Phytosterols and Triterpenes in the Roots of the "Kidney Bean" (*Phaseolus vulgaris* L.)[1]

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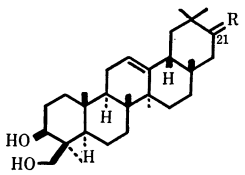
In connection with the studies of hatching substances for soybean cyst nematodes, the neutral fraction of the roots of the "kidney bean" (*Phaseolus vulgaris* L.) has been examined. It was found that phytosterols and triterpenes exist in the roots of plants.

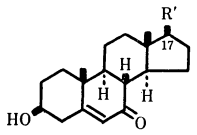
Recently the hatching of eggs and larval emergence from the soybean cyst nematode (*Heterodera glycines*) has been found to be stimulated by root diffusates of several host plants.[2] Among the host plants, soybean (*Glycine Max* Merrill) has been studied extensively and reported to contain γ-sitoserol (clionasterol), stigmasterol, and soyasapogenols-A~E[3,4] as its neutral components. On the other hand, root diffusates of the "kidney bean" (*Phaseolus vulgaris* L.) are known to be more active for the hatching,[2] but no paper on the components of this plant seems to have been published. Accordingly, in connection with studies on the relevant hatching substances, we have examined the neutral fraction of the "kidney bean".

The dried powdered roots of the "kidney bean" were percolated with water and then extracted with methanol, after removal of the aqueous solution which was active for the hatching. The methanol extracts were subjected to column and thin layer chromatography as well as fractional recrystallization to isolate and identify triterpenes and phytosterols. The results deserve some comment.

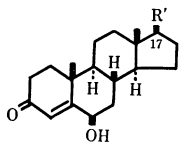
(1) Compound II, $C_{32}H_{48}O_5$, was presumed to be a 21-dehydro derivative of I on the basis of mass, IR, and NMR spectra. In fact, compound I was transformed *via* its acetonide to 21-dehydrosoyasapogenol-B,



I R=·····OH, −H
II R=O



IV R′=R¹
V R′=R²



VI R =R¹
VII R′=R²

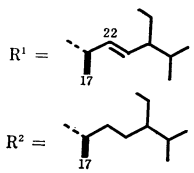


Table 1. Triterpenes and phytosterols[a] in the roots of the "kidney bean"

	Compound	Mp (°C)	Yield (%)	$[\alpha]_D$	Ref.
I	Soyasapogenol-B[b]	259—261	0.005	+89°	3
II	Soyasapogenol-E	249—250	0.0013	+34°	4
III	Stigmast-5-en-3β-ol (β-sitosterol)	141—142	0.003		
IV	Stigmasta-5,22-dien-3β-ol-7-one	160—162[c]	0.00024	−78°	5, 6a
V	Stigmast-5-en-3β-ol-7-one	128—130[c]	0.00012	−85°	7
VI	Stigmasta-4,22-dien-6β-ol-3-one	210—212[d]	0.00014	+ 8°	
VII	Stigmast-4-en-6β-ol-3-one	211—213[d]	0.00014	+29°	

a) For nomenclature, see, *J. Org. Chem.*, **34**, 1517 (1969).
b) The authors are indebted to Professors C. Djerassi and O. Jeger for their kind donation of the sample.
c) These compounds have been obtained by synthesis (Ref. 5—7), but do not appear to have been isolated from natural sources.
d) New compounds.

