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In addition to trans-communol and trans-communic acid (obtained in the form of the methyl ester), seven new diterpenoids were isolated as non basic constituents from fresh bulbs of Fritillaria thunbergii Miq. (Liliaceae). Their structures were determined to be isopimarain-19-ol (3), isopimarain-19-oic acid [obtained in the form of the methyl ester (4)], ent-kauran-16β,17-diol (5), ent-kauran-16α,17-diol (6), ent-16β,17-epoxy-kaurane (7), ent-16α-methoxy-kauran-17-ol (8), and ent-kaur-15-en-17-ol (9).

Keywords—Fritillaria thunbergii Miq.; isopimarane-type diterpenoid; ent-kaurane-type diterpenoid; 1H-NMR; 13C-NMR

Fritillaria thunbergii Miq. (Liliaceae) is a Chinese plant cultivated in Japan. The bulbs which are treated with lime then bleached in the sun are called “Bai-mo” in Japanese and are used as a principle in Chinese medicine.

As for the constituent alkaloids of fresh bulbs of Fritillaria thunbergii Miq. grown in Japan, Fukuda isolated verticline, verticinone, verticilline and an amorphous base.2) Morimoto and Kimata obtained pemine (verticline), and its glucoside, peminoside.3) The structures of verticline and verticinone were determined by Ito et al.4) Recently, Kaneko and Mitsushashi isolated isoverticline (the 6-epimer of verticline)5) and we identified a minor alkaloid, 11-deoxy-6-oxo-5α,6-dihydrojervine.6) From the aerial parts of this plant, three glycosidal Solanum alkaloids (basic steroid saponins) were isolated and characterized together with minor amounts of two alkaloids, verticline and verticinone.1) However, the non basic constituents have not been examined.

This paper describes the structure elucidation of diterpenoids isolated from the fresh bulbs of Fritillaria thunbergii Miq.

The sliced fresh bulbs (19.6 kg), cultivated in Nara prefecture, were collected in May and extracted with MeOH. The extracts were fractionated and purified according to the procedure shown in Chart 1 to give nine kinds of diterpenoids. Compounds (Compds.) II and IV were obtained as their methyl ester derivatives after methylation.

Compds. I [C29H42O, a colorless oil, \([\alpha]_D^{19} +14.5^\circ (\text{CHCl}_3)] (1) and II [C21H32O2, mp 104—105°C, \([\alpha]_D^{19} +48.0^\circ (\text{CHCl}_3)] (2) were identified as trans-communol and trans-communic acid methyl ester from their physical and spectral data7) (Chart 2).

Compds. III[C20H32O, mp 86°C, \([\alpha]_D^{19} -39.0^\circ (\text{CHCl}_3)] (3) and IV [C21H32O2, colorless oil, \([\alpha]_D^{19} +26.7^\circ (\text{CHCl}_3)] (4) showed the signals of three tertiary (lert) methy groups (excluding the signal of the methyl ester of 4), one exo-methylene, and one tri-substituted double bond in the proton nuclear magnetic resonance (1H-NMR) spectrum (Table 1).

Compd. 3 was derived from 4 by treatment with LiAlH4 in tetrahydrofuran (THF). Thus, 3 and 4 were considered to be a tricyclic diterpenoid alcohol and the corresponding acid ester, respectively. Comparison of the 1H-NMR spectral data of 3 with those of pimarinal (11),8) isopimarinal (12)9) and sandaracopimarinal (13)10) which are representative diterpenoid monoalcohols, showed good similarity between 3 and 12, except for the downfield shift of the 4-methyl (δ 0.97) and hydroxymethyl (δ 3.49 and 3.90, each doublet, J = 11 Hz) groups (Chart 3). These results indicated the presence of axial hydroxymethyl. Thus, 3 and 4 were assumed
to be isopimarane-7,15-diene type diterpenoids bearing an O-function at C-19.\textsuperscript{11}

