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The Constituents of *Gymnopilus spectabilis*

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Cerevisterol (**1**) and a new acetylenic compound, 4,6-decadiyne-1,3,8-triol (**2**) were isolated and characterized from a hallucinogenic mushroom, *Gymnopilus spectabilis* (FR.) A. H. SMITH, along with ergosterol, ergosteryl peroxide and choline.

Psychoactive compounds such as psilocybin and related compounds have not been detected in our collections of this mushroom, though some psilocybin has been found in several other Japanese mushrooms.

Keywords——*Gymnopilus spectabilis*; hallucinogenic mushroom; cerevisterol; 4,6-dicadiyne-1,3,8-triol; ergosterol; ergosteryl peroxide; choline

Previously we reported the isolation and structural elucidation of gymnoprenol-A, -B, -D and -E and a bitter principle, gymnopilin, all of which have a novel type of polyisoprene chain, from the fruiting bodies of *Gymnopilus spectabilis* (FR.) A. H. SMITH.[1-5] During further investigation of the constituents of the same mushroom, we isolated cerevisterol (**1**) and 4,6-decadiyne-1,3,8-triol (**2**), along with ergosterol, ergosteryl peroxide and choline. Cerevisterol (**1**) was identified after direct comparison with a synthetic sample, which was prepared from ergosterol according to the reported method.[6] The acetylenic compound (**2**) has not been described previously, although many similar compounds have been reported. These results are presented here.

Cerevisterol (**1**), mp 251—253 °C, $C_{28}H_{46}O_3$, was isolated from fresh fruiting bodies of *Gymnopilus spectabilis* (Japanese name: Ohwaraitake) as described in the experimental section. The molecular formula was deduced on the basis of the microanalysis and the mass spectrum (MS). The fragment ions (*m/z* 269, $M^+ - C_9H_{17} - 2H_2O$; *m/z* 251, $M^+ - C_9H_{17} - 3H_2O$) in the MS were thought to arise from fragmentations similar to those of ergosterol (*m/z* 271, $M^+ - C_9H_{17}$; *m/z* 253, $M^+ - C_9H_{17} - H_2O$).

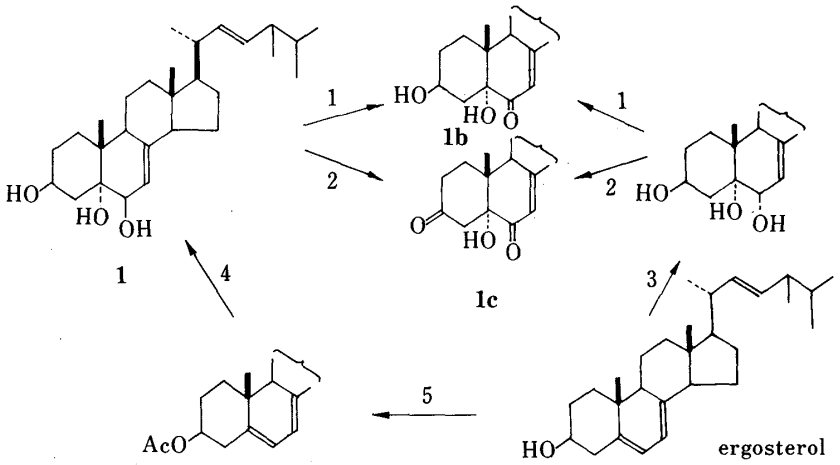
The following signals of the nuclear magnetic resonance (NMR) spectrum (δ, 5.20—5.36 ppm, 2H, m, $C_{22,23}$-2H; 0.65 ppm, 3H, s, C_{18}-3H; 0.90 ppm, 3H, s, C_{19}-3H; 0.96 ppm; 3H, d, J=7.0 Hz, C_{21}-3H; 1.07 ppm, 3H, d, J=6.0 Hz, C_{28}-3H; 0.88 ppm, 6H, d, J=7.0 Hz, $C_{26,27}$-6H) are similar to those of ergosterol.

