Constituents of *Prunus zippeliana* Leaves and Branches

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Received January 27, 1993

The following substances were identified in the fresh leaves and branches of *Prunus zippeliana* MIQ.: 22-dehydroclerosteryl acetate, stigmasteryl acetate, β-sitosterol, stigmasterol, clerosterol, 22-dehydroclerosterol, β-sitosterol and stigmasterol 3-*O*-β-D-glucopyranoside, ursolic acid, oleanolic acid, 2α-hydroxyursolic acid, tormentic acid, methyl linolate, phytol, prunasin, *dl*-mandelic acid, kaempferol 3-*O*-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside] and *d*-mandelic acid β-D-glucopyranoside.

Worthy of note is that 24α-ethylsterols (β-sitosterol and stigmasterol) and 24β-ethylsterols (clerosterol and 22-dehydroclerosterol) were obtained together from the leaves of a higher plant.

Keywords *Prunus zippeliana*; 24-ethylsterol; mandelic acid glucoside; 2α-hydroxy ursolic acid; prunasin; mandelic acid

The leaves of *Prunus zippeliana* MIQ. (Rosaceae) are used in Japanese folk medicement, but prunasin was the only known chemical component.[1] Here, we report the separation and identification of seventeen compounds including 24β-ethyl-25(27)-dehydrocholesterols from the fresh leaves, and seven compounds from the fresh branches of this plant.

The methanol extract of fresh leaves of *P. zippeliana* was dissolved in water and successively extracted with ether and *n*-butanol. From the ether extract three types of sterol mixture (acetyl, free and glucosyl sterols) were obtained, and from the mixture of acetyl sterols, two compounds [**1** (main, 65%) and **2** (minor, 35%)] were isolated by high-performance liquid chromatography (HPLC).

The main component of steryl acetate **1** ($C_{31}H_{48}O_2$, mp 149 °C, $[\alpha]_D$ −41°) showed strong ion peaks at *m/z* 392 $[M-CH_3COOH]^+$ and 253 $[M-CH_3COOH-C_{10}H_{19}$ (side chain)$]^+$ in the electron impact mass spectrum (EI-MS), indicating that **1** was C_{29}-steryl acetate with one double bond in the sterol skeleton, and two double bonds in the side chain at C-17. The proton nuclear magnetic resonance (^{1}H-NMR) and the carbon-13 (^{13}C)-NMR spectral data of **1** agreed with the presence of $\Delta^{5,22,25(27),2)}$ and the ^{1}H-chemical shift of signals due to the side chain [δ 0.83 (3H, d, J=7.3 Hz, H-21), 1.65 (3H, s, H-26), 4.70 (2H, br s, H-27), 5.17, 5.25 (each 1H, dd, J=15.2, 7.4 Hz, H-22, 23)] suggested that **1** possessed the 24β-ethyl group as previously observed for $\Delta^{22,25(27)}$-cholesterol.[2b] From these data, **1** was concluded to be 22-dehydroclerosteryl acetate (24β-ethyl-22,25(27)-bis-dehydrocholesteryl acetate). This is the first example of natural occurrence of **1**.

A minor component of steryl acetate **2** was identified as stigmasteryl acetate (24α-ethyl-22-dehydrochoresteryl acetate) by comparison of ^{1}H-NMR with authentic sample.[2b] As mostly 24-ethylsterol, **2** possesses the 24α-ethyl group.

A mixture of free sterol showed two peaks by gas liquid chromatography (GLC) analysis, but examination of ^{1}H- and ^{13}C-NMR spectra, revealed it to be composed of four kinds of sterols. By comparison of ^{13}C-NMR spectrum of this sterol mixture with those of published data, it was concluded to be a mixture of stigmasterol (**3a**, 24α-ethyl-22-dehydrocholesterol, 34%),[2b] 22-dehydroclerosterol (**3b**, 24β-ethyl-22,25(27)-bis-dehydrocholesterol, 26%),[2a] β-sitosterol (**3c**, 24α-ethylcholesterol, 22%),[2b] and clerosterol (**3d**, 24β-ethyl-25(27)-dehydrocholesterol, 18%).[3] As reported by Akihisa *et al.*, in the ^{13}C-NMR spectrum of 24-ethylsterol mixture, the chemical shift and relative intensity of signals due to C-24 carbon was useful to identify and quantify of composed sterols.[2b] Though the coexistence of 24α-ethylsterol and 24β-ethylsterol have been reported in a few cases,[2b-d,f,g] it is interesting that these two types of sterol were found in leaves of a higher plant in the ratio of 14 : 11.

