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SUGIOL AND 5 $\alpha$ -STIGMASTANE-3,6-DIONE FROM THE CHINESE DRUG  
"TI-KU-PI" (*LYCII RADICIS CORTEX*)<sup>1</sup>

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"Ti-ku-p'i" (root bark of *Lycium chinense* Mill., Solanaceae) has been used in traditional Chinese medicine for the treatment of fever, hemorrhagic inflammation, hypertension, and ulcers. Several compounds (betaine, linoleic acid, linolenic acid, melissic acid,  $\beta$ -sitosterol, cinnamic acid, and kukoamine A) have been isolated previously from the crude drug (1-4). As part of our search for the constituents of "Ti-ku-p'i", we reported the isolation of a new dipeptide, lyciumamide (5). In this communication, we describe the isolation and identification of sugiol and 5 $\alpha$ -stigmastane-3,6-dione from the neutral fraction of the crude drug extracts. In the course of identification of the steroidal diketone, an exact coincidence of <sup>1</sup>H-nmr spectra in CDCl<sub>3</sub> with reported data (6) was not obtained (e.g., the chemical shift for the C-18 angular methyl was observed as  $\delta$ 0.70, while  $\delta$ 0.76 was reported). As the authentic sample was not available for direct comparison, 5 $\alpha$ -stigmastane-3,6-dione<sup>3</sup> was synthesized from  $\beta$ -sitosterol (8). Identity of the isolated steroidal diketone and the synthetic compound was then fully established, including exact coincidence of <sup>1</sup>H-nmr spectra as described in the experimental section.

EXPERIMENTAL

MATERIAL.—The crude drug (dried root bark) was obtained from Mikuni & Co., Ltd., Osaka, Japan.

<sup>1</sup>This paper forms Part II of "Studies on the Constituents of Chinese Drug 'Ti-ku-p'i'." For Part I, see Noguchi *et al.* (5).

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<sup>3</sup>The compound was also synthesized according to the method described by Fieser for 5 $\alpha$ -cholestane-3,6-dione (7).

EXTRACTION and ISOLATION.—The ground crude drug (50.5 kg) was percolated with 50% EtOH at 60°, and the extract was concentrated *in vacuo* to give a resinous precipitate (1.3 kg) and a H<sub>2</sub>O soluble residue (3.8 kg). A part of the former (365 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was washed with 3% citric acid and 3% NaHCO<sub>3</sub> solution. The remaining neutral fraction was chromatographed on silica gel. The fraction eluted with petroleum ether-Et<sub>2</sub>O (9:1) gave sugiol (30 mg), while the fraction eluted with petroleum ether-Et<sub>2</sub>O (8:2) contained 5 $\alpha$ -stigmastane-3,6-dione (100 mg).

Compound	Identification	Reference
sugiol	mp, uv, ir, ms, <sup>1</sup> H nmr, elemental analysis	(9)
	acetate (mp, mmp, [ $\alpha$ ] <sub>D</sub> , ir, <sup>1</sup> H nmr, elemental analysis)	(10)
5 $\alpha$ -stigmastane-3,6-dione	mp, mmp, ir, <sup>1</sup> H nmr, ms, cd, elemental analysis	(6, 8)

Full details of the isolation and identification of the compounds are available on request to the senior author.

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