On acetylation, **1** provided a diacetyl derivative (**1a**), and on oxidation with active manganese dioxide, **1** provided an α,β-unsaturated ketone (**1b**), the NMR spectrum of which showed no signal attributable to the carbinyl hydrogen found at 4.29 ppm in that of **1**. These results suggested the presence of a secondary allylic alcohol in **1**.

On Jones' oxidation, **1** provided a diketone (**1c**), the NMR spectrum of which showed disappearance of the signals of an allylic carbinyl hydrogen and another secondary carbinyl hydrogen. The latter hydrogen appeared as an unresolved multiplet at 3.61 ppm in the NMR spectrum of **1** and there was a close similarity of the chemical shift and the pattern of the signal to that attributed to 3α-hydrogen of ergosterol.

Ergosterol gave 5α-ergosta-7,22-diene-3β,5α,6α-triol on treatment with osmium tetroxide.[7] This triol was converted to 3β,5α-dihydroxy-ergosta-7,22-dien-6-one by oxidation with active manganese dioxide and to 5α-hydroxy-5α-ergosta-7,22-diene-3,6-dione by Jones' oxidation.

The monoketo derivative (**1b**) and the diketo derivative (**1c**) prepared from **1** were identified as 3β,5α-dihydroxy-5α-ergost-7,22-dien-6-one and 5α-hydroxy-5α-ergosta-7,22 diene-3,6-dione prepared above, respectively, by direct infrared (IR), ultraviolet (UV) and NMR comparisons with authentic samples, while **1** was different from 5α-ergosta-7,22-diene-3β,5α,6α-triol. These results suggested that **1** is cerevisterol, which was synthesized according to Alt and Barton[6] as follows. Ergosteryl acetate was treated with perphthalic acid, then refluxed with 5% KOH–MeOH. Cerevisterol, mp 253—255 °C was obtained by chromatography of the products; this synthesized compound and the isolated compound (**1**) were identical on the basis of spectral comparison.



1: active MnO_2, 2: Jones reagent, 3: OsO_4,
4: perphthalic acid, then reflux with 5% KOH (MeOH),
5: Ac_2O–pyr.

Fig. 1

A new acetylenic compound (**2**), bp 122 °C (0.4 mmHg), $C_{10}H_{14}O_3$, was isolated from the ethyl acetate fraction of the aqueous extract of the fruiting bodies, and from the culture fluid of the isolated mycelia.

The IR spectrum showed a hydroxy band at 3300 cm^{-1} and acetylenic bands at 2150, 2250 cm^{-1}. On acetylation with acetic anhydride in pyridine, **2** gave a triacetyl derivative (**2a**), which produced an octahydro derivative (**2b**).

The NMR spectrum of **2** showed a triplet (3.79 ppm, 2H, $J=6$ Hz), a second triplet (4.36 ppm, 1H, $J=6$ Hz) and a third triplet (4.69 ppm, 1H, $J=6$ Hz), which shifted to 4.20, 5.35 and 5.53 ppm in **2a**, respectively, while retaining the multiplicities. These results suggested the presence of the partial structures A and B in the structure of **2**. The NMR

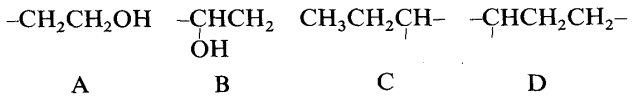
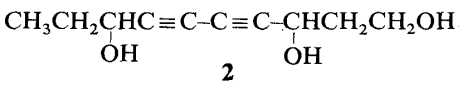


Fig. 2

spectrum of **2** in pyridine-d_5 also showed a triplet (1.10 ppm, 3H, $J=7.0$ Hz), a quintet (1.76 ppm, 2H, $J=7$ H), and a quartet (2.35 ppm, 2H, $J=7.0$ Hz), suggesting the presence of

the partial structures C and D.

Because this compound showed no olefinic hydrogens, the unsaturation number 4 was explained in terms of two acetylenic bonds. Therefore, **2** was concluded to be 4,6-decadiyne-1,3,8-triol (Fig. 3).



