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24-METHYLENE-25-METHYLCYCLOARTANOL AND 24α-ETHYL-5α-CHOLESTAN-3α-OL FROM *NEOLITSEA SERICEA*

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Key Word Index—*Neolitsea sericea*; Lauraceae; triterpene alcohol; sterol; 24-methylene-25-methylcycloartanol; 24α-ethyl-5α-cholestan-3α-ol.

Abstract—A new triterpene alcohol isolated from the stems of *Neolitsea sericea* was shown to have the structure 24-methylene-25-methylcycloartanol. Moreover, in addition to the common triterpene alcohols and sterols, the following uncommon compounds were isolated from the plant material and were identified: (24*E*)- and (24*Z*)-24-ethylidene-cycloartanol, (24*E*)- and (24*Z*)-24-ethylidene-5α-lanost-8-en-3β-ol, 24-methylene-24(25)-dihydroparkeol, 24-methylene-5α-lanosta-7,9(11)-dien-3β-ol, 24-methylenedammarenol, both C-24 epimers of 14α,24-dimethyl-5α-cholest-9(11)-en-3β-ol,14α-methyl-24α- ethyl-5α-cholest-9(11)-en-3β-ol, and 24α-ethyl-5α-cholestan-3α-ol.

INTRODUCTION

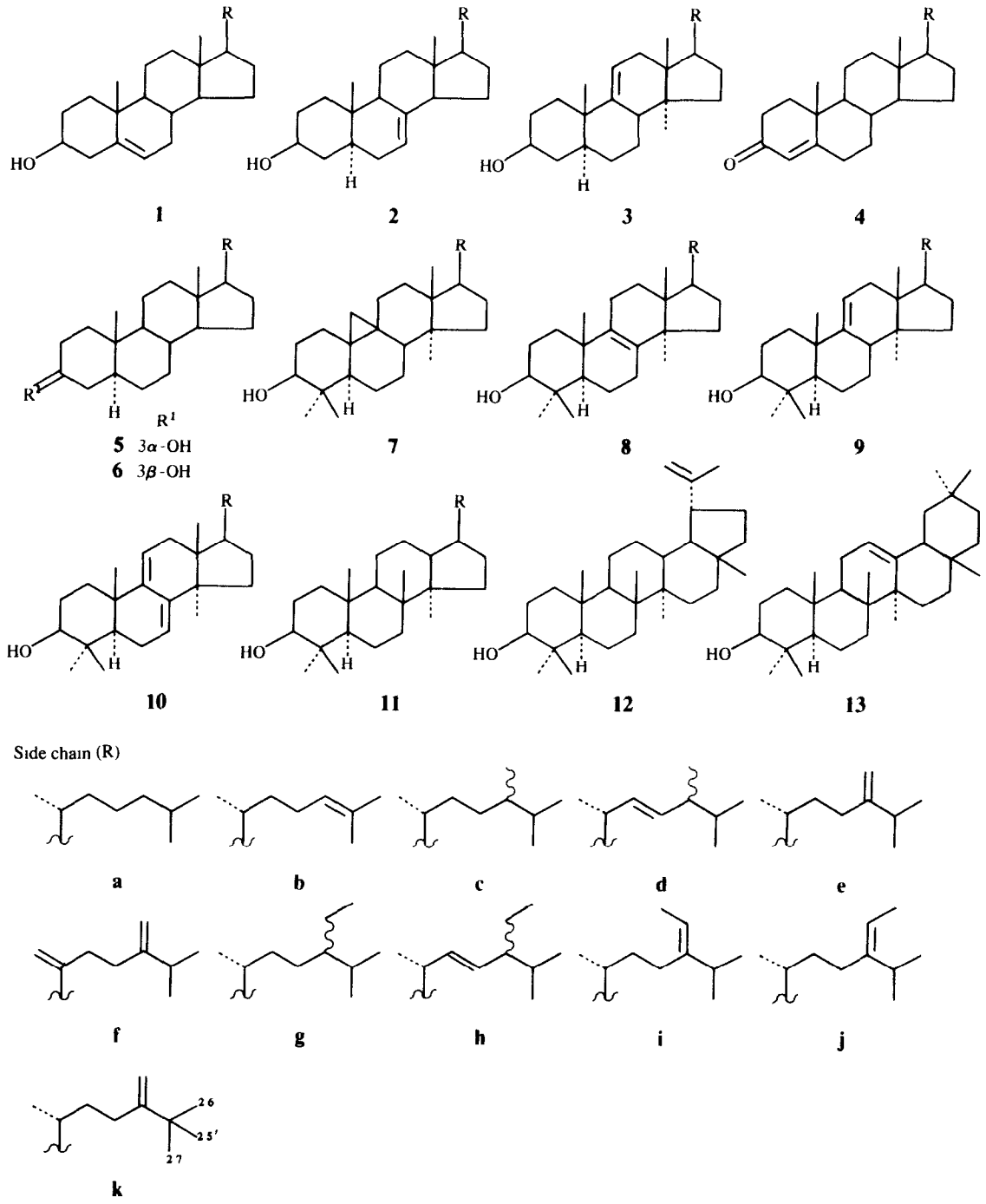
Our recent studies [1, 2] have shown that the unsaponifiable lipid of a stem (bark and heartwood) extract of *Neolitsea sericea* Koidz. (Japanese name: Shirodamo) contains several uncommon and new triterpene alcohols, viz., 24*E*-ethylidene-9β,19-cyclo-5α-lanostan-3β-ol (**7i**), and 24*Z*-ethylidene-9β,19-cyclo-5α-lanostan-3β-ol (**7j**), 24-methylene-5α-lanost-8-en-3β-ol (**8e**), 24*E*-ethylidene-5α-lanost-8-en-3β-ol (**8i**), 24*Z*-ethylidene-5α-lanost-8-en-3β-ol (**8j**), in addition to the common triterpene alcohols. This characteristic feature of *N. sericea* prompted us to undertake more detailed investigation on the unsaponifiable lipid constituents. This paper describes our further study on the triterpene alcohols and sterols from *N. sericea* extract which led to the isolation and characterization of further compounds including 24-methylene-25-methylcycloartanol (**7k**, 24-methylene-25-methyl-9β,19-cyclo-5α-lanostan-3β-ol), a new triterpene alcohol, and stigmastan-3α-ol (**5g**, 24α-ethyl-5α-cholestan-3α-ol).