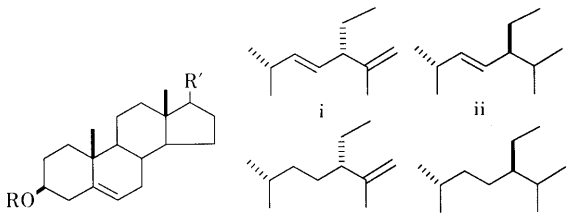
A mixture of glucosyl sterol was hydrolyzed to aglycone and glucose and the former was characterized as a mixture of **3c** (70%) and **3a** (30%) by GLC analysis and NMR. It was thus concluded to be a mixture of 3-*O*-β-D-glucopyranosides of β-sitosterol (**4c**) and stigmasterol (**4a**) in the ratio of 7 : 3.[2h]

As the triterpenoid fraction, two fractions were separated from the ether extract. From one, an equivalent mixture of ursolic acid (**5a**) and oleanolic acid (**5b**) was obtained as white powder. The other was shown to be a mixture of dihydroxy and trihydroxy triterpenoid acids, and these acids were isolated as acetates. The ^{1}H-NMR spectra of these two diacetates showed two typical proton signals which were assigned to 2β-H [δ 4.74, 4.75 (d, J=10.3 Hz)] and 3α-H [δ 5.05 (ddd, J=11.0, 10.3, 4.0 Hz)].[4] They were saponificated with 5% KOH in methanol, and saponificated compounds were identified as 2α-hydroxyursolic acid (**6**)[5] and tormentic acid (**7**, 2α,19α-dihydroxyursolic acid)[6] by ^{1}H- and ^{13}C-NMR analysis.[5b,6b,7] Although **5** was found in most *Prunus* species, this is the first report of the isolation of **6** and **7** in *Prunus* species.

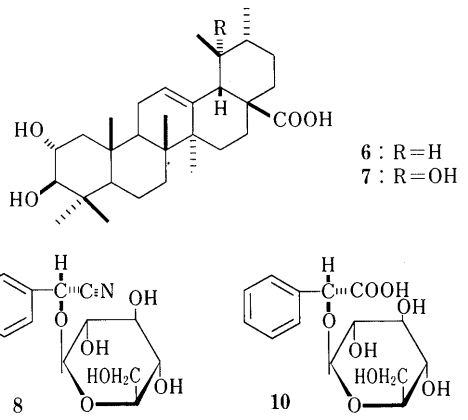
Two oily compounds were also obtained from the ether extract, and they were identified as methyl linolate and phytol by spectral data.[8]

From the *n*-butanol extract, prunasin (**8**)[9] was obtained as the main constituent of this leaf. Together with **8**, an aromatic compound was isolated as a minor constituent, and it was identified as *dl*-mandelic acid (**9**) by physical and spectral data.[10] Members of the genus *Prunus* are known to be particularly rich in flavonoids, and from this extract, kaempferol 3-*O*-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside][11] was obtained as the main flavonoid.

We also examined the constituents of methanol extract of the fresh branches of this plant, and compared the compounds found in the fresh leaves and the fresh branches.



1 : R=Ac, R′=i 2 : R=Ac, R′=ii 3a : R=H, R′=ii
3b : R=H, R′=i 3c : R=H, R′=iv 3d : R=H, R′=iii
4a : R=β-D-glc, R′=ii 4c : R=β-D-glc, R′=iv



6 : R=H
7 : R=OH

Chart 1

TABLE I. Sterol Constituents of *Prunus zippeliana* MIQ.