2

Fig. 3

This structure was supported by the MS of **2b**, [*m/z* 316 (M^+), 287 ($M^+ - C_2H_5$), 256 (M^+ −AcOH), 196 ($M^+ - 2AcOH$), 136 ($M^+ - 3AcOH$)] and the similarity of the UV spectrum with that of 4,6-decadiyn-1-ol.[8)]

Discussion

Previously we reported the isolation of psilocybin [4-phosphoryloxy-3-(2-dimethylaminoethyl) indole], a hallucinogenic tryptamine derivative, from a Japanese mushroom, *Psilocybe argentipes* K. YOKOYAMA, and the determination of psilocybin in some Japanese

TABLE I. Occurrence of Psilocybin

Species analyzed	Origin	Concentration of psilocybin
Psilocybe argentipes (Hikageshibiretake)	Aobayama, Sendai, July, 1979	0.14—0.16 (2.97—3.43)
	Aobayama, Sendai, Sept., 1979	0.53—0.55 (3.95—3.65)
	Izumigatake, Miyagi, July, 1979	0.018—0.02 (0.38—0.55)
	Kyoto, 1979	0.002—0.004 (2.32—2.53)
	Takahata, Yamagata, Oct., 1985	1.21—1.35[a)] (12.8—13.9)
P. subcaerulipes (Aizomeshibahutake)	Hiroshima, July, 1981	0.34—0.81
P. caprophila	Shiga, Oct., 1980	0.08—0.15
Panaeolus papilionaceus (Waraitake)	Shiga, May, 1981	0.04—0.05
P. subbalteatus (Senbonsaigyogasa)	Shiga, May, 1981	0.64—0.70
	Aobayama, Sendai, July, 1983	0.16 (1.33—1.46)
	Aobayama, Sendai, July, 1985	0.061 (0.60—0.61)[a)]
P. semiovatus (Jingasatake)	Shiga, May 1981	0.0007—0.001
P. antillarum (Jingasatakemodoki)	Shiga, Sept., 1980	0.045—0.083
P. sphinctrinus (Hikagetake)	Shiga, May, 1981	0.014—0.017
Gymnopilus spectabilis	Oguni, Yamagata, Sept., Oct., 1979, 1980, 1981, 1985	N.D.
	Miyagi, Sept., 1979, 1985[a)]	N.D.
	Germany, 1977	N.D.

N.D. not detectable. Figures are based on partially dry weight of specimens and those in parentheses are based on the MeOH extracts. The values were determined by combined anion exchange resin chromatography and HPLC except where indicated by *a*), where the values were determined by the TLC densitometric method.

mushrooms of *Psilocybe* species, *Panaeolus* species and others by high-performance liquid chromatography (HPLC) as summarized in Table I.[9,10]

As described in the previous report,[9,10] psilocybin was not detected in several specimens of *Gymnopilus spectabilis* (FR.) A. H. SMITH, although this mushroom has been believed to be psychoactive in Japan. Because Hatfield *et al.* reported the isolation of psilocybin from an American hallucinogenic mushroom, *Gymnopilus validipes* (PK.) HESLER (0.12% yield from the freeze-dried carpophores) and because of the detection of the same compound in four specimens of 13 collections of American *G. spectabilis* (0.0004%), psilocybin was expected to be an active principle of Japanese *G. spectabilis*. Almost all the specimens of our collections were obtained in a mountainous area (Oguni in Yamagata prefecture, Japan), where the people cook this mushroom in a specific way. They treat the mushroom in boiling water until the bitter principles are transferred to the water layer and, after removal of the fluid, they eat the residual fruiting bodies. Some people have described intoxication as a result of accidental ingestion of incorrectly cooked mushrooms. However, the reported procedures and the use of paper chromatography (PPC), thin layer chromatography (TLC) and HPLC failed to detect psilocybin. Therefore, other constituents were sought in our investigation.