1) Part I of Constituents from the "Kindney Bean."
2) M. Tsutsumi and K. Sakurai, *Rev. Plant Protec. Rec.*, **2**, 128 (1962).
3) a) E. Ochiai, K. Tsuda, and S. Kitagawa, *Ber.*, **70**, 2083 (1936). b) A. Meyer, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **33**, 672, 687, 1835 (1950). c) H. G. Smith and F. S. Spring, *Tetrahedron*, **4**, 111 (1958).
4) D. Willner, B. Gestetner, D. Lavie, Y. Birk, and A. Bondi, *J. Chem. Soc.*, **1964**, 5884.
5) O. Linsert, *Z. Phys. Chem.*, **241**, 125 (1936).
6) It is known that steroids with Δ^5-3-ol structure are partially oxidized by passing oxygen into the colloidal suspension to give those with Δ^5-3,7-diol and/or Δ^5-3-ol-7-one. However, no examples of the formation of steroids with Δ^4-6β-ol-3-one structure under the conditions have been reported. *Cf.* a) S. Bergstrom and O. Wintersteiner, *J. Biol. Chem.*, **141**, 597 (1941); b) S. Bergstrom, *ibid.*, **145**, 327 (1942).
7) W. Wunderlich, *Z. Phys. Chem.*, **241**, 116 (1936).

mp 247—248°C and $[\alpha]_D$+32°, which was identical with II. As a compound corresponding to the above structure, Willner *et al.*[4] obtained a triterpene, soyasapogenol-E, from soybean. While their compound is amorphous and its crystalline derivatives, acetonide and diacetate, differ slightly from ours in physical constants, we consider that II should be assigned soyasapogenol-E.

(2) Occurrence of phytosterols IV, V, VI, and VII is a noticeable fact in the sense that these compounds appear to have been isolated newly from natural source. The latter two compounds, hitherto unknown, involve 6β-hydroxy-Δ^4-3-ketone structure, and the former two contain a ketonic group at C_7.[8] In view of the fact that no detectable amount of stigmast-5-en-3β-ol (VIII, stigmasterol) could be found, it would be certain that these four sterols, at least IV and VI, are not artifacts formed by air oxidation[6] or microbiological oxidation[9] during the course of isolation.

Experimental

The melting points are uncorrected. The optical rotations, UV and IR spectra were measured in chloroform, 99% ethanol, and Nujol, respectively, unless otherwise stated. The NMR spectra were recorded at 60 and/or 100 MHz in deuterochloroform, TMS being used as an internal standard, unless otherwise stated. The abbreviations "s, d, t, q, br, and m" in the NMR spectra denote "singlet, doublet, triplet, quartet, broad, and multiplet," respectively. Thin layer chromatography (tlc) was carried out on silica gel (Merck G), using benzene-ether 5: 1 (solvent A) or chloroform-ether 1: 1 (B). Column chromatography was carried out over silica gel (Mallinckrodt A.R. 100 mesh).

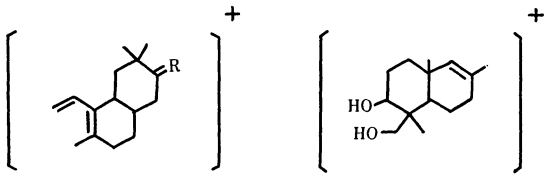
Extraction of Roots of the "Kidney Bean" (Phaseolus vulugaris L.). The dried, powdered roots (22 kg) were percolated with water (3×100 *l*) and, after removal of the aqueous solution, extracted with methanol (2×125 *l*). The extracts were concentrated to about 20 *l in vacuo* and extracted continuously with chloroform to give resinous material (124 g), which was treated with *n*-hexane. The hexane-insoluble materials (97 g) were redissolved in chloroform and washed with 2N sodium hydroxide solution and then 1N hydrochloric acid. The neutral substances (16 g) thus obtained were chromatographed over a mixture of silica gel (250 g) and celite (100 g), using *n*-hexane, benzene, chloroform, and ether, successively. Elution with benzene gave an oily, complex mixture (3.3 g, probably esters), which was not examined further. Elution with chloroform afforded phytosterols (2.2 g) and a mixture of ketones (4.4 g), and that with ether crude soyasapogenol-B (4.3 g).

β-Sitosterol (III). The phytosterol mixture was crystallized from methanol to give crude β-sitosterol (0.90 g), mp 126—130°C, which on recrystallization from methanol afforded III (0.54 g), colorless plates, mp 141—142°C in pure state.