Type	Leaves	Branches
Acetyl sterol	**1** [24β(24*R*), 65%]	
	2 [24α(24*S*), 35%]	
Free sterol	**3a** [24α(24*S*), 34%]	
	3b [24β(24*R*), 26%]	
	3c [24α(24*R*), 22%]	**3c**
	3d [24β(24*S*), 18%]	
Glucosyl sterol	**4a** [24α(24*S*), 30%]	
	4c [24α(24*R*), 70%]	

The methanol extract of fresh branches was treated in almost the same way as that of the leaves. By repeated column chromatography, one free sterol and three triterpenoid acids were isolated from the ether extract, and three aromatic compounds were obtained from the ethyl acetate extract and *n*-butanol extract. The free sterol of the fresh branches was identified as **3c** by GLC analysis and NMR spectral data,[2b] and the three triterpenoid acid constituents were identified as **5a**, **6** and **7** by thin layer chromatography (TLC) and spectral data.

As a constituent of the aromatic compounds, **10** ($C_{14}H_{18}O_8$, an amorphous powder, $[\alpha]_D -126°$) was isolated together with **8** and **9**. Compound **10** was not hydrolyzed by alkaline and was identified as *d*-mandelic acid β-D-glucopyranoside [(2*R*)-2-(β-D-glucopyranosyl)-2-phenylacetic acid][12] by an examination of acid hydrolysis products, and ^{1}H- and ^{13}C-NMR spectral data. As far as we know, this is the first report of the isolation of **10** from nature. The coexistence of **8**, **9** and **10** strongly suggests a biosynthetic sequence of cyanogenic glucoside→mandelic acid glucoside→mandelic acid.

It is notable that acetyl, free and glucosyl sterols coexisted and that 24α- and 24β-ethylsterols coexisted in fresh leaves, but only free 24β-ethylsterol was isolated from the fresh bransches [Table I].

Further, it is interesting that the constituents of aromatic compounds were quite different between the fresh leaves and the fresh branches, the main constituent of the former being **8** and that of the latter being **9**.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were obtained with a JASCO A-103 IR spectrophotometer. Optical rotations were determined with a JASCO DIP-140 automatic polarimeter at 20—22 °C. MS were recorded with a JEOL JMS D-300 and HX-110 spectrometer. ^{1}H (100, 270 MHz) and ^{13}C (25, 67.5 MHz)-NMR spectra were taken with a JEOL FX-100 and a JEOL JNM GX-270 spectrometer. Column chromatography was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Silica Woelm TSC (silica gel for dry column, Woelm), aluminum oxide neutral (grade III, Woelm), Sephadex LH-20 (25—100 μm, Pharmacia) and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721) and spots were detected with anisaldehyde reagent. GLC was performed on a GC-380 (GL Sciences) with Chromosorb G AW DMCS coated with SE-30 (1.4%) at 260 °C in a flow of nitrogen (*ca.* 20 ml/min), and cholestane was used as int. reference. HPLC separation was carried out on a JASCO liquid chromatograph (880-system) with a JASCO 830 RI detector.