Hatfield and Brady isolated bis-noryangonin from an American specimen (Tenino, Washington) and suggested it to be an active principle because of the structural similarity to α-pyrones found in Kawa, an intoxicating beverage prepared from *Piper methylsticum*.[11] However, Hatfiled and Valdes later found that this compound was inactive at doses of up to 50 mg/kg in rats.[12] Hearn *et al.* reported the isolation of (−)-hepta-1,3-diyn-5-ol from the culture fluid of *G. spectabilis* and its structural elucidation,[13] along with the determination of the absolute configurations.[14]

Experimental[15]

Isolation Procedure——Fresh fruiting bodies (200 g) of *Gymnopilus spectabilis* collected at the mountainous area of Oguni, Yamagata prefecture, in the autumn of 1977 were extracted with MeOH at room temperature three times. The filtered solution was concentrated under reduced pressure and the residual extract was partitioned between AcOEt and water. The AcOEt layer was evaporated to provide the residue (2.1 g). On the other hand, the aqueous layer was concentrated under reduced pressure to half the initial volume and subjected to column chromatography on Amberlite XAD-2. The column was washed with water, and the adsorbed constituents were eluted with MeOH. The solvent was evaporated off under reduced pressure and the residue (0.5 g) was obtained.

The AcOEt extract (2.1 g) was chromatographed on silica gel (50 g) and eluted with mixtures of *n*-hexane–AcOEt and AcOEt–MeOH. Ergosterol (40 mg), mp 160 °C, was obtained as colorless needles from the fraction eluted with *n*-hexane–AcOEt (5 : 1) after recrystallization from AcOEt. The spectroscopic data [MS *m/z*: 396 (M^+), 271, 253. IR ν_{max}^{KBr} cm^{-1}: 3350, 1620. NMR ($CDCl_3$, 100 MHz) ppm: 0.63 (3H, s), 0.84 (6H, d, J=8.0 Hz), 0.92 (3H, d, J=7.0 Hz), 0.94 (3H, s), 1.04 (3H, d, J=7.0 Hz), 3.60 (1H, br s), 5.16—5.30 (2H, m), 5.41 (1H, m), 5.59 (1H, dd, J=1.0, 5.0 Hz)] were identical with those of an authentic specimen.

Ergosteryl peroxide (70 mg), mp 180—182 °C, was obtained as colorless needles from the fraction eluted with *n*-hexane–AcOEt (2 : 1) after recrystallization from AcOEt. The spectroscopic data [MS *m/z*: 428 (M^+), 396. IR ν_{max}^{KBr} cm^{-1}: 3350, 1620. NMR ($CDCl_3$, 60 MHz) ppm: 0.77 (3H, s), 0.85 (6H, d, J=5.0 Hz), 0.88 (6H, s), 0.96 (3H, s), 1.10 (3H, d, J=6.0 Hz), 5.18—5.35 (2H, m), 6.31 (1H, d, J=14.0 Hz), 6.60 (1H, d, J=14.0 Hz)] were identical with those of an authentic specimen.

Cerevisterol (**1**) was obtained as colorless leaflets (12 mg) from the fraction eluted with AcOEt–MeOH (10 : 1) after repeated chromatographies on silica gel and recrystallization from AcOEt. The following data was obtained: mp 251—253 °C. *Anal.* Calcd for $C_{28}H_{46}O_3$: C, 78.14; H, 10.70. Found: C, 77.72; H, 10.74. MS *m/z*: 412 (M^+-H_2O), 394 (M^+-2H_2O), 376 (M^+-3H_2O), 269, 251, 227, 209. IR ν_{max}^{KBr} cm^{-1}: 3400, 1620. NMR (pyridine-d_5 + CD_3OD, 100 MHz) ppm: 0.65 (3H, s), 0.88 (6H, d, J=7.0 Hz), 0.90 (3H, s), 0.96 (3H, d, J=7.0 Hz), 1.07 (3H, d, J=6.0 Hz), 3.61 (1H, m), 4.29 (1H, br d, J=5.0 Hz), 5.20—5.36 (2H, m), 5.74 (1H, br d, J=5.0 Hz).

The fraction eluted with MeOH in the chromatography of the AcOEt extract provided a spot sensitive to Dragendorff's reagent on TLC. The same spot was found in the fraction that passed through the Amberlite XAD-2 column. The combined fractions (26 g) were chromatographed on cellulose (1.3 kg) and eluted with *n*-BuOH saturated with water. The eluted fraction (5.2 g), sensitive to Dragendorff's reagent, was chromatographed on alumina (50 g).