The electron impact mass (EI-MS) spectrum of 4 lacked the ion peak at \( m/z \) 121, \([\text{C}_9\text{H}_{14}]^+\), which appeared as the base peak due to the C-ring in pimamic acid methyl ester (14) and sandaracopimamic acid methyl ester (15), both of which contain a double bond at C-8/C-14.\textsuperscript{12}

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**Chart 1. Isolation of Diterpenoids**

\( a) \) see Part VI of this series.
The carbon nuclear magnetic resonance (\(^{13}\text{C}\)-NMR) spectral data of 3 and 4 were very similar to those of 12, isopimaric acid (16), and isopimara-7,15-dien (17'), except for the chemical shifts of C-18 and C-19 (Table II). Thus, it was confirmed that 3 and 4 are isopimarane type diterpenoids.
TABLE II. $^{13}$C-NMR Spectral Data for 3 and 4.$^{a,b}$

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<td>16.1 (q)</td>
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</tr>
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</table>

a) Reference substances: $^{40}$ 11, 12, pimarin acid (14'), sandaracopimarinic acid (18'), 16, pimara-8 (14), 15-dienc (17) and 17'.

b) Solvent: 3, 4, 14' and 16' (CDCl$_3$), 11, 12, 16, 17 and 17' (CCl$_4$).

Aiyar and Seshadri obtained oblongifolic acid (18) from the Euphorbiaceous plant Croton oblongifolium, and determined the structure to be ent-isopimar-19-0ic acid.$^{14}$ They also obtained the methyl ester (19), monoalcohol (20) and monoacetate (21) of 18, and the physical properties of 19 through 21 were identical with those of 4, 3 and 3-acetate (22), respectively, except for optical rotations. Thus, 3 and 4 are isopimar-19-0l and isopimar-19-0ic acid methyl ester, respectively (Chart 4).

Compds. V [C$_{26}$H$_{34}$O$_2$, mp 188—189°C, [a]$_D$ $-47.0^\circ$ (CHCl$_3$)] (5) and VI [C$_{26}$H$_{34}$O$_2$, mp 177°C, [a]$_D$ $-45.5^\circ$ (CHCl$_3$)] (6) showed an infrared (IR) absorption band due to the hydroxy group, and their $^1$H-NMR spectra showed signals due to three tert methyl and one hydroxymethyl groups. Thus, 5 and 6 were considered to be tetracyclic diterpenoids having two O-functions (Table III).

On acetylation with Ac$_2$O-pyridine at room temperature, 5 and 6 each yielded a monoacetate, 23 and 24, and their IR spectra still showed the presence of a hydroxy group. Therefore, it was clarified that 5 and 6 each contain one secondary and one tert hydroxy group.

On treatment with HIO$_4$ in MeOH, 5 and 6 yielded the same product (25) [C$_{19}$H$_{30}$O, mp 117—118°C, [a]$_D$ $-29.0^\circ$ (CHCl$_3$)], which was identified as ent-17-norkauran-16-one by comparison with an authentic sample.$^{15}$ Consequently, 5 and 6 are ent-kaurane type diterpenoids, which have hydroxy groups at C-16 and C-17 (Chart 5). The $^{13}$C-NMR signals of C-1 through C-11, C-14, C-18, C-19 and C-20 of compounds 5 and 6 (Table IV) were similar to those of ent-
TABLE III. \textsuperscript{1}H-NMR Spectral Data for 5, 6, 7, 8, and 9

<table>
<thead>
<tr>
<th>5 (ppm)</th>
<th>6 (ppm)</th>
<th>7 (ppm)</th>
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<td>tert-CH\textsubscript{3}</td>
<td>0.80</td>
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<tr>
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<td>1.02</td>
<td>tert-CH\textsubscript{3}</td>
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<td>3.80</td>
<td>-CH\textsubscript{2}OH</td>
<td>3.51</td>
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(each 1H, d, $J = 11$ Hz) (each 1H, d, $J = 12$ Hz) (each 1H, d, $J = 5$ Hz)
kaurane. However, the chemical shifts of C-12, C-13, C-15, C-16, and C-17, which are influenced by the hydroxy groups, were found to be consistent with those of ent-kauran-16β,17-diol-19-oic acid (27). The melting point and optical rotation of 5 showed good agreement with those of ent-kauran-16β,17-diol, which was derived from 26. Thus, 5 and 6 are ent-kauran-16β,17-diol and ent-kauran-16α,17-diol, respectively.