Extraction and Separation of Leaf Constituents *P. zippeliana* MIQ. was collected at Sata in Kagoshima prefecture of Japan in January, 1989. The fresh leaves (1.61 kg) were extracted with methanol (10 l) at room temperature. After evaporation of solvent, the residue (158 g) was successively partitioned into ether–water and *n*-butanol–water. Removal of the solvent from each phase gave the ether (36.2 g), the *n*-butanol (36.3 g) and the aqueous (85.5 g) extracts. The ether extract was chromatographed on silica gel (*n*-hexane : EtOAc = 9 : 1→1 : 1, EtOAc, EtOAc : MeOH = 9 : 1→7 : 3) which furnished eight fractions, and one fraction containing acetyl sterol was purified by alumina (*n*-hexane : benzene = 4 : 1) column chromatography to afford a phytol (40 mg) and acetyl sterol mixture. This mixture was subjected to HPLC [ODS-3251-D (Senshu pack), $CH_3CN : CHCl_3 = 9 : 1$] to give **1** (58 mg) and **2** (32 mg). From a fraction containing sterol, methyl linolate and a mixture of sterol (60 mg) were obtained by silica gel (*n*-hexane : EtOAc = 4 : 1) column chromatography. From a glucosyl sterol fraction, a mixture of **4a** and **4c** (20 mg) was obtained by silica gel ($CHCl_3$: MeOH = 4 : 1) column chromatography. A triterpenoid acid fraction was treated with charcoal in methanol, and chromatographed on silica gel ($CHCl_3$: EtOAc = 4 : 1) to afford a mixture of **5a** and **5b** (890 mg) and a fraction containing more polar triterpenoid acid (350 mg). The latter fraction was acetylated with Ac_2O and pyridine, and the acetylated fraction was purified by repeated silica gel column chromatography (*n*-hexane : EtOAc = 4 : 1) to afford diacetates of **6** (190 mg) and **7** (140 mg). They were hydrolyzed to **6** and **7** by treatment with 3% NaOH : 80% MeOH in the usual way; the *n*-butanol extract was subjected to column chromatography on Amberlite XAD-II (H_2O→MeOH). The methanol elute (17.7 g) was chromatographed on silica gel ($CHCl_3$: MeOH = 9 : 1→3 : 2) to give four fractions. From the main fraction, **8** (10.8 g) and **9** (30 mg) were isolated by silica gel column chromatography ($CHCl_3$: MeOH = 23 : 2). Further, from a fraction of flavonoid glycoside, kaempferol 3-*O*-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside] (80 mg) was obtained by silica gel column chromatography ($CHCl_3$: MeOH = 4 : 1) and Sephadex LH-20 (MeOH).

22-Dehydroclerosteryl Acetate (1) Colorless needles, mp 149 °C, $[\alpha]_D^{22}$ −41° (*c* = 0.23, $CHCl_3$). GLC (Rt_R): 3.33. CI-MS *m/z*: 453 $[M+H]^+$. EI-MS *m/z*: 392.3487 $[M(C_{31}H_{48}O_2) - CH_3COOH]^+$, 253.1960 ($C_{19}H_{25}$, base). ^{1}H-NMR [270 MHz, $CDCl_3$] δ: 0.69 (3H, s, 18-H_3), 0.83 (3H, t, *J* = 7.3 Hz, 29-H_3), 1.01 (3H, d, *J* = 6.8 Hz, 21-H_3), 1.02 (3H, s, 19-H_3), 1.65 (3H, s, 26-H_3), 2.03 (3H, s, OAc), 2.32 (2H, d, *J* = 7.8 Hz, 4-H_2), 2.42 (1H, dd, *J* = 14.2, 7.4 Hz, 24-H), 4.60 (1H, m, 3-H), 4.70 (2H, br s, 27-H_2), 5.17, 5.25 (each 1H, dd, *J* = 15.2, 7.4 Hz, 22-H, 23-H), 5.37 (1H, br d, *J* = 4.9 Hz, 5-H). ^{13}C-NMR [67.5 MHz, $CDCl_3$] δ: 12.04 (C-18), 12.14 (C-29), 19.30 (C-19), 20.22 (C-26), 20.80 (C-21), 21.00 (C-11), 24.31 (C-15), 25.70 (C-28), 27.77 (C-2), 28.69 (C-16), 31.85 (C-8), 31.87 (C-7), 36.60 (C-10), 36.99 (C-1), 38.12 (C-4), 39.62 (C-12), 40.19 (C-20), 42.24 (C-13), 50.04 (C-9), 51.99 (C-24), 55.85 (C-17), 56.76 (C-14), 73.97 (C-3), 109.52 (C-27), 122.62 (C-6), 130.05 (C-23), 137.19 (C-22), 139.65 (C-5), 148.60

(C-25), 21.43, 170.54 (OAc).