The mother liquors were treated with bromine to check the presence of stigmasterol (VIII), but no crystalline substance corresponding to its tetrabromide[10] was obtained.

Soyasapogenol-B (I). The crude soyasapogenol-B was recrystallized repeatedly from methanol to give I (1.1 g), mp 253—254°C, in pure state, which gave green color by the Lieberman-Burchards test. This was recrystallized from methanol to yield an analytical sample (0.99 g), mp 259—261°C and $[\alpha]_D$+89° (*cf.* Ref. 3c); mass, *m/e* 458 (M^+), 234 (base peak, IX), 224 (X), and 219 (IX−Me);[11] IR, ν_{max} 3300, 1388, 1379, and 845 cm^{-1}; NMR (deuteropyridine), δ 0.99, 1.08, and 1.23 (each 3H, s), 1.28 (6H, s), 1.56 (3H, s), and 3.73 (3H, br m). This compound was identical (mixed mp, tlc, mass, IR, and NMR spectra) with authentic specimens donated by Professors C. Djerassi[12] and O. Jeger.[3b]

Found: C, 78.36; H, 10.94%. Calcd for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99%.



IX R=OH, H
XI R=O

X

Compound I (51 mg) was acetylated with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at room temperature for 24 hr to give the triacetate (Ia, 55 mg), colorless prisms, mp 176—177°C from methanol and $[\alpha]_D$+80° (*cf.* Ref. 3c); mass, *m/e* 584 (M^+), 276 and 261; IR, ν_{max} 1724 cm^{-1}; NMR, δ 0.83 and 0.91 (each 3H, s), 1.00 (9H, s), 1.04 and 1.16 (each 3H, s), 2.03 (6H, s, OAc), 2.06 (3H, s, OAc), 4.14 and 4.38 (each 1H, ABq J=12 Hz, CH_2OAc), 4.62 (2H, br m, 2 CH-OAc) and 5.25 (1H, br t J=4.5 Hz, H at C_{12}) (*cf.* Ref. 13).

Found: C, 74.02; H, 9.40%. Calcd for $C_{36}H_{56}O_6$: C, 73.90; H, 9.65%.

Soyasapogenol-E (II). The mixture of ketones was rechromatographed over a mixture of silica gel (80 g) and celite (20 g) using chloroform as solvent, and separated into four fractions. The first fraction gave a brown-red oil (1.3 g, probably esters), which was not examined further. The second yielded a mixture of ketones (0.97 g), which was submitted to separation. The next fraction afforded crude soyasapogenol-E (1.7 g), and the last fraction was proved to contain I (0.17 g) as a main component by tlc (solvent B).

Crude soyasapogenol-E was recrystallized from methanol to give colorless needles (260 mg), mp 233—234°C, which on recrystallizations from methanol afforded an analytical sample of II (80 mg), mp 249—250°C (amorphous[4]) and $[\alpha]_D$ +34°; mass,[11] *m/e* 456 (M^+) and 232 (base peak, XI); IR, ν_{max} 1705 cm^{-1}; NMR, δ 0.86, 0.89, and 0.92 (each 3H, s), 0.98 (6H, s), 1.20 and 1.23 (each 3H, s), 3.36 (2H, br CH_2-OH), 4.33 (1H, br CHOH), and 5.29 (1H, br H at C_{12}) (*cf.* Ref. 4).

Found: C, 78.93; H, 10.76%. Calcd for $C_{30}H_{48}O_3$: C, 78.89; H, 10.51%.

The second crops (70 mg), obtained from the mother liquor on recrystallizations of II, gave the diacetate (IIa, 50 mg),

8) Tremulone and antheridiol have been reported as the only natural sterols containing a ketonic group at C_7;
a) R. A. Abramovitch and R. G. Micetich, *Can. J. Chem.*, **40**, 2017 (1962); b) J. A. Edwards, J. S. Mills, J. Sundeen, and J. H. Fried, *J. Amer. Chem. Soc.*, **91**, 1248 (1969).

