of mp 83—85°, $[\alpha]_D^{20}$ +33.9° (c=4.0, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{36}O_6$: C, 67.36; H, 7.00. Found: C, 67.22; H, 6.98.

Similar treatment of Xb afforded XIb as needles of mp 89—91°, $[\alpha]_D^{20}$ −79.4° (c=5.2, $CHCl_3$), in the same yield. *Anal.* Found: C, 67.22; H, 6.98.

Methyl 2,3-Di-O-benzyl-α(and β)-L-*arabino*-pentodialdo-1,4-furanoside (IIIa and IIIb)——(i) To a solution of 6.27 g of VIIa and 18.7 g of dicyclohexylcarbodiimide in 91 ml of dimethyl sulfoxide was added 9.1 ml of 1M H_3PO_4 solution in dimethyl sulfoxide, and the mixture was allowed to stand at room temperature for 20 hr. The reaction mixture was diluted with cold water and, after standing for a few minutes, extracted with ether. The H_2O layer was also extracted several times with ether. The combined extracts were washed with H_2O, dried over anhyd. Na_2SO_4, evaporated *in vacuo* to give a thick syrup which was chromatographed on 180 g of silica gel. The fraction eluted with benzene–AcOEt (97:3 v/v) afforded 4.9 g (79%) of IIIa as a syrup which formed a semicarbazone of mp 124°, $[\alpha]_D^{20}$ −46.6° (c=1.1, $CHCl_3$). Similar treatment of VIIb afforded the β-anomer (IIIb) in 83% yield. IIIb formed a semicarbazone of mp 154—156°, $[\alpha]_D^{20}$ +20.1° (c=2.1, $CHCl_3$), and a 2,4-dinitrophenylhydrazone of mp 122—123°. (ii) To a solution of 1 g of XIa dissolved in 15 ml of dry benzene, 1.58 g of $Pb(OAc)_4$ was added in small portions with stirring. After standing at 50—55° for 15 min, excess of the reagent was decomposed by the addition of a small amount of ethylene glycol, and the mixture was evaporated *in vacuo*, giving the same IIIa which was analogously characterized as a semicarbazone of mp 124°. Similar oxidation of XIb yielded the same IIIb, and yields in both cases were almost quantitative.

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Isolation of A_1-Barrigenol from *Camellia Sasanqua*

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In a previous paper,[2] we have reported the isolation of eight sapogenols from the seeds of *Camellia Sasanqua* Thunb., camelliagenin A,[3] B,[3] C,[3] D, E, barringtogenol C,[4] theasapogenol A[5] and another unknown sapogenol, and assigned the structures for camelliagenins D and E.[6] We now wish to report the identity of the eighth sapogenol with A_1-barrigenol.[8,9]

Silica gel chromatography of the crude sapogenol mixture, followed by a repeated recrystallization, afforded a compound I, $C_{30}H_{50}O_5$, mp 271—274°. Acetylation of I with acetic anhydride in pyridine yielded a tetraacetate II, $C_{38}H_{58}O_9$, mp 190—193°, ν^{KBr} 1738 cm^{-1}. NMR spectrum of II in deuterochloroform exhibited seven singlets due to tertiary methyl groups at 0.85, 0.87, 0.93, 0.96, 1.00, 1.00, 1.53 ppm together with signals at 3.70 (1H, d,

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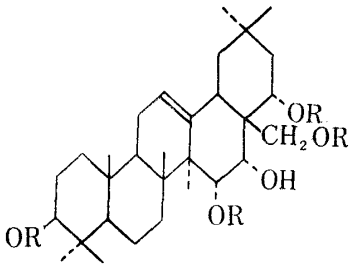

I : R=H
II : R=Ac

J=11.5), 3.99 (1H, d, J=11.5), 4.22 (1H, d, J=4), 4.48 (1H, t, J=7.5), 5.11 (1H, d, J=4), 5.33 (1H, q, J=6.5, 11.5), 5.43 ppm (1H, m).

The IR spectra of I and II and the NMR spectrum of II are superimposable on those of A_1-barrigenol and its tetraacetate,[9] respectively. Their identity was further confirmed by comparison of *Rf* values in TLC and the respective mixed melting point determinations with the authentic A_1-barrigenol and its tetraacetate.

Experimental

Isolation of the Sapogenol——The crude sasanqua saponins (10 g) obtained by Aoyama's procedure,[10] was heated under reflux in 83% MeOH (180 ml) with conc. hydrochloric acid (12 ml) for 10 hr. The reaction mixture was poured into excess water and the brown powder obtained (4.8 g) by filtration was again heated under reflux in 83% MeOH (120 ml) containing 3 g KOH for 2 hr and poured into excess water. Dark brown powder (2.1 g) formed was filtered, dried and chromatographed on 90 g silica gel to give the following fractions:

Fraction No.	Solvent ($CHCl_3$:MeOH)	Vol. (ml)	Compounds obtained	Yield (mg)
1	20:1	140	Camelliagenin A and B	467
2	20:1	60	A_1-Barrigenol	32
3	20:1	100	Camelliagenin D and Barringtogenol C	86
4	10:1	100	Camelliagenin E	136
5	10:1	250	Theasapogenol A	100

The second fraction was purified by further chromatography on silica gel and recrystallization from acetone to give fine needles, mp 271—274° (14 mg). IR spectrum was superimposable with that of A_1-barrigenol[9] and *Rf* value (0.74) on silica gel TLC (solvent: $CHCl_3$–MeOH 10:1) was same as that of A_1-barrigenol. They exhibited no depression of melting point upon admixture.

Tetraacetyl-A_1-barrigenol——The sapogenin (65 mg) was allowed to stand for 2 days in 1 ml pyridine with 0.5 ml acetic anhydride at room temperature. The reaction mixture was poured into water containing dil. hydrochloric acid, extracted with $CHCl_3$, and washed successively with satd. sodium bicarbonate soln. and water. Purification of crude product (81 mg, oil) by silica gel chromatography and recrystallization from aq. MeOH gave colorless scales, mp 190—193°, which showed no melting point depression with authentic tetraacetyl-A_1-barrigenol (195—197°) Its IR and NMR spectra were superimposable with those of the authentic specimen, respectively, and the *Rf* value in TLC was same as that of the authentic sample.

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