Stigmasteryl Acetate (2) Colorless needles, mp 141 °C, $[\alpha]_D^{22}$ −50° (c=0.20, $CHCl_3$). GLC (Rt_R): 3.33. The results of ^1H- and ^{13}C-NMR showed it to be identical with those of authentic sample.

Mixture of Free Sterol [Stigmasterol (3a), 22-Dehydroclerosterol (3b), β-Sitosterol (3c) and Clerosterol (3d)] From the results of EI-MS and NMR, **3a**, **3b**, **3c** and **3d** were identical with those of published values. White needles, mp 132—134 °C, GLC of acetate (Rt_R): 3.33 (**3a**, **3b**), 3.82 (**3c**, **3d**). EI-MS m/z: 414 $[M(C_{29}H_{50}O)]^+$ of **3c**, 412 $[M(C_{29}H_{48}O)]^+$ of **3a** and **3d**, 410 $[M(C_{29}H_{46}O)]^+$ of **3b**. ^1H-NMR [100 MHz, $CDCl_3$] δ: 0.69 (3H, s, 18-H_3), 1.00 (3H, s, 19-H_3), 2.27 (2H, d, J=6.6 Hz, 4-H_2), 3.48 (1H, m, 3-H), 4.69 (br s, 27-H_2 of **3b** and **3d**), 5.02 (m, 22, 23-H of **3a**), 5.17 (m, 22, 23-H of **3b**), 5.35 (1H, br d, J=4.2 Hz, 5-H). ^{13}C-NMR [25 MHz, $CDCl_3$] δ: 12.1 (C-18), 19.4 (C-19), 21.2 (C-11), 24.4 (C-15), 31.8 (C-2), 32.0 (C-7, C-8), 36.6 (C-10), 37.4 (C-1), 42.4 (C-4, C-13), 50.3 (C-9), 71.3 (C-3), 121.6 (C-6), 140.8 (C-5), **3a** [12.3 (C-29), 19.1 (C-27), 21.1 (C-21), 21.3 (C-26), 25.4 (C-28), 28.9 (C-16), 31.9 (C-25), 39.8 (C-12), 40.4 (C-20), 51.3 (C-24), 56.1 (C-17), 57.0 (C-14), 129.4 (C-23), 138.3 (C-22)], **3b** [12.2 (C-29), 20.2 (C-26), 20.9 (C-21), 25.8 (C-28), 28.8 (C-16), 39.8 (C-12), 40.1 (C-20), 52.0 (C-24), 56.1 (C-17), 57.0 (C-14), 109.6 (C-27), 130.1 (C-23), 137.1 (C-22), 148.5 (C-25)], **3c** [11.9 (C-29), 18.9 (C-21), 19.1 (C-27), 19.8 (C-26), 23.2 (C-28), 26.4 (C-23), 28.3 (C-16), 29.4 (C-25), 34.1 (C-22), 36.2 (C-20), 39.9 (C-12), 46.0 (C-24), 56.2 (C-17), 56.9 (C-14)], **3d** [11.9 (C-29), 18.0 (C-26), 18.9 (C-21), 26.6 (C-28), 28.3 (C-16), 29.4 (C-23), 33.8 (C-22), 35.6 (C-20), 39.9 (C-12), 49.5 (C-24), 56.1 (C-17), 56.9 (C-14), 111.3 (C-27), 147.4 (C-25)].

Mixture of Glucosyl Sterol [β-Sitosterol 3-*O*-β-D-glucopyranoside (4c) and Stigmasterol 3-*O*-β-D-Glucopyranoside (4a)] White powder [mp 265—267 °C (dec.)]. From comparison with the results of TLC, NMR and examination of the acid hydrolyzed products, it was characterized as a mixture of **4c** (70%) and **4a** (30%).

Mixture of Ursolic Acid (5a) and Oleanolic Acid (5b) White powder (mp 275—280 °C). From comparison with the results of TLC and NMR, it was characterized as an equal mixture of **5a** and **5b**.