RESULTS AND DISCUSSION

The composition of the triterpene alcohol fraction of *N. sericea* determined by GC as the acetyl derivative is shown in Table 1. (Two 3-oxosteroids and a 3 α-hydroxy steroid were also included in Table 1 because these compounds exhibited the same mobility as 3β-hydroxy triterpenes on silica gel column chromatography.) The RR_t data on GC and HPLC, and the mp of the acetyl derivatives of the triterpene alcohols are also given in Table 1.

The mass spectrum of **7k**-acetate showed $[M]^+$ at *m/z* 496 ($C_{34}H_{56}O_2$) accompanied with the major fragment ions at *m/z* 481 $[M-Me]^+$, 436 $[M-HOAc]^+$, 421 $[M-Me-HOAc]^+$, 357 $[M-C_{10}H_{19}$ (side chain)$]^+$, 297 $[M-C_{10}H_{19}-HOAc]^+$, and 295 (*m/z* 297−2H), which suggested that this compound was the acetate of a C_{32}-triterpene alcohol with two degrees of unsaturation. The other fragment ions at *m/z* 379 (*m/z* 436-C_4H_9), 338 $[M-HOAc-C_7H_{14}]^+$, 255 [*m/z* 297-C_3H_6 (ring D)], and 241 (*m/z* 255-CH_2) suggested that this had the tetracyclic skeleton with one double bond and a monounsaturated C_{10}-side chain. The peak at *m/z* 338 due to a McLaffety rearrangement involving cleavage of the C-22/C-23 bond with one H transfer from C-20, suggested that the double bond was located in the side chain either at $\Delta^{24(25)}$ or $\Delta^{24(24')}$ [3–5]. The ions at *m/z* 255 and 241 suggested that the additional methyl group in the nucleus was located at C-14 [5, 6]. Moreover, the further ion at *m/z* 314 $[M-C_{11}H_{18}O_2$ (ring A)$]^+$, corresponding to the loss of ring A and characteristic of the 9β,19-cyclo tetracyclic triterpenes [5, 6], suggested the presence of 9β,19-cyclo group in the skeleton. The presence of an ion at *m/z* 379 further suggested that the side chain double bond was located at $\Delta^{24(24')}$. The skeletal proton signals observed in the ^{1}H NMR spectrum of **7k**-acetate at δ0.971 (3H, *s*, H_3-18), 0.342, 0.580 (each 1H and *d*, H_2-19), 0.848 (3H, *s*, H_3-28), 0.890 and 0.904 (each 3H, *s*, H_3-29 and H_3-30), 2.052 (3H, *s*, OAc-3β), and 4.569 (1H, *dd*, H-3α) (Table 2) were almost consistent with the corresponding signals for 24-methylenecycloartanyl (**7e**) acetate, and hence, **7k**-acetate had the cycloartane skeleton. The ^{1}H NMR spectrum of **7k**-acetate showed the side chain signals at δ0.911 (3H, *d*, $J=5.8$ Hz, H_3-21), 1.061 (9H, *s*, H_3-26, H_3-27 and H_3-25′), and 4.667 and 4.836 (each 1H, *d*, $J=1.1$ Hz) (H_2-24′). The *t*-butyl singlet deshielded to δ1.061 suggested the presence of an additional methyl group at C-25 which is linked to the double bond, and the signals were consistent with those of the sterols possessing a 24-methylene-25-methyl side chain structure [7–11]. Thus, triterpene alcohol **7k** was considered to have the structure 24-methylene-25-methylcycloartanol.

Identification of **10e**-acetate was supported by UV, MS and ^{1}H NMR data. A triterpene alcohol with Δ^8-monounsaturated skeleton is known to yield the corresponding $\Delta^{7,9(11)}$-diene upon dehydrogenation with SeO_2–AcOH



[12–14]. Thus, the reference triterpene with a $\Delta^{7,9(11)}$-diene system, 5α-lanosta-7,9(11)-dien-3β-yl (**10a**) acetate, was prepared from 5α-lanost-8-en-3β-yl (**8a**) acetate. Identifications of **4g** and **4h** were based on further mass spectra and ^{1}H NMR data.

The mass spectrum of **5g**-acetate gave $[M]^+$ at *m/z* 458 ($C_{31}H_{54}O_2$) with the major fragment ions at *m/z* 443 $[M-Me]^+$, 398 $[M-HOAc]^+$, 383 $[M-Me-HOAc]^+$, and 257 $[M-HOAc-C_{10}H_{21}$ (side chain)$]^+$, which suggested that this compound was the acetate of a saturated C_{29}-sterol with a C_{10}-side chain. Further ions at *m/z* 355 [*m/z* 398-C_3H_7 (part of side chain)], 255 (*m/z* 257-2H), and 215 (*m/z* 275-HOAc) suggested that this sterol has a tetracyclic skeleton with a C_{10}-side chain. The ion observed at *m/z* 203 $[M-C_{10}H_{21}$ (side chain)$-C_6H_{10}O_2$ (ring A)$]^+$, due to the cleavage of ring A, was typical for sterols with saturated A, B ring system [15]. The ^{1}H NMR spectrum of **5g**-acetate gave the side chain proton signals at δ0.910 (H_3-21), 0.835 (H_3-26), 0.814 (H_3-27), and 0.845 (H_3-24″) which were consistent with the

Table 1. Composition (%), chromatographic data and mp of triterpene alcohols* from *Neolitsea sericea*