9) Ch. Tamm, *Angew. Chem.*, **74**, 225 (1962).

10) A. Windaus and A. Hauth, *Ber.*, **39**, 4378 (1906).

11) *Cf.*, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3688 (1963).

12) E. D. Walter, E. M. Bickoff, C. R. Thompson, C. H. Robinson, and C. Djerassi, *ibid.*, **77**, 4936 (1955).

13) M. Shamma, R. E. Glick, and R. O. Mumma, *J. Org. Chem.*, **27**, 4512 (1962).

mp 243—244°C and $[\alpha]_D+21°$ (*cf.* Ref. 4); mass, *m/e* 540 (M^+) and 232; IR, ν_{max} 1706, 1740, and 1745 cm^{-1} (*cf.* Ref. 4); NMR, δ 0.87 (3H, s), 0.98, 0.99, and 1.01 (total 15H, each s), 1.20 (3H, s), 2.01 and 2.03 (each 3H, s, OAc), 4.16 and 4.32 (each 1H, ABq $J=12$ Hz, CH_2OAc), 4.52 (1H, dd $J=$ 7.5 and 2.5 Hz, CHOAc), and 5.26 (1H, br d $J=$ 5 Hz, H at C_{12}) (*cf.* Ref. 4). Compound IIa was reconverted into II by hydrolysis under the same conditions as those[4] reported.

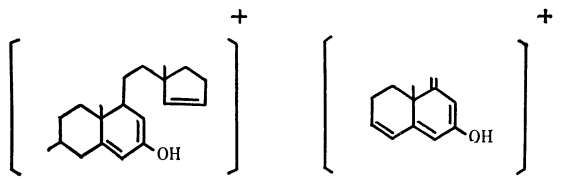
Found: C, 75.08; H, 9.72%. Calcd for $C_{34}H_{52}O_5$: C, 75.51; H, 9.69%.

Soyasapogenol-B (I, 786 mg) dissolved in a 4: 1 mixture (10 m*l*) of chloroform and ether was passed through a column of silica gel (Wakogel Q-23), freshly washed successively with methanol, acetone, and *n*-hexane, using *n*-hexane containing 8% acetone. The eluate was recrystallized from methanol to give the acetonide (Ib, 500 mg), mp 177—178°C and $[\alpha]_D+111°$ (*cf.* Ref. 3c); IR, ν_{max} 3430, 1150, 1100, 1080, 1052, and 1025 cm^{-1}; NMR, δ 0.88, 0.90, 0.99, 1.03, 1.11, 1.15, 1.20, 1.35, and 1.40 (each 3H, s), 3.35 (2H, br), 4.03 (1H, br d $J=10$ Hz), and 5.25 (1H, br).

Compound Ib (450 mg) in pyridine (10 m*l*) was oxidized with chromic anhydride (530 mg) in pyridine (4 m*l*) at room temperature for 20 hr under stirring. The product was treated with water and ether, and the ether solution afforded amorphous keto-acetonide (495 mg). This was converted into crystalline glycol on heating with methanol, which was recrystallized from methanol to give II (300 mg), mp 246—248°C and $[\alpha]_D+32°$. This compound and its diacetate, mp 243—244°C and $[\alpha]_D+24°$, were identical with the corresponding natural specimens.

Stigmasta-5,22-dien-3β-ol-7-one (IV) and Stigmast-5-en-3β-ol-7-one (V). A mixture of ketones (970 mg), the second fraction obtained on rechromatography, was triturated with methanol to give crystalline material (340 mg), which was separated into two fractions (150 and 65 mg) by preparative tlc (chloroform: ether 3 : 1). Recrystallization of the former from ethanol afforded crystal A (IV and V, 80 mg), and that of the latter crystal B (VI and VII, 50 mg), each showing a single spot on tlc (solvent A).