Compd. VII [C_{20}H_{32}O, mp 114—116°C, [α]_D -18.5° (CHCl_3)] (7) showed an IR absorption band assignable to an epoxy group instead of the hydroxy group. Its 1H-NMR spectrum showed signals of three tert methyl groups and the presence of a methylene group bearing an O-function (Table III). Therefore, 7 was considered to be a tetracyclic diterpenoid with one epoxy group.

Comparison of the 13C-NMR spectra of 5, 6, and 7 showed that the chemical shifts of C-1 through C-12, C-14, C-18, and C-20 of 7 were in agreement with those of 5 and 6 (Table IV). Thus, 7 was considered to be ent-16,17-epoxy-kaurane.

Alkaline hydrolysis of 7 with 2.5% NaOH-dil. MeOH afforded a methoxy compound (28) [C_{21}H_{36}O_2, mp 174—176°C, [α]_D -33.0° (CHCl_3)], which was derived from 5 by application of the Kuhn method. Compd. 7 could also be connected with 5 via epoxidation of 5-tosylate (29) (see Chart 5). Thus, 7 was determined to be ent-16β,17-epoxy-kaurane.
Compd. VIII [C_{21}H_{22}O_2, mp 171-173°C, [x]_D -45.6° (CHCl_3)] (8) showed the ^1H-NMR signals of one methoxy, three tert methyl, and one hydroxymethyl groups. The EI-MS spectrum of 8 lacked the M^+ ion peak, but elemental analysis of 8, and the presence of a fragment ion at m/z 289 (M-CH_2CHO)^+ gave C_{21}H_{30}O_2 as the formula of 8 (Table III).

Compd. 8 showed a distinctive absorption due to the hydroxy group in its IR spectrum, and acetylation of 8 with Ac_2O-pyridine at room temp. yielded a monoacetate (30). Therefore, 8 was considered to be a tetracyclic diterpenoid bearing one methoxy and one hydroxymethyl groups.

Comparison of the ^13C-NMR spectra of 5, 6 and 8 showed that the chemical shifts of C-1 through C-12, C-14, C-18, C-19, and C-20 of 8 were in accord with those of 5 and 6. Therefore, 8 was considered to be ent-16-methoxy-kauran-17-ol (Table IV).

Hydrolysis of 7 with 3% Na_2CO_3-dil. MeOH yielded two compounds in a ratio of ca. 1:1; they were identified as 5 and 8, respectively. It is known that the cleavage of the exo-epoxide ring, in neutral or basic media, proceeds in a usual S_n2 manner^{19} (Chart 6). Therefore, the C-16 methoxy group of 8 must be β-oriented. From these results it is evident that 8 is ent-16α-methoxykauran-17-ol, which is probably formed during the isolation procedures.

Compd. IX [C_{20}H_{22}O, mp 134-136°C, [x]_D -26.1° (CHCl_3)] (9) showed an IR absorption band due to a hydroxy group, and ^1H-NMR spectral signals due to three tert methyl groups, one hydroxymethyl group, and one tri-substituted double bond (Table III). The ^13C-NMR spectrum of 9 was similar to those of 5, 6, and 7, especially in the signals of C-1 through C-12, C-14, C-18, C-19, and C-20 (Table IV). Therefore, 9 was considered to be ent-kaur-15-en-17-ol,
which has been derived from 26 by Briggs et al.. In fact, both compounds showed identical properties (melting point, $^1$H-NMR spectrum and optical rotation$^{20}$). The melting point of 9-acetate (10) coincided with that reported for ent-kaur-15-en-17-ol monooacetate [lit.$^{20}$ mp 70°C]. Thus, 9 was determined to be ent-kaur-15-en-17-ol.