Choline (0.7 g) was obtained as a colorless oil from the fraction eluted with $CHCl_3$–MeOH (4:1). NMR (CD_3OD, 60 MHz) ppm: 3.22 (6H, s), 3.28 (3H, m), 3.50 (2H, m), 4.20 (2H, m). It was identified by comparison of the NMR spectrum and *Rf* value on TLC with those of an authentic specimen.

A new acetylenic compound (**2**) was obtained from the fraction eluted with MeOH from Amberlite XAD-2 after chromatographies on silica gel.

Sufficient of this compound for structural analysis was obtained from another isolation. Fresh fruiting bodies (1.1 kg) of this mushroom collected at Oguni, Yamagata prefecture, in the autumn of 1978 were extracted with hot water three times. The solution was concentrated to 1 l under reduced pressure and the extract was partitioned with AcOEt. The extract was evaporated under reduced pressure to leave the residue (3.9 g). This was chromatographed on silica gel (49 g) and eluted with AcOEt to provide the acetylenic compound (520 mg) in a crude state.

After HPLC (column, 8 mm × 250 mm; packing material, Lichrosorb SI-60; elution, AcOEt with a flow rate of 0.7 ml/min) of a part of the product, compound **2**, t_R 6.1, 30 mg, was obtained as a colorless oil, bp 122 °C (0.4 mmHg). MS *m/z*: 164 ($M^+ - H_2O$). UV λ_{max}^{MeOH} nm (log ε): 256 (3.03), 243 (3.24), 228 (3.32), 220 (3.33). IR ν_{max}^{KBr} cm^{-1}: 3300, 2250, 2150. NMR (CD_3OD, 100 MHz)ppm: 1.06 (3H, t, J=7.0 Hz), 1.76 (2H, quintet, J=7.0 Hz), 1.96 (2H, q, J=7.0 Hz), 3.79 (2H, t, J=6.0 Hz), 4.36 (1H, t, J=6.0 Hz), 4.69 (1H, t, J=6.0 Hz). NMR (pyridine-d_5, 100 MHz) ppm: 1.10 (3H, t, J=7.0 Hz), 1.76 (2H, quintet, J=7.0 Hz), 2.35 (2H, q, J=7.0 Hz), 4.04—4.36 (2H, m), 4.67 (1H, t, J=6.0 Hz), 5.21 (1H, t, J=6.0 Hz).

Acetylation of Cerevisterol (1)——Cerevisterol (5 mg) was dissolved in 2 ml of pyridine, and acetic anhydride (1 ml) was added to the solution. After being stirred overnight at room temperature, the reaction solution was poured into cold water and extracted with AcOEt. Usual treatment (washing the AcOEt layer with water, drying over anhydrous sodium sulfate, removing the drying reagent and evaporation of the solvent) was carried out. The product (**1a**) was obtained as colorless needles (4 mg) after recrystallization from Me_2CO. mp 157—159 °C. MS *m/z*: 454 (M^+ – AcOH), 251, 125. IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1710. NMR ($CDCl_3$, 100 MHz) ppm: 0.61 (3H, s), 0.83 (3H, d, J=6.0 Hz), 0.84 (6H, d, J=7.0 Hz), 0.98 (3H, d, J=4.0 Hz), 1.08 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 4.82 (1H, br d, J=5.0 Hz), 4.92—5.32 (3H, m).

Oxidation of Cerevisterol (1) with Active Manganese Dioxide——Cerevisterol (5 mg) was dissolved in MeOH (5 ml) and activated MnO_2 (3 mg) was added. The mixture was stirred overnight at room temperature. After removal of the precipitate by filtration, the reaction product was subjected to chromatography on precoated thin layer plates. The purified product (**1b**) was obtained as colorless plates (3.5 mg) after recrystallization from AcOEt. mp 247—248 °C. MS *m/z*: 410 ($M^+ - H_2O$), 392 ($M^+ - 2H_2O$). UV λ_{max}^{MeOH} nm (ε): 247 (11800). IR ν_{max}^{KBr} cm^{-1}: 3350, 1670, 1620. NMR (pyridine-d_5, 100 MHz) ppm: 0.63 (3H, s), 0.91 (6H, d, J=7.0 Hz), 1.00 (3H, d, J=7.0 Hz), 1.09 (3H, d, J=7.0 Hz), 1.12 (3H, s), 5.28 (2H, m), 5.93 (1H, s), 7.13 (1H, br s, exchangeable with D_2O).