Crystal A had mp 144—146°C and $[\alpha]_D-80°$; mass, *m/e* 428 (M^+), 426 (M^+), 410, 408, 396, 383, 314, 287 (base peak, XII), and 174 (XIII);[14] UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 3360 and 1675 cm^{-1}; NMR, δ 0.69 (s, 18-Me), 0.74, 0.78, 0.84, 0.88, 0.96, and 1.07 (each sharp), 1.19 (s, 19-Me), 3.58 (1H, br CH–OH), 5.06 (*ca.* 1.5H, br $W_H=12$ Hz, 2H at C_{22} and C_{23}), and 5.64 (1H, s, H at C_6).



XII XIII

XIV XII$-H_2O$

Crystal A (50 mg) was converted into the acetate, which on preparative tlc (benzene: chloroform 2 : 1) followed by trituration with acetone afforded a sample (35 mg) showing a single spot, mp 176—179°C and $[\alpha]_D-102°$; mass, *m/e* 410 (M^+–AcOH), 408 (M^+–AcOH), 396, 365, and 269 (base peak, XIV) and 174; UV, λ_{max} 238 mμ (ε 15000); IR, ν_{max} 1740 and 1670 cm^{-1}; NMR, δ 0.68 (3H, s, 18-Me), 0.75, 0.79, 0.86, 0.89, 0.97, and 1.08 (each sharp), 1.18 (3H, s, 19-Me), 2.00 (3H, s, OAc), 4.68 (1H, br CH-OAc), 5.08 (1.3H, t $J=6$ Hz, 2H at C_{22} and C_{23}), and 5.68 (1H, s, H at C_6).

Attempted purifications of crystal A [preparative tlc over silica gel (benzene: *n*-hexane 1 : 1), over silica gel containing silver nitrate, or over alumina or bromination followed by debromination] failed and only repeated recrystallization from methanol effected isolation of IV (10 mg from 80 mg of A) in pure state, which had mp 138—140°C and, after drying, 160—162°C and $[\alpha]_D-78°$; mass, *m/e* 426 (M^+), 408, 383, 287 (XII), and 269 (XIV); UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 3360 and 1675 cm^{-1}; NMR, δ 0.69 (s, 18-Me), 0.83 (t $J=7$ Hz, 29-Me), 0.83 (d $J=6$ Hz, 26- and 27-Me), 1.00 (d $J=7$ Hz, 21-Me), 1.19 (s, 19-Me), 3.60 (1H, br CH–OH), 5.08 (2H, br t $J=5$ Hz, 2H at C_{22} and C_{23}), and 5.65 (1H, s, H at C_6). This compound was identified as IV by direct comparison with an authentic sample.

Found: C, 81.54; H, 10.84%. Calcd for $C_{29}H_{46}O_2$: C, 81.63; H, 10.87%.

A 2: 1 mixture of synthetic samples IV and V had mp 144—146°C and $[\alpha]_D-81°$, and that of the respective acetates mp 176—179°C and $[\alpha]_D-101°$. The former and the latter mixtures revealed mass, UV, IR, and NMR spectra, superimposable over the corresponding spectra of crystal A and its acetate, respectively.