2α-Hydroxyursolic Acid (6) White powder [mp 255—260 °C (dec.)]. CI-MS m/z: 473 $[M(C_{30}H_{48}O_4)+H]^+$, 455 $([M+H-H_2O]^+$, base), 437 $[M+H-2H_2O]^+$. ^1H-NMR [100 MHz, C_5D_5N] δ: 0.98, 1.00, 1.08, 1.22, 1.27 (each 3H, s, 23-H_3, 24-H_3, 25-H_3, 26-H_3, 27-H_3), 1.01 (6H, d, J=7.0 Hz, 29-H_3, 30-H_3), 2.63 (1H, d, J=10.6 Hz, 18-H), 3.40 (1H, d, J=9.3 Hz, 3α-H), 4.09 (1H, m, 2β-H), 5.46 (1H, m, 12-H), diacetate [$CDCl_3$] δ: 4.74 (1H, d, J=10.3 Hz, 3α-H), 5.05 (1H, ddd, J=11.0, 10.3, 4.0 Hz, 2α-H). ^{13}C-NMR [25 MHz, C_5D_5N] δ: 17.0 (C-25), 17.5 (C-26, C-30), 17.6 (C-24), 18.9 (C-6), 21.4 (C-29), 23.7 (C-11), 23.9 (C-27), 24.9 (C-16), 28.7 (C-15), 29.3 (C-23), 31.1 (C-21), 33.5 (C-7), 37.4 (C-22), 38.4 (C-10), 39.5 (C-19, C-20), 39.8 (C-4), 40.0 (C-8), 42.5 (C-14), 48.0 (C-1, C-9, C-17), 53.5 (C-18), 55.9 (C-5), 68.6 (C-2), 83.8 (C-3), 125.4 (C-12), 139.3 (C-13), 179.9 (C-28).

Tormentic Acid (7) White powder [mp 262—265 °C (dec.)]. FAB-MS m/z: 489 $[M(C_{30}H_{48}O_5)+H]^+$. ^1H-NMR [100 MHz, C_5D_5N] δ: 1.02, 1.09, 1.12, 1.28 (each 3H, s, 23-H_3, 25-H_3, 24-H_3, 26-H_3), 1.12 (3H, d, J=6.5 Hz, 30-H_3), 1.45 (3H, s, 29-H_3), 1.72 (3H, s, 27-H_3), 3.06 (1H, br s, 18-H), 3.39 (1H, d, J=9.3 Hz, 3α-H), 4.12 (1H, m, 2β-H), 5.59 (1H, m, 12-H), diacetate [$CDCl_3$] δ: 4.75 (1H, d, J=10.3 Hz, 3α-H), 5.05 (1H, ddd, J=11.0, 10.3, 4.0 Hz, 2β-H). ^{13}C-NMR [25 MHz, C_5D_5N] δ: 16.8, 16.9 (C-24, C-30), 17.3 (C-25), 17.7 (C-26), 19.0 (C-6), 24.1 (C-11), 24.7 (C-27), 26.4 (C-16), 26.9 (C-21), 27.1 (C-29), 29.3 (C-15, C-23), 33.5 (C-7), 38.5 (C-10, C-22), 39.9 (C-4), 40.4 (C-8), 42.2 (C-14), 42.4 (C-20), 47.9 (C-1, C-17), 48.3 (C-9), 54.6 (C-18), 56.0 (C-5), 68.6 (C-2), 72.7 (C-19), 83.9 (C-3), 127.9 (C-12), 140.0 (C-13), 180.7 (C-28).

Methyl Linolate Colorless oil. From the results of ^1H- and ^{13}C-NMR, it was identified as methyl linolate.

Phytol Colorless oil. The results of ^1H- and ^{13}C-NMR were identical with those of authentic samples.

Prunasin (8) Colorless needles, mp 148—150 °C, $[\alpha]_D^{20}$ −31° (c=0.7, H_2O). The results of ^{13}C-NMR showed **8** to be identical with published values.