### Experimental

Melting points are uncorrected. Optical rotations were taken with a JASCO DIP-SL automatic polarimeter at 17—27°C. IR spectra were obtained with a JASCO IR-G spectrometer. $^{13}$C-NMR data were obtained in CDCl$_3$ solution on a JEOL-FX-100 spectrometer (25.05 MHz) under the following conditions: pulse width 5 μs, repetition time 1 s, and data points 8192. $^1$H-NMR spectra were recorded at 100 MHz on a JEOL-PS-100 spectrometer: in the $^{13}$C-NMR and $^1$H-NMR studies, a 5 mm$^3$ sample tube was used. Chemical shifts are expressed in ppm from tetramethylsilane as an internal reference, and coupling constants (J) are given in Hz. Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. EI-MS spectra were measured on a JEOL JMS-01SG double focusing mass spectrometer with direct insertion of the probe into the ion source. The spectra were recorded with an accelerating potential of 6.5—6.7 kV, an ionizing potential of 75 eV, and a sample temperature of 47—196°C. Thin layer chromatography (TLC) was performed on DC-Alufolien Kieselgel 60 F$_{254}$ (Merck) using anisaldehyde reagent$^{21}$ and 10% H$_2$SO$_4$ as the detector. Column chromatography was carried out using Kieselgel (silica gel 0.063—0.2 mm, Merck), Silica Woelm TSC (silica gel for dry column (dry), Woelm Pharma.), Aluminiumoxide standardisiert (grade III, Merck), and Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemicals) in an amount equivalent to fifty to two hundred fold excess over the material. Gas-liquid chromatography (GLC) was run on a JEOL JGC-1100 machine with a flame ionization detector using a glass column (1.5 m x 7 mm$^3$) packed with 10% SE-30 Chromosorb W (80—80 mesh).

### Extraction and Isolation of Diterpenoids

The bulbs were collected in May from plants cultivated in Nara prefecture, and the isolation procedure is shown in Chart 1.

#### Compd. I — Colorless oil, $[\alpha]_D^{25} +14.5^\circ$ ($c=1.8$, CHCl$_3$). IR $\nu_{\text{max}}$ cm$^{-1}$: 3300 (OH), 1645, 1605 (double bond), 888 (exo-methylene). $^1$H-NMR (CDCl$_3$) $\delta$: 0.71, 1.00, 1.77 (each 3H, s, tert CH$_3$), 3.40, 3.77 (each 1H, d, $J=11$ Hz, C$_{19}$H$_2$), 4.46, 4.82 (each 1H, s, C$_{15}$H$_2$), 4.82—5.32 (2H, m, C$_{15}$H$_2$), 5.42 (1H, t, C$_{15}$H), 6.35 (1H, q, $J=17$ Hz and 11 Hz, C$_{15}$H) — EI-MS $m/z$: 288 (M$^+$, base peak), 257, 81. 1-Acetate: colorless oil. $^1$H-NMR (CDCl$_3$) $\delta$: 0.84, 0.98, 1.86 (each 3H, s, tert CH$_3$), 2.04 (3H, s, $-$OAc), 4.25, 4.16 (each 1H, d, $J=11$ Hz, C$_{19}$H$_2$), 4.46, 4.82 (each 1H, s, C$_{15}$H$_2$), 4.82—5.32 (2H, m, C$_{15}$H$_2$), 5.41 (1H, t, C$_{15}$H), 6.35 (1H, q, $J=17$ and 12 Hz, C$_{11}$H) — EI-MS $m/z$: 330 (M$^+$), 288, 257 (base peak), 81. GLC (column temp.: 210°C, N$_2$: 1.0 kg/cm$^2$, H$_2$: 1.5 kg/cm$^2$) $\Lambda$ 10.49°.

