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Triterpenic Constituents of *Stewartia monadelpha* Sieb. et Zucc. Camelliagenin A 16-Cinnamate as a Sapogenin

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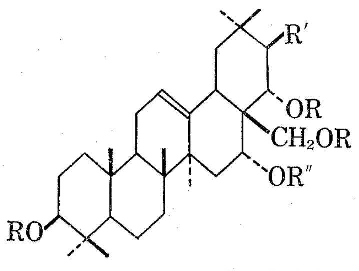
As the continuation of our study[2)] of triterpenic sapogenins isolated from the plants of Theaceae, we have investigated the wood of *Stewartia monadelpha* Sieb. et Zucc. (Japanese name: Himeshara) of the natural genus very closely related to *Camellia*.

The crude saponin mixture gave, after acid hydrolysis and subsequent silica gel chromatography, amorphous powder (I) together with camelliagenin A[2a)] (II) and barringtogenol C[3)] (III). The infrared (IR) and nuclear magnetic resonance (NMR) spectra of I revealed the presence of a conjugated ester group [ν_{max}^{KBr} cm^{-1}: 1705, 1638, 1270, $\delta_{ppm}^{CDCl_3}$: 5.77 (1H, multiplet)], a disubstituted double bond [$\delta_{ppm}^{CDCl_3}$: 6.43, 7.75 (two doublets, J=16 cps)] and a monosubstituted benzene ring [ν_{max}^{KBr} cm^{-1}: 1603, 1580, 770, 715, $\delta_{ppm}^{CDCl_3}$: 7.44 (5H, multiplet)] in the molecule. Alkaline hydrolysis of I yielded II and cinnamic acid, clearly showing I to be camelliagenin A cinnamate.

The position of the cinnamoyl group in I was determined as follows: A mild acetylation of I under conditions in which the 16α-hydroxyl group in II is not affected, yielded the triacetate (IV) with no hydroxyl band in its IR spectrum and signals due to the $-\overset{|}{\underset{|}{C}}-CH_3$ groups at 0.87 (6H), 0.93 (3H), 0.97 (6H), 1.04 (3H) and 1.26 ppm (3H) in its NMR spectrum. The chemical shift values for all methyl signals in IV are identical (deviation, 0.01) with those of camelliagenin A tetraacetate (V)[2a)] except that at lowest field for which the deviation is 0.04 ppm.



I : R=R'=H, R''=COCH=CHPh
Ⅱ : R=R'=R''=H
Ⅲ : R=R''=H, R'=OH
Ⅳ : R=Ac, R'=H, R''=COCH=CHPh
Ⅴ : R=R''=Ac, R'=H
Ⅵ : R=Ac, R'=H, R''=H

The lowest field methyl signal in the NMR spectrum of IV, appears at the same field as in the NMR of I [$\delta_{ppm}^{CDCl_3}$: 0.79 (3H), 0.96 (15H), 1.27 (3H)] and at higher field than for camelliagenin A triacetate VI (1.44ppm). Since the 27-methyl signal appears at the lowest field in derivatives of II and related compounds, and since its regular up-field shift on acetylation of the 16α-hydroxyl group is well known,[2,4)] the observed chemical shifts of the 27-methyl signals in I, and IV and VI can only be explained by the presence of the cinnamoyl group at 16α-position.

As far as we are aware, this is the first instance of a 16α-cinnamate of olean-12-ene to be found in nature.

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1) Location: *a*) *Katahiracho, Sendai*; *b*) *Meguro, Tokyo*.
2) *a*) S. Itô, M. Kodama and M. Konoike, *Tetrahedron Letters*, **1967**, 591; *b*) S. Itô and T. Ogino, *ibid.*, **1967**, 1127; *c*) T. Ogino, T. Hayasaka and S. Itô, *Chem. Pharm. Bull.* (Tokyo), **16**, 1132 (1968).
3) I. Yoshioka, T. Nishimura, A. Matsuda and I. Kitagawa, *Tetrahedron Letters*, **1966**, 5979.
4) *a*) S. Itô, T. Ogino, H. Sugiyama and M. Kodama, *Tetrahedron Letters*, **1967**, 2289; *b*) S. Itô, M. Kodama, M. Sunagawa, T. Ôba and H. Hikino, to be published.

