

Studies on the constituents of Formosan

Dioscorea Colletii Hook. f. (I)

The Isolation of Dimethyl Terephthalate

By

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The constituents of Formosan *Dioscorea colletii* Hook. f. were studied. Dimethyl terephthalate (I) was isolated from the MeOH extract of the tubers of this plant. Hydrolysis of (I) afforded an acidic compound which was confirmed as terephthalic acid (II) by direct comparison of its IR spectrum with that of authentic sample. The synthetic dimethyl terephthalate was identical to the isolated compound in all respects.

The genus *Dioscorea* has served as a uniquely profuse source of steroidal sapogenins¹⁻⁹⁾. We report herewith the isolation and identification of dimethyl terephthalate (I) from the MeOH extract of the tubers of *Dioscorea colletii* Hook. f. growing in Formosa.

The methanolic extract of the tubers of this plant, on concentration, gave a large amount of sublimable crystalline compound (I). After removal of crystals, the filtrate was further concentrated and the syrupy brown residue is now under examination.

Crystalline compound (I) mp. 141-2°C from EtOH, $[\alpha]_D^{27} = 0^\circ$ (CHCl₃) gave negative Lieberman-Burchard's, Mayer's and Mg-HCl tests. It showed a characteristic UV spectrum, $\epsilon_{\text{max}}^{\text{EtOH}}$ (log ϵ): 240 μ (4.27), 285 μ (3.23), of simple benzenoid skeleton. The IR. (nujol) spectrum indicated the presence of carboxylic acid ester absorptions at 1720 cm⁻¹ and 1260 cm⁻¹. The NMR. (CDCl₃) exhibited one singlet of four aromatic protons at 1.88 τ and six protons singlet of two methoxyl signal at 6.06 τ . Based on the above spectral evidences, compound (I) is appeared as a highly symmetric dicarboxylic acid ester structure.

Hydrolysis of (I) with 10% NaOH afforded a crystalline compound (II), mp. >300° (sublimes without melt), which was confirmed as terephthalic acid by direct comparison of IR. (KBr) spectrum with that of authentic sample. Thus, the compound (I) is suggested to be dimethyl ester of terephthalic acid. The identity with dimethyl terephthalate was proved by the mixed mp. and IR. (KBr) comparison with that of authentic specimen which was synthesized by known method¹⁰⁾.



(I). R=CH₃

(II). R=H

This is the first instance that dimethyl terephthalate being isolated from natural source. It has been reported¹⁾ that the blood levels of tetracyclines, sulfonamides and sulfaethylthiadiazole were increased by simultaneous administration of terephthalic acid (II), a hydrolytic product of compound (I), and it has been used together with antibiotics for treating and preventing diseases of poultry.

EXPERIMENTAL

M. Ps. were measured by use of the micro melting point apparatus (Yanagimoto Co. Ltd. Kyoto) and uncorrected. UV. absorption spectrum was taken on Hitachi Perkin-Elmer 139 UV-VIS Spectrophotometer. IR. spectra were recorded on the Hitachi Grating Infrared Spectrophotometer, model EPI-G2. Optical rotation was determined with Rex Photoelectric Polarimeter, model NEP-2. The NMR spectrum was measured in CDCl₃ with (CH₃)₄ Si as internal standard.

Isolation of crystalline compound (I), dimethyl terephthalate:

The dried tubers (4.8kg) of *Dioscorea colletii* Hook. f., collected in "Thumb Mountain" near to Taipei in May 1967 by the department of pharmacognosy of this college, were successively extracted with MeOH. The total MeOH extract was concentrated under reduced pressure to about 2 liters and a large amount of sublimable colorless needle crystals were produced. After removal of colorless needle crystals (Compound (I), yield 7.5g), the filtrate was further evaporated and the residue is now under examination.

Crystalline compound (I), Dimethyl terephthalate:

Colorless needles from EtOH, mp. 141-2°C, sublimable, $[\alpha]_D^{27} = 0^\circ$ (c=1, CHCl₃), negative to Lieberman-Burchard's, Mayer's and Mg-HCl tests. UV. λ_{max}^{EtOH} (log ϵ): 240(4.27), 285(3.23). IR. (nujol): 1720cm⁻¹, 1260cm⁻¹ (ester carbonyl). The NMR spectrum in CDCl₃ showed the following signals; 1.88 τ (singlet, 4H, aromatic) and 6.06 τ (singlet, 6H, 2xOCH₃). On admixture with synthetic dimethyl terephthalate, the mp. was not depressed. Its IR. (KBr) spectrum was also found to be superimposable with that of authentic sample.

Hydrolysis of crystalline compound (I), terephthalic acid (II):

130 mg of compound (I) was heated with 10.5ml of 10% NaOH on boiling water bath for 2 hours, cooling and filtration, the filtrate was extracted with ether. The aqueous layer was warmed on boiling water bath for 5 mins. and acidified with c-HCl, cooled, the white precipitate was gathered by suction filtration and purified by recrystallization from EtOH to give a microcrystalline compound (II), mp >300°C (sublimes without melt). The IR. (KBr) spectrum was superimposable with that of authentic sample of terephthalic acid.

Synthesis of dimethyl terephthalate (I):

170mg of reagent grade terephthalic acid (II) (Tokyo Kasei Kogyo Co. Ltd.) was refluxed with 5 ml of thionyl chloride on boiling water bath for 7 hrs. The reaction mixture, after

cooled, was evaporated to dryness under reduced pressure. The residue was then treated with 5 ml of CH_3OH and stand aside for crystallization. Collected the crystals and purified by recrystallization from MeOH to give colorless needles, mp. $140-2^\circ\text{C}$, yield 128 mg. On admixture with compound (I), the mp. showed no depression. The IR. (KBr) spectra also found to be identical.

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中文摘要

臺灣產 *Dioscorea colletii* Hook. f. 之成分研究 (I)

Dimethyl Terephthalate 之分離

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由 *Dioscorea Colletii* Hook. f. 之塊根, 分離一種昇華性白色針狀結晶 mp. $141-2^\circ\text{C}$, $[\alpha]_D^{27} = \pm 0^\circ$,

$\lambda_{\text{max}}^{\text{EtOH}}$ $\mu(\log \epsilon)$: 240(4.27), 285(3.23). 由其 IR, NMR 等性質, 得知為一極對稱性之 dicarboxylic acid ester. 經水解反應及合成證明本物質為 dimethyl terephthalate.