Stigmasterol acetate (VIIIa) and β-sitosterol acetate (IIIa) were oxidized[8a] to give the respective 7-oxo derivatives (IVa), mp 183—184°C (*cf.* Refs. 5 and 6a) and $[\alpha]_D-103°$ (*cf.* Ref. 6a); mass, *m/e* 408, 365, 297, and 269 (base peak); UV, λ_{max} 238 mμ (ε 15000); IR, ν_{max} 1740 and 1670 cm^{-1}; NMR, δ 0.69 (3H, s, 19-Me), 0.83 (t $J=7$ Hz, 29-Me), 0.83 (d $J=$ 7 Hz, 26- and 27-Me), 1.02 (d $J=7$ Hz, 21-Me), 1.21 (s, 19-Me), 2.02 (3H, s, OAc), 4.63 (1H, br CH–OAc), 5.02 (2H, br t $J=5.5$ Hz, 2H at C_{22} and C_{23}), and 5.61 (1H, s, H at C_6), and (Va), mp 174—176°C and $[\alpha]_D-95°$ (*cf.* Ref. 7); mass, *m/e* 410, 396, and 174 (base peak); UV, λ_{max} 238 mμ (ε 15000); IR, ν_{max} 1740 and 1670 cm^{-1}; NMR, δ 0.69 (3H, s, 18-Me), 0.86 (d $J=6$ Hz, 21-, 26-, and 27-Me), 0.88 (t $J=$ 7 Hz, 29-Me), 1.22 (s, 19-Me), 2.06 (3H, s, OAc), 4.67 (1H, br CH–OAc), and 5.70 (1H, s, H at C_6).

The resulting 7-oxo-compounds (IVa and Va) were saponified[6a] to yield the respective alcohols IV and V. Compound IV had mp 138—140°C (from methanol) and mp 158—160°C (after drying at 90°C) (154°C[5] and 130—135°C[6a]) and showed $[\alpha]_D-78°$ ($-113°$[5]). Compound V had mp 128—130°C and $[\alpha]_D-85°$ (144—145°C and $-116°$[7]); mass, *m/e* 428, 410, 396, and 174 (base peak); UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 3380 and 1675 cm^{-1}; NMR, δ 0.68 (3H, s, 18-Me), 0.82 (d $J=6$ Hz, 21-, 26-, and 27-Me), 0.85 (t $J=7$ Hz, 29-Me), 1.19 (s, 19-Me), 3.63 (1H, br CH–OH), and 5.70 (1H, s, H at C_6).

Stigmasta-4,22-dien-6β-ol-3-one (VI) and Stigmast-4-en-6β-ol-3-one (VII). Crystal B (50 mg) had mp 210—213°C and $[\alpha]_D+16°$; mass, *m/e* 428 (M^+) and 426 (M^+); UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 3400, 1680, 1035, and 1010 cm^{-1}; NMR, δ 0.76 (s, 18-Me), 0.81, 0.84, 0.87, 0.91, 0.98, and 1.09 (each sharp), 1.39 (3H, s, 19-Me), 4.34 (1H, br s $W_H=5$ Hz, CH–OH), 5.12 (1H, br t $J=5$ Hz, 2H at C_{22} and C_{23}), and 5.80 (1H, s, H at C_4). This crysatal resisted further purification.

Treatment of crystal B (43 mg) with acetic anhydride (0.4 m*l*) and pyridine (0.4 m*l*) gave its acetate, amorphous, showing $[\alpha]_D+21°$; mass, *m/e* 470, 468, 428, 426, and 149 (base peak); UV, λ_{max} 237 mμ (ε 15000); IR, ν_{max} 1740 and 1680 cm^{-1}; NMR, δ 0.76 (s, 18-Me), 0.84, 0.88, 0.90, 0.98, and 1.09 (each sharp), 1.28 (3H, s, 19-Me), 2.02 (3H,

14) S. Sasaki, "Interpretation of Mass Spectra," Hirokawa Publishing Co., Tokyo (1965), p. 172.

s, OAc), 5.09 (1H, br t J=5 Hz, 2H at C_{22} and C_{23}), 5.40 (1H, br t J=3 Hz, CH–OAc), and 5.91 (1H, s, H at C_4) (*cf.*, NMR spectrum[15] of cholest-4-en-6β-ol-3-one).