#### Compd. II (2) — Needles (MeOH), mp 104—105°C, $[\alpha]_D^{25} +48.0^\circ$ ($c=1.0$, CHCl$_3$). IR $\nu_{\text{max}}$ cm$^{-1}$: 1710 (C=O), 1642, 1605 (double bond), 885, 882 (exo-methylene). $^1$H-NMR (CDCl$_3$) $\delta$: 0.56, 1.77, 1.19 (each 3H, s, tert CH$_3$), 3.61 (3H, s, COOCH$_3$), 4.46, 4.82 (each 1H, s, C$_{15}$H$_2$), 4.82—5.32 (2H, m, C$_{15}$H$_2$), 5.42 (1H, t, C$_{15}$H), 6.34 (1H, q, $J=17$ Hz and 11 Hz) — EI-MS $m/z$: 316 (M$^+$, base peak), 257, 235, 181, 175, 121. Anal. Calc'd for C$_{30}$H$_{32}$O$_2$: C, 79.70; H, 10.91. Found: C, 79.41; H, 10.91.

#### Compd. III (3) — Needles (MeOH), mp 86°C, $[\alpha]_D^{25} -39.0^\circ$ ($c=1.2$, CHCl$_3$). IR $\nu_{\text{max}}$ cm$^{-1}$: 3350, 1028 (OH), 1640, 907 (exo-methylene). $^1$H-NMR (CDCl$_3$) $\delta$: see Table I. EI-MS $m/z$: 288 (M$^+$), 273, 257, 205, 181.
(base peak). $^{13}$C-NMR (CDCl₃) δ: see Table II. Anal. Calcd for C₆₈H₄₂O·1/4H₂O: C, 81.99; H, 11.18. Found: C, 82.49; H, 11.13.

Compd. IV (4)—Colorless oil, $[a]_D^{25} + 26.7^\circ$ (c=3.3, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 1725 (C=O), 1640, 908 (exomethylene). $^{1}H$-NMR (CDCl₃) δ: see Table I. EI-MS m/z: 316 (M+, base peak), 301, 287, 257, 241. $^{13}$C-NMR (CDCl₃) δ: see Table II.

3-Monoacetate (22)—The conventional acetylation of 3 (20 mg) with Ac₂O-pyridine (1:1 ml each) at room temperature overnight, and subsequent purification of the crude product by silica gel column chromatography (dry, 10 g, solv.: n-hexane-EtOAc=9:1) gave 22, colorless oil, $[a]_D^{25} + 30.0^\circ$ (c=1.9, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 1743 (OAC), 1640, 910 (exo-methylene). $^{1}H$-NMR (CDCl₃) δ: 0.87 (6H, s, tert CH₂×2), 0.94 (3H, s, tert CH₃), 2.05 (3H, s, OAC), 3.95, 4.35 (each 1H, d, J=11 Hz, C₈H₅-H), 4.86(CH₂), 4.95 (br), 5.81 (s) (each 1H, J=8-17 Hz, J=10 Hz, J=2 Hz, C₈H₅-H, C₈H₅-H), 5.36 (1H, t, J=2 Hz, C₈H₅-H).

LiAlH₄ Reduction of 4—A mixture of 4 (25 mg), THF (5 ml), and LiAlH₄ (15 mg) was stirred for 1 h at room temperature. After quenching of excess LiAlH₄ with MeOH (10 ml), the reaction mixture was poured into water and extracted with EtO. The organic layer was washed with dil. H₂SO₄ and water, and concentrated to give the residue, which was chromatographed on a silica gel column (dry, 30 g, solv.: n-hexane-EtOAc=4:1) to give 3, 6.5 mg of needles from MeOH.

Compd. V (5)—Needles (MeOH), mp 188–189°C. $[a]_D^{25} -47.0^\circ$ (c=2.1, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 3350 (OH). $^{1}H$-NMR (CDCl₃) δ: see Table III. EI-MS m/z: 306 (M⁺), 288, 275 (base peak), 257, 123. $^{13}$C-NMR (CDCl₃) δ: see Table IV. Anal. Calcd for C₈H₄O₂·1/2H₂O: C, 76.14; H, 11.18. Found: C, 76.48; H, 11.24.