Experimental[5]

Extraction of the Saponin and Isolation of the Sapogenins——The chopped wood (7.46 kg) of *Stewartia monadelpha* Sieb. et Zucc. was percolated with methanol (80 liters) for 24 hr. The extract was concentrated to about 1.35 liters and to it was added acetone (6.7 liters) and the solution kept overnight. The dark brown amorphous solid which precipitated was collected by filtration and washed with acetone in a Soxhlet extractor for 4 days to give a brown crude saponin mixture (12 g). The mixture was heated under reflux in 83% EtOH (250 ml) with conc. HCl (17 ml) for 10 hr. The reaction mixture was poured into water (1.2 liters) and the solution was made alkaline by potassium hydroxide solution in order to dissolve colored matter. The insoluble powder was collected by filtration (4 g) and dissolved in methanol. Filtration of the insoluble matter and evaporation of the solvent yielded a resinous, pale-brown sapogenin mixture (1.2 g). This was separated by chromatography on silica gel (60 g) to give the following fractions.

Fraction No.	Solvent ($CHCl_3$–MeOH)	Volume (ml)	Compounds obtained	Yield (mg)
1	99:1	190	camelliagenin A 16-cinnamate (I)	489
2	99:1	120	camelliagenin A (II)	279
3	90:10	150	barringtogenol C (III)	67

The first fraction (amorphous) shows the following spectral properties. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3450, 1705, 1633, 1603, 1580, 1270, 770, 715. NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$: 0.79 (3H, singlet), 0.96 (15H, broad singlet), 1.27 (3H, singlet), 3.22 (1H, broad triplet, J=7 cps), 3.4—4.2 (3H, unresolved multiplet), 5.34 (1H, multiplet), 5.77 (1H, multiplet), 6.43 (1H, doublet, J=16 cps), 7.44 (5H, multiplet), 7.75 (1H, doublet, J=16 cps).

The second fraction was recrystallized from methanol to give fine needles, mp 283—285°, which have IR spectrum and *Rf* value on silica gel thin-layer chromatography (TLC) identical with those of camelliagenin A. No depression of the melting point was observed upon admixture with an authentic sample.

The third fraction, on recrystallization from methanol, yielded needles, mp 286—289°, which are identical with barringtogenol C from IR spectrum, *Rf* value on silica gel TLC and mixed melting point.

Alkaline Hydrolysis of I——A methanol solution of I (224 mg) was refluxed with 10% aq. potassium hydroxide (0.7 ml) for 2 hr. The reaction mixture was poured into excess water. The solid precipitate was collected by filtration and recrystallized from methanol to yield fine needles, mp 283—285°, IR spectrum and *Rf* value on silica gel TLC identical with those of camelliagenin A. Their mixed melting point show no depression.

The filtrate was acidified by hydrochloric acid and extracted with ether to yield a yellow solid (60 mg). Recrystallization from water gave colorless plates, mp 132—133°, NMR and IR spectra of which are superimposable with authentic cinnamic acid, and the melting point showed no depression upon admixture with the authentic sample.

Acetylation of I——The first fraction (51 mg) and acetic anhydride (0.5 ml) in pyridine (1 ml) were kept overnight at room temperature to give, by usual work-up, an amorphous acetate (52 mg). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1733, 1630, 1240, 770, 715. NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$: 0.87 (6H, singlet), 0.93 (3H, singlet), 0.97 (6H, singlet), 1.04 (3H, singlet), 1.26 (3H, singlet), 2.04 (9H, broad singlet), 3.85 (2H, broad singlet), 4.51 (1H, broad triplet, J=7 cps), 5.1—5.8 (3H, unresolved multiplet), 6.43 (1H, doublet, J=16 cps), 7.47 (5H, multiplet), 7.73 (1H, doublet, J=16 cps).

Camelliagenin A Triacetate (VI)——Camelliagenin A (94 mg) and acetic anhydride (0.5 ml) in pyridine (1.5 ml) were kept overnight at room temperature. The reaction mixture was poured into water (20 ml), extracted with chloroform and washed successively with 2 N hydrochloric acid, aq. sodium bicarbonate solution and water. Evaporation of the solvent after drying, gave glassy residue (126 mg), which was purified by chromatography and crystallization from methanol to give colorless plates, mp 207—209°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3520, 1735, 1250. NMR $\delta_{\text{ppm}}^{\text{CDCl}_3}$: 0.87 (6H, singlet), 0.92 (3H, singlet), 0.93 (3H, singlet), 0.96 (3H, singlet), 1.02 (3H, singlet), 1.44 (3H, singlet), 2.03 (9H, singlet), 3.71 (2H, broad singlet), 4.26 (1H, multiplet), 4.49 (1H, broad triplet, J=7 cps), 5.30 (1H, quartet, J=6.5, 11.5 cps), 5.31 (1H, multiplet).

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[5] All melting points were not corrected. In NMR spectra, chemical shifts were measured from the signal of tetramethylsilane as an internal reference.