These spectral data suggest crystal B to be a 1:1 mixture of VI and VII. In fact, a 1:1 mixture of synthetic samples of VI and VII, had mp 209—212°C and $[\alpha]_D$+15°, and the corresponding acetate, amorphous, showed $[\alpha]_D$+23°. These synthetic alcohol and acetate mixtures exhibited the mass, UV, IR, and NMR spectra superimposable over the corresponding spectra of crystal B and its acetate, respectively.

Preparation of VI and VII. To a solution of stigmasterol (VIII, 2.40 g) in benzene (11 m*l*) and acetic acid (10 m*l*) was added sodium bichromate (1.5 g as hydrate) in acetic acid (5 m*l*) at room temperature (*cf.* Ref. 16). The mixture was stirred at room temperature overnight and, after addition of ethanol (*ca.* 10 m*l*), diluted with water (50 m*l*), and then extracted with ether (50 m*l*). The ether solution was washed with a 5% sodium bicarbonate solution and then with water, dried and evaporated to leave amorphous residue. This was purified by chromatography over silica gel (100 g), using a 10:1 mixture of chloroform and ether, and it gave a crude sample of VI (1.1 g), mp 198—203°C, showing a single spot on tlc. Recrystallization from ethanol afforded a pure sample, mp 210—212°C and $[\alpha]_D$+8°; mass, *m/e* 426; UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 1680 and 1620 cm^{-1}; NMR, δ 0.77 (3H, s, 18-Me), 1.39 (s, 19-Me), 4.33 (1H, br s W_H=6 Hz, CH–OH), 5.11 (2H, br t J=5 Hz, 2H at C_{22} and C_{23}), and 5.79 (1H, s, H at C_4).

Found: C, 81.25; H, 10.99%. Calcd for $C_{29}H_{46}O_2$; C, 81.63; H, 10.84%.

Compound VI was converted into the acetate (VIa), mp 107—109°C (from *n*-hexane) and $[\alpha]_D$+16°; mass, *m/e* 468, 426, and 149 (base peak); UV, λ_{max} 238 mμ (ε 15,000); IR, ν_{max} 1740, 1680, and 1620 cm^{-1}; NMR, δ 0.77 (3H, s, 18-Me), 1.29 (s, 19-Me), 2.02 (3H, s, OAc), 5.12 (2H, br t J=5 Hz, 2H at C_{22} and C_{23}), 5.40 (1H, br s W_H=5 Hz, CH–OAc), and 5.90 (1H, s, H at C_4).

Found: C, 79.50; H, 10.15%. Calcd for $C_{31}H_{48}O_3$; C, 79.43; H, 10.32%.

Compound VII (1.49 g) was likewise obtained from β-sitosterol (III, 2.2 g) in crude state and had mp 188—194°C. Recrystallization from ethanol gave a pure sample, mp 211—213°C and $[\alpha]_D$+29°; mass, *m/e* 428; UV, λ_{max} 238 mμ (ε 16000); IR, ν_{max} 1680 and 1620 cm^{-1}; NMR, δ 0.76 (3H, s, 18-Me), 1.39 (s, 19-Me), 4.31 (1H, br s W_H=6 Hz, CH–OH), and 5.79 (1H, s, H at C_4).

Found: C, 81.48; H, 11.37%. Calcd for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29%.

An acetate (VIIa) of VII was obtained only in amorphous state and showed $[\alpha]_D$+27°; mass, *m/e* 470, 428, and 149; UV, λ_{max} 238 mμ (ε 15000); IR, ν_{max} 1740, 1680, and 1620 cm^{-1}, NMR, δ 0.77 (3H, s, 18-Me), 1.29 (s, 19-Me), 2.02 (3H, s, OAc), 5.39 (1H, br s W_H=5 Hz, CH–OAc), and 5.90 (1H, s, H at C_4).

Found: C, 79.35; H, 10.50%. Calcd for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71%.

15) K. Tori and K. Kuriyama, *Chem. Ind.*, **1963**, 1525.
16) L. F. Fieser, *J. Amer. Chem. Soc.*, **75**, 4377 (1953).