Triterpene alcohols*	Composition (%)	Acetate		
		RR_t† on GC	RR_t† on HPLC	Mp
Cycloartenol (**7b**)	1.1	1.87	0.88	122–124°
24-Methylenecycloartanol (**7e**)	40.4	2.07	0.96	116–118°
24*E*-24-Ethylidenecycloartanol (**7i**)	0.9	2.65	1.44	—
24*Z*-24-Ethylidenecycloartanol (**7j**)	0.8	2.77		—
24-Methylene-25-methylcycloartanol (**7k**)	0.8	2.54	1.23	137–139°
24-Methylenelanost-8-enol (**8e**)	15.9	1.76	1.00	146–148°
24*E*-24-Ethylidenelanost-8-enol (**8i**)	0.8	2.25	1.28	148–150°
24*Z*-24-Ethylidenelanost-8-enol (**8j**)	4.7	2.35	1.23	156–157°
24-Methylene-24(25)-dihydroparkeol (**9e**)	2.6	1.99	1.00	156–158°
24-Methylenelanosta-7,9(11)-dienol (**10e**)	1.5	1.72	0.77	183–187°
24-Methylenedammarenol (**11f**)	1.3	1.78	0.75	136–137°
Lupeol (**12**)	14.6	1.92	0.78	222–223°
β-Amyrin (**13**)	6.1	1.65	0.97	241–244°
24α-Ethylcholestan-3α-ol (**5g**)	1.1	1.44	n.d.‡	84–85°
24α-Ethylcholest-4-en-3-one (**4g**)	2.0	1.89	0.48	78°
24α-Ethylcholesta-4,22-dien-3-one (**4h**)	0.7	1.52	0.44	124–126°
Others, unidentified	4.7	—	—	—

*The triterpene alcohol fraction of *N. sericea* contained a 3α-hydroxy (**5g**) and 3-oxosteroids (**4g** and **4h**) in addition to the usual 3β-hydroxy triterpenes, and therefore the former three steroids were also included in this Table.

†RR_t in GC and HPLC were expressed relative to cholesteryl acetate.

‡Not determined.

Table 2. ^{1}H NMR data of some triterpene alcohols isolated from *Neolitsea sericea* (400 MHz, $CDCl_3$; TMS as int. standard)*

Protons	Acetate		
	7k	**10a**†	**10e**
H_3-18 (*s*)	0.971	0.564	0.567
H_2-19 (2 × *d*)	0.342 (4.1)	—	—
	0.580 (4.7)	—	—
H_3-19 (*s*)	—	1.008	1.006
H_3-28 (*s*)	0.848	0.889	0.889
H_3-29 (*s*)	0.890	0.955	0.955
H_3-30 (*s*)	0.904	0.881	0.881
OAc-3β (*s*)	2.052	2.056	2.059
H-3α (*dd*)	4.569 (11.0, 5.8)	4.516 (11.2, 4.9)	4.512 (11.2, 4.9)
H-7 (*m*)	—	5.314	5.320
H-11 (*m*)	—	5.458	5.461
H_3-21 (*d*)	0.911 (5.8)	0.872 (6.8)	0.918 (6.4)
H_3-26 (*d*)	1.061 (*s*)	0.867 (6.8)	1.028 (6.8)
H_3-27 (*d*)		0.867 (6.8)	1.033 (6.8)
H_3-25′ (*s*)		—	—
H-25 (*sept.*)	—	—	2.239 (7.1)
H_2-24′	4.667 (*d*, 1.1)	—	4.667 (*d*, 1.5)
	4.836 (*d*, 1.1)	—	4.721 (*s*)

*Given as δ values. Figures in parentheses denote *J* values (Hz).

