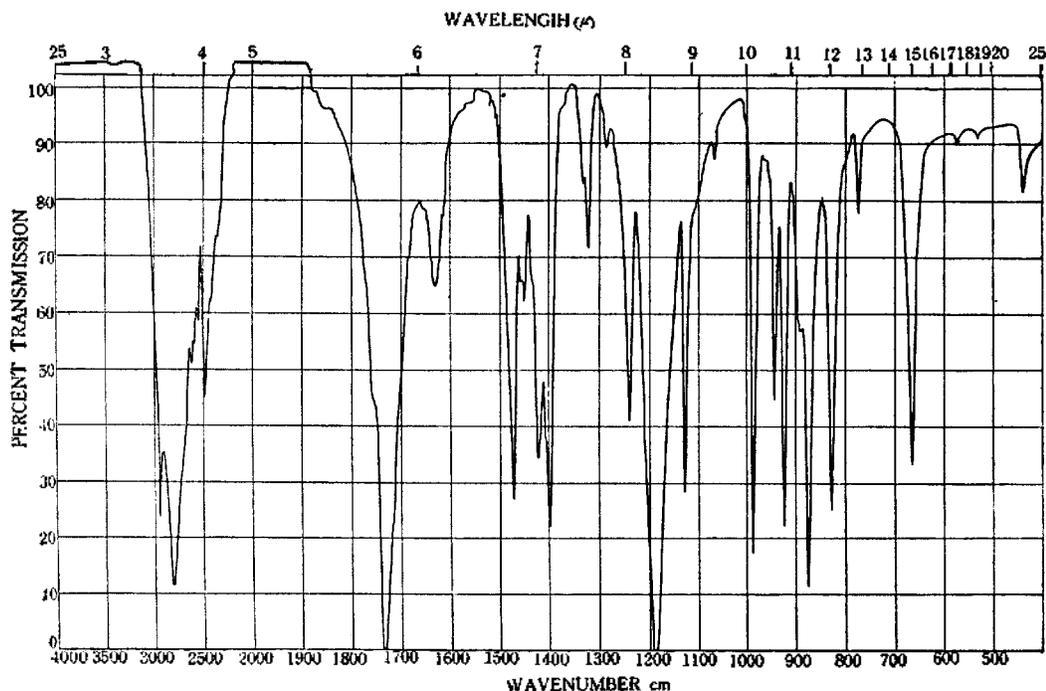


Fig. 1. Infrared absorption spectra of the sample in the solid state

EXPERIMENTAL⁴⁾

Separation: A finely-ground sample of 20kgm. of fruits of *Forsythia Koreana* was extracted by methanol and this extract was distilled at reduced pressure. This concentrated methanol extract was treated with 5% sulfuric acid. The residue was discarded and the sulfuric acid solution was extracted with ether. The saturated solution of ammonium reineckate was added to the above extract. The solution was cooled and the resulted precipitate was filtered, washed well with methanol, and recrystallized in acetone. Pink crystalline powder (42 gm.) m. p., 270°C (dec.) were obtained.

Base picrate: The reineckate (6 gm.) was dissolved in 500ml. of acetone. 5 grams of silver sulfate, dissolved in 500ml. of water at 60°C, were added to the 500ml. of reineckate solution. The silver reineckate precipitate was filtered. The excess silver ion was precipitated by hydrochloric acid and the precipitate was discarded. The acetone was removed by evaporation and the base picrate was recrystallized from water. Yellow needle-like picrate base m. p. 182°C (lit., 180-181°C) was obtained⁸⁾.

Base chloride: The picrate base crystals were dissolved in water and diluted hydrochloric acid was added. The free picric acid was extracted by ether. Upon the concentration of the aqueous solution under reduced pressure a white crystalline precipitate was obtained. This was recrystallized from isopropyl alcohol, white prism-shaped crystals (0.3gm.) were obtained. (m. p., 230°C (dec.) lit., 228°C⁹⁾) (Calcd. for C₅H₁₂NO₂Cl: C 39.03, H 7.82, N 9.10, O 20.85, Cl 23.15, found: C 38.33, H 7.66, N 8.86, O 22.18, Cl 22.97).

These crystals gave negative bromine test,

Baeyer test and 2,4-dinitrophenylhydrazine reagent test.

CONCLUSION

From the fruits of *Forsythia Koreana* NAKAI, a quaternary base was separated and purified. White prism-shaped crystals m. p., 237°C (dec.) were obtained.

Through the mass spectrogram and elementary analysis, a molecular weight of 152 and molecular formula of C₅H₁₂NO₂Cl were determined. Further, by ultraviolet and infrared spectra and colour reaction, this compound was identified as betaine. By the perfectly identical spectra of the sample and betaine the identification was confirmed.

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