***dl*-Mandelic Acid (9)** Colorless needles, $[\alpha]_D^{22}$ −0.1° (c=0.8, methanol), mp 119 °C (the melting point of *d*-mandelic acid was 133 °C and the melting point of *dl*-mandelic acid was 118—119 °C). The results of ^{13}C-NMR and melting point, **9** was identified as *dl*-mandelic acid. IR ν_{max}^{Nujol} cm^{-1}: 3400 (OH), 1650 (COOH), 1610, 740. CI-MS m/z: 152 $[M(C_8H_8O_3)]^+$. ^{13}C-NMR [25 MHz, C_5D_5N] δ: 75.0, 134.5 (×2), 135.5, 136.5 (×2), 142.5, 176.3.

Kaempferol 3-*O*-[*O*-α-L-Rhamnopyranosyl-(1→6)-β-D-glucopyranoside] Pale yellow powder (mp 175—177 °C). From the results of ^1H- and ^{13}C-NMR,[13] it was identified as kaempferol 3-*O*-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside].

Extraction and Isolation of Branch Constituents The fresh branches (1.1 kg) were extracted with methanol (10 l) at room temperature. After evaporation of the solvent, the residue (64.3 g) was partitioned into ether–water, ethyl acetate–water and *n*-butanol–water successively. Removal of the solvent from each phase under reduced pressure gave the ether (5.7 g), the ethyl acetate (1.7 g), the *n*-butanol (6.8 g) and the aqueous (50.1 g) extract. The ether extract was chromatographed on silica gel (*n*-hexane : EtOAc = 9 : 1 → 1 : 1, EtOAc, EtOAc : MeOH = 9 : 1 → 7 : 3) to furnish six fractions. From a sterol fraction and a triterpenoid acid fraction, **3c** (120 mg), **5a** (80 mg), diacetate of **6** (30 mg) and **7** (10 mg) were obtained in the same way as described for the leaf constituents. From the ethyl acetate extract, **9** (300 mg) was obtained by column chromatography of silica gel ($CHCl_3$: MeOH = 9 : 1) and Sephadex LH-20 (MeOH). The *n*-butanol extract was separated by a combination of silica gel ($CHCl_3$: MeOH = 4 : 1 → 3 : 2) and Sephadex LH-20 (MeOH) column chromatography to afford **8** (90 mg) and **10** (130 mg).

β-Sitosterol (3c) White needles, mp 138—139 °C, $[\alpha]_D^{22}$ −40° (c=0.3, $CHCl_3$). GLC of acetate (Rt_R): 3.82. The results of ^1H- and ^{13}C-NMR were identical with those of authentic sample.

Ursolic Acid (5a) White powder (mp 288—290 °C). From the results of ^1H- and ^{13}C-NMR, it was identified as **5a**.

***d*-Mandelic Acid β-D-Glucopyranoside (10)** Amorphous powder, $[\alpha]_D^{20}$ −126° (c=1.4, C_5H_5N). IR ν_{max}^{Nujol} cm^{-1}: 3350 (OH), 1650 (COOH), 1620, 750. FAB-MS m/z: 314 $[M(C_{14}H_{18}O_8)]^+$, 152 (base). ^1H-NMR [100 MHz, C_5D_5N] δ: 5.04 (1H, d, J=6.8 Hz, anomeric proton of glucose). ^{13}C-NMR [25 MHz, C_5D_5N] δ: 79.3, 128.5 (×4), 128.6, 137.8, 179.1, glucosyl [62.3, 71.2, 75.0, 77.9, 78.4, 101.0].

Acid Hydrolysis of 10 A solution of **10** (20 mg) in 2 N H_2SO_4 was heated on a water bath for 3 h. From the reaction mixture, *d*-mandelic acid (mp 130 °C) and D-glucose were obtained.

Acknowledgement The authors thank Mr. Y. Takase of the Central Analytical Department of this college for NMR and MS measurements.

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