Oxidation of Cerevisterol (1) with Jones' Reagent——Cerevisterol (4.3 mg) was dissolved in Me_2CO (0.5 ml) and two drops of Jones' reagent were added. The mixture was stirred under cooling on ice for 10 min. After neutralization with $NaHCO_3$, the reaction product was extracted with AcOEt. Usual treatment was carried out and the purified product (**1c**) was obtained as colorless needles (2.6 mg) after recrystallization from AcOEt. mp 232—233 °C. MS *m/z*: 426 (M^+), 408 ($M^+ - H_2O$). UV λ_{max}^{MeOH} nm (ε): 250 (8400). IR ν_{max}^{KBr} cm^{-1}: 3350, 1720, 1670, 1620. NMR ($CDCl_3$, 100 MHz) ppm: 0.64 (3H, s), 0.84 (6H, d, J=7.0 Hz), 0.92 (3H, d, J=7.0 Hz), 1.08 (3H, d, J=7.0 Hz), 1.16 (3H, s), 5.16—5.28 (2H, m), 5.72 (1H, br s).

Oxidation of Ergosterol with Osmium Tetroxide——Ergosterol (248 mg, 0.68 mmol) was dissolved in pyridine (0.5 ml), and OsO_4 (127 mg) was added. The mixture was stirred at room temperature for 3 d. A solution of $NaHSO_3$ (0.25 g) in water (3.8 ml) and pyridine (1.8 ml) was added to the above reaction solution and stirring was continued for another hour. Extraction with $CHCl_3$ and usual treatment provided the reaction products (283 mg), which were chromatographed on silica gel (8 g). 5α-Ergosta-7,22-diene-3β,5α,6α-triol (86 mg) was obtained as colorless leaflets after recrystallization of the fraction eluted with AcOEt–MeOH (10:1). mp 242—244 °C. MS *m/z*: 412 (M^+-H_2O), 394 ($M^+ - 2H_2O$), 379, 269, 251. IR ν_{max}^{KBr} cm^{-1}: 3400. NMR (pyridine-d_5, 100 MHz) ppm: 0.63 (3H, s), 0.88 (6H, d, J=7.0 Hz), 0.93 (3H, d, J=4.0 Hz), 1.02 (3H, d, J=4.0 Hz), 1.13 (3H, s).

Synthesis of 3β,5α-Dihydroxy-5α-ergosta-7,22-dien-6-one from 5α-Ergosta-7,22-diene-3β,5α,6α-triol——5α-Ergosta-7,22-diene-3β,5α,6α-triol (2 mg), which was prepared by oxidation of ergosterol with OsO_4 as mentioned above, was dissolved in $CHCl_3$ (1.0 ml). Active MnO_2 (2.2 mg) was added and the mixture was stirred at room temperature overnight. Removal of the precipitate by filtration and evaporation of the solvent under reduced pressure provided the product, 3β,5α-dihydroxy-5α-ergosta-7,22-dien-6-one (1.8 mg), the spectroscopic data and *Rf* values of which were identical with those of the oxidation product (**1b**) of cerevisterol with active MnO_2.

Synthesis of 5α-Hydroxy-5α-ergosta-7,22-diene-3,6-dione from 5α-Ergosta-7,22-diene-3β,5α,6α-triol——5α-Ergosta-7,22-diene-3β,5α,6α-triol (9 mg) was dissolved in Me_2CO (1 ml) and 5 drops of Jones' reagent were added. The mixture was stirred under cooling on ice for 10 min. Neutralization with $NaHCO_3$ solution was followed by extraction with AcOEt. Usual treatment of the extract provided 5α-hydroxy-5α-ergosta-7,22-diene-3,6-dione (6 mg) as colorless needles, the spectroscopic data and *Rf* value on TLC of which were identical with those of the oxidation product (**1c**) of cerevisterol (**1**) with Jones' reagent.