5-Monoacetate (23)—Acetylation of 5 (25 mg with Ac₂O-pyridine (1:1 ml each) at room temperature overnight gave 23, 20.5 mg of needles from acetone. mp 159°C. IR $\nu_{max}$ cm$^{-1}$: 3480 (OH), 1730 (OAc). $^{1}H$-NMR (CDCl₃) δ: 0.70, 0.84, 1.03 (each 3H, s, tert CH₃), 2.10 (3H, s, OAc). 4.23 (2H, s, C₈H₅-H). EI-MS m/z: 348 (M⁺), 330, 315, 275 (base peak), 270, 257, 123.

HIO₄ Oxidation of 5—A mixture of 5 (100 mg), MeOH (10 ml), and HIO₄ (50 mg) was stirred for 2 h at room temperature. The reaction mixture was poured into water and extracted with EtO. The organic layer was concentrated to give the residue, which was chromatographed on a silica gel column (dry, 30 g, solv.: n-hexane-EtOAc=9:1) to afford 25 as prisms, 52 mg from MeOH. mp 117–118°C, $[a]_D^{25} -29.0^\circ$ (c=1.3, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 1742 (C=O). $^{1}H$-NMR (CDCl₃) δ: 0.83, 0.87, 1.08 (each 3H, s, tert CH₃). EI-MS m/z: 274 (M⁺, base peak), 261.

Compd. VI (6)—Needles (MeOH), mp 177°C, $[a]_D^{25} -45.5^\circ$ (c=1.2, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 3350 (OH). $^{1}H$-NMR (CDCl₃) δ: see Table III. EI-MS m/z: 306 (M⁺), 288, 275 (base peak), 257, 123. $^{13}$C-NMR (CDCl₃) δ: see Table IV. Anal. Calcd for C₈H₄O₂·3/2H₂O: C, 76.14; H, 11.18. Found: C, 76.38; H, 11.21.

5-Monoacetate (24)—Acetylation of 6 (25 mg with Ac₂O-pyridine (1:1 ml each) at room temperature overnight gave 24, 20 mg of needles from acetone. mp 127–129°C. IR $\nu_{max}$ cm$^{-1}$: 3480 (OH), 1730 (OAc). EI-MS m/z: 348 (M⁺), 330, 315, 288, 275 (base peak), 270, 257, 123.

HIO₄ Oxidation of 6—A mixture of 6 (50 mg), MeOH (6 ml), and HIO₄ (30 mg) was stirred for 2 h at room temperature. After the usual work-up, the residue was purified by silica gel column chromatography (dry, 10 g, solv.: n-hexane-EtOAc=9:1) to afford prisms 25, 32 mg from MeOH.

Compd. VII (7)—Needles (MeOH), mp 114–116°C, $[a]_D^{25} -18.5^\circ$ (c=2.0, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 792 (epoxy). $^{1}H$-NMR (CDCl₃) δ: see Table III. EI-MS m/z: 288 (M⁺), 273 (base peak). $^{13}$C-NMR (CDCl₃) δ: see Table IV. Anal. Calcd for C₈H₄O₂: C, 83.27; H, 11.18. Found: C, 83.02; H, 11.09.

Alkaline Hydrolysis of 7—7 (30 mg) was refluxed in 2.5% NaOH-dil. MeOH (10 ml) on a hot water bath for 2 h, then the solution was poured into water and extracted with EtO. The organic layer was washed with water and concentrated to give a residue, which was chromatographed on silica gel (dry, 10 g, solv.: n-hexane-EtOAc=4:1) to afford 28, 25 mg of needles from MeOH. mp 174–176°C, $[a]_D^{25} +33.0^\circ$ (c=1.0, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 3430 (OH). $^{1}H$-NMR (CDCl₃) δ: 0.81, 0.85, 1.02 (each 3H, s, tert CH₃), 3.40 (3H, s, OCH₃), 3.40, 3.58 (each 1H, d, J=9 Hz, C₈H₅-H). EI-MS m/z: 320 (M⁺). 302, 289 (base peak), 257.

Methylation of 5—A mixture of NaH (35 mg), DMF (4 ml) and 5 (70 mg) was stirred for 10 min at room temperature, then CH₂Cl₂ (4 ml) was added. After being stirred for 2 h, the reaction mixture was poured into water and extracted with EtO. The organic layer was washed with water and concentrated to give a residue, which was chromatographed on silica gel column (dry, 15 g, solv.: n-hexane-EtOAc=9:1) to afford 29, 57 mg of needles from MeOH.