†Synthetic compound.

corresponding signals of **1g**-acetate suggesting that **5g**-acetate possessed a 24α-ethyl substituted side chain. The skeletal ^{1}H NMR signals of **5g**-acetate at δ0.654 (H_3-18), 0.787 (H_3-19), 2.052 (OAc-3α), and δ5.008 (H-3β) were consistent with the corresponding signals of 5α-cholestan-3α-yl (**5a**) acetate, thus suggesting that **5g**-acetate possesses a 3α-acetoxy-5α-cholestane skeleton. Hence, **5g** was considered to have the structure 24α-ethyl-5α-cholestan-3α-ol (stigmastan-3α-ol). Alkaline hydrolysis of **5g**-acetate afforded a free sterol **5g**. The ^{1}H NMR

spectrum of sterol **5g** was consistent with the corresponding signals of the same sterol isolated from a marine sponge [16].

Identifications of **7b** (cycloartenol), **7e** (24-methylenecycloartanol), **8i**, **8j**, **12** (lupeol), and **13** (β-amyrin) were by GC, HPLC, and mp data after isolation as the acetyl derivatives [1, 2]. Identifications of **7i** and **7j** were based on the GC data [2]. The identifications of **3c**, **3g**, **9e** and **11f** were supported by MS and ^{1}H NMR data after isolation as the acetyl derivatives.

The composition of the sterol fraction of *N. sericea* determined by GC of the acetyl derivatives is shown in Table 3. The RR_t on GC and HPLC and the mp of the acetates from *N. sericea* are given in Table 3. The ratio of the 24α- and 24β-epimers of **3c**-acetate was estimated to be 81:19 based on the averaged intensity of the relevant ^{1}H NMR signals. 24-Methylcholesterol (**1c**), 24α-ethylcholesterol (**1g**), 24α-ethyl-22-dehydrocholesterol (**1h**), and 24α-ethylcholestanol (**6g**) were identified as the acetyl derivatives by the GC, HPLC, and mp data.

This appears to be the first case of the isolation and characterization of 24-methylene-25-methylcycloartanol (**7k**) although two 4-demethylsterols [8–11] and a 4α-methylsterol [7] possessing a 24-methylene-25-methyl substituted side chain have previously been reported in plants. The occurrence of a sterol possessing a 3α-hydroxy group in the skeleton in higher plants is very rare. *Daemia extensa* R. Br. (Asclepiadaceae) [17] seems to be the only other case in which the occurrence of 3α-hydroxy steroids has been reported. A marine sponge *Esperiopsis edwardii* [16] and marine sediments [18] contain the 3α-hydroxy steroids, cholestan-3α-ol (**5a**) and stigmastan-3α-ol (**5g**). This study constitutes the first case for the detection of stigmastan-3α-ol (**5g**) in a higher plant. 24-Methylene-5α-lanosta-7,9(11)-dien-3β-ol (**10e**) has so far been detected only in *Artabotrys odoritissimus* (Annonaceae) [19], and this study represents its second detection. In addition, this appears to be the second instance for the detection of 24α- and 24β-epimers of 14α,24-dimethyl-5α-cholest-9(11)-en-3β-ol (**3c**) [20] and 14α-methyl-24α-ethyl-5α-cholest-9(11)-en-3β-ol (**3g**) [21] as the natural products. The occurrence of 24α-ethylcholest-4-en-3-one (**4g**) and 24α-ethylcholesta-4,22-dien-3-one (**4h**), has so far been reported in some plants [22–26] and marine organisms [16, 27].

EXPERIMENTAL

Mp: uncorr. Recrystallizations were performed in Me_2CO–MeOH. Prep. TLC on silica gel (0.5 mm thick) of the unsaponifiable lipids were developed ×3 with hexane–EtOAc (6:1). Argentation (silver nitrate–silica gel, 1:4) prep. TLC (0.5 mm thick) was developed ×5 using CCl_4–CH_2Cl_2 (5:1). HPLC: Partisil 5 ODS-2 column (25 cm × 10 mm i.d.), MeOH as a mobile phase (flow rate, 4 ml min^{-1}), RI detector. GC: OV-17 glass capillary column (30 m × 0.3 mm i.d.), column temp. 260°. RR_t values on the HPLC and GC were taken relative to cholesteryl (cholest-5-en-3β-yl) acetate. High resolution EIMS (70 eV): probe. ^{1}H NMR: 400 MHz, $CDCl_3$, TMS as an int. standard. Acetylation: Ac_2O–pyridine at room temp. overnight. Alkaline hydrolysis of sterol acetate: 5% KOH–MeOH at room temp. overnight. UV spectrum was recorded in EtOH (Shimadzu UV-300 spectrometer).