Synthesis of Cerevisterol (1) from Ergosterol——Ergosterol (200 mg) was dissolved in dried pyridine (6 ml) and

acetic anhydride (3 ml) was added. The mixture was stirred at room temperature for 6 h. Water (10 ml) was added to the above reaction solution and extranction with AcOEt was carried out. The AcOEt layer was washed with $KHSO_4$ solution and then water, and dried over Na_2SO_4. Removal of the drying reagent and evaporation of the solvent left ergosteryl acetate as a crystalline material. This acetate was dissolved in ether solution (20 ml) containing perphthalic acid (400 mg), and the mixture was left at 0 °C for 2 d. The reaction solution was washed with 5% NaOH, and then water, and the ether solution was dried over Na_2SO_4. After removal of the drying agent, the solvent was evaporated off under reduced pressure. The products were chromatographed on alumina (3 g). After elution with benzene, the benzene–ether (1 : 1) eluate yielded 3β-acetoxyergosta-7,22-diene-5α, 6β-diol (53 mg). This monoacetate (34 mg) was dissolved in 5% KOH–MeOH (3 ml), and refluxed for 1 h. The mixture was allowed to cool to room temperature, then extraction was carried out with $CHCl_3$. After usual treatment, cerevisterol (26 mg) was obtained as colorless leaflets, mp 253—255 °C. Its identity was confirmed by mass, NMR and IR spectral comparisons with an authentic sample. No depression was shown in mixed melting point.

Acetylation of 4,6-Decadiyne-1,3,8-triol (2)——Acetic anhydride (1.5 ml) was added to dry pyridine solution (3 ml) containing **2** (137 mg), and the reaction solution was left at room temperature for 12 h. Water was added and the products were extracted with AcOEt (3 × 10 ml). The combined AcOEt layer was washed with water, dil. HCl, $NaHCO_3$ solution and water, then dried over Na_2SO_4. The drying agent was removed and the solvent was evaporated off. The residue was chromatographed on silica gel (10 g). Elution with *n*-hexane–AcOEt (10 : 1) provided an acetate (**2a**, oil, 112 mg). bp 87 °C (0.4 mmHg, bath). MS *m/z*: 248 ($M^+ - AcOH$). NMR ($CDCl_3$, 100 MHz) ppm: 1.00 (3H, t, $J=7.0$ Hz), 1.80 (2H, quintet, $J=7.0$ Hz), 2.06 (3H, s), 2.10 (6H, s), 2.04—2.28 (2H, m), 4.20 (2H, t, $J=6.0$ Hz), 5.35 (1H, t, $J=6.0$ Hz), 5.53 (1H, t, $J=6.0$ Hz).

Catalytic Hydrogenation of the Acetate (2a)——A solution of **2a** (45 mg) in EtOH (5 ml) was stirred under hydrogen gas in the presence of 5% Pd–C (50 mg); 44 ml of hydrogen gas was taken up. The catalyst was removed by filtration and the filtered solution was concentrated under reduced pressure. The residue was chromatographed on Al_2O_3 (5 g). Elution with *n*-hexane–AcOEt (20 : 1) provided an octahydro derivative (**2b**). bp 83 °C (0.4 mmHg, bath). MS *m/z*: 316 (M^+), 287 ($M^+ - C_2H_5$), 256 ($M^+ - AcOH$), 196 ($M^+ - 2AcOH$), 136 ($M^+ - 3AcOH$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1230. NMR ($CDCl_3$, 100 MHz) ppm: 0.86 (3H, t, $J=7.0$ Hz), 2.05 (9H, s, $OCOCH_3 \times 3$), 4.10 (2H, t, $J=7.0$ Hz), 4.90 (2H, quintet, $J=7.0$ Hz).

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15) Melting points were measured using a Yanagimoto micro hot plate and are uncorrected. IR spectra were measured with a Shimadzu IR-27G infrared spectrometer. ^{1}H-NMR spectra were taken with a Hitachi R-20 spectrometer at 60 MHz and a JEOL FX100 at 100 MHz. Chemical shift values are expressed in ppm relative to internal tetramethylsilane. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. MS were measured with a Hitachi M-52 mass spectrometer.