Preparation of p-Toluenesulfonate (29)—A mixture of 5 (80 mg), pyridine (5 ml), and p-toluenesulfonyl chloride (150 mg) was stirred overnight at room temperature. The reaction mixture was poured into water and extracted with CHCl₃. The organic layer was taken up and concentrated to give a residue, which was chromatographed on silica gel chromagram (dry, 10 g, solv.: n-hexane-EtOAc=9:1) to afford 29, 57 mg of needles from MeOH.

Compd. VIII (8)—Needles (MeOH), mp 171–173°C, $[a]_D^{25} -45.0^\circ$ (c=1.1, CHCl₃). IR $\nu_{max}$ cm$^{-1}$: 3400
(OH). $^1$H-NMR (CDCl$_3$) $\delta$: see Table III. EI-MS $m/z$: 280 (M−OCH$_3$)$^+$, 274 (base peak). $^{13}$C-NMR (CDCl$_3$) $\delta$: see Table IV. Anal. Calculated for C$_9$H$_{12}$O$_2$: C, 78.69; H, 11.32. Found: C, 78.07; H, 11.23.

8-Monoacetate (30)—Acetylation of 8 (20 mg) with Ac$_2$O-pyridine (each 1 ml) at room temperature overnight gave 30, 18 mg of prism from MeOH. mp 127−128°C. $^1$H-NMR (CDCl$_3$) $\delta$: 0.77, 0.83, 0.99 (each 3H, s, tert CH$_3$), 2.08 (3H, s, OAc), 3.12 (6H, s, OCH$_3$), 4.14, 4.37 (each 1H, d, $J=12$ Hz, N$_2$−H$_2$).

Alkaline Hydrolysis of 7—7 (50 mg) was refluxed in 3% Na$_2$CO$_3$-dil. MeOH (10 ml) on a hot water bath for 4 h, then the solution was poured into water and extracted with EtO$_2$. The organic layer was washed with water and concentrated to give a residue, which was chromatographed on silica gel (dry, 10 g, solv.: $n$-hexane-EtOAc=3:2) to afford 8, 17 mg of needles from MeOH, and 5, 16 mg of needles from MeOH. 5, mp 188−189°C. IR $\nu_{max}$ cm$^{-1}$: 3350 (OH). 8, mp 171−172°C, $[\alpha]_D^{19}$ −45.5° ($c=1.2$, CHCl$_3$).

Compd. IX (9)—Needles (MeOH), mp 134−136°C, $[\alpha]_D^{19}$ −26.1° ($c=3.3$, CHCl$_3$). IR $\nu_{max}$ cm$^{-1}$: 3300 (OH). $^1$H-NMR (CDCl$_3$) $\delta$: see Table III. EI-MS $m/z$: 288 (M$^+$, base peak), 263, 163. $^{13}$C-NMR (CDCl$_3$) $\delta$: see Table IV. Anal. Calculated for C$_9$H$_{12}$O$_2$: C, 83.27; H, 11.18. Found: C, 83.39; H, 11.12.

9-Monoacetate (10)—Acetylation of 9 (30 mg) with Ac$_2$O-pyridine (each 1 ml) at room temperature overnight gave 10, 26 mg of needles from MeOH. mp 69°C. EI-MS $m/z$: 330 (M$^+$). GLC: (column temp.: 210°C, N$_2$; 1.0 kg/cm$^2$, H$_2$: 1.5 kg/cm$^2$) $t_k$ 10′43′.

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References and Notes

1) J. Kitajima, T. Komori, T. Kawasaki, and H.-R. Schulten, *Phytochemistry*, 21, 187 (1982) (Basic Steroid Saponins from Aerial Parts of *Fritillaria thunbergii* is designated as Part II of this series. Part of the present work was presented at the 26th Annual Meeting of the Japanese Society of Pharmacognosy, Tokyo, November 1979, Abstr., p. 17.