The acetates of the following triterpene alcohols and sterols were used as the reference specimens: **2d** [28, 29], **3c** [20], **3g** [21], **5a** [30], **6g** [31, 32], **9e** [33], **11f** [34].

Extraction and fractionation of triterpene alcohols and sterols. The stems of *N. sericea* were collected at the bank of Akigawa river of Nishi-Tama area of Tokyo. Milled and dried *N. sericea* stems (14 kg) were extracted with CH_2Cl_2 for 8 hr giving extracted lipid (86 g). Saponification of the lipid with 5% KOH in MeOH under reflux followed by extraction with isopropyl ether gave unsaponifiable lipid (22 g). CC of the unsaponifiable lipid on silica gel (300 g) [hexane (1 l), hexane–Et_2O (9:1, 1.5 l, then 4:1, 1.5 l)], hexane–EtOAc [6:1, 3.5 l, then, 2:1, 2 l] gave the triterpene alcohol fr. (5.2 g) and sterol fr. (2.25 g). (The elution was monitored by TLC on precoated silica gel.) The triterpene alcohol fr. was subjected again to CC [silica gel, 200 g; eluent, hexane–EtOAc (6:1, 2 l)] yielding the purified triterpene alcohol fraction (1.28 g) [1, 2]. The triterpene alcohol fraction was acetylated, and the resulting acetate (1.49 g) was subjected to argentation TLC to give 5 major bands (referred to as bands 1–5 in order of polarity, beginning with the least polar). The fr. (49 mg) from band 1 was subjected to further argentation TLC and HPLC which eventually yielded a 3α-acetoxy steroid, **5g**-acetate (1.2 mg), and **13**-acetate (6 mg). The fr. (20 mg) from band 2 was subjected to HPLC and afforded **7b**-acetate (1.1 mg). The fr. (108 mg) from band 3 was subjected to a further argentation TLC which afforded **12**-acetate (6.3 mg), **7e**-acetate (5 mg), a mixture of **8i**- and **8j**-acetate (8.9 mg), and a mixture of **7i**- and **7j**-acetate (1.7 mg). The fraction (318 mg) from band 4 was subjected to a further argentation TLC and HPLC giving **8e**-acetate (12 mg), **7k**-acetate (0.5 mg), **7e**-acetate (30 mg), **4g** (2.6 mg) and **4h** (0.8 mg), respectively. The fr. (173 mg) from the most polar band 5 was subjected to a further argentation TLC and afforded a mixture from which was isolated **10e**-acetate (1.2 mg) (UV λ_{max} nm: 235, 242, 251), **9e**-acetate (1.9 mg), and **11f**-acetate (1.3 mg) was isolated by HPLC. The sterol fraction was acetylated, and the resulting acetate fraction (2.35 g) was crystallized to give crystalline (1786 mg) and filtrate portions. After evaporating the solvent of the filtrate (563 mg), this was subjected to argentation TLC to give 7 bands (referred to bands 1–7). HPLC of the fr. recovered from band 3 yielded **3c**-acetate (2.1 mg) and **3g**-acetate (1.5 mg). The fr. from band 4 on further HPLC afforded **2d**-acetate (2.1 mg). The crystallized portion contained **1c**-, **1g**-, **1h**- and **6g**-acetate of which isolation was undertaken by GC and HPLC.

Synthesis of 5α-lanosta-7,9(11)-dien-3β-yl (**10a**) *acetate from 5α-lanost-8-en-3β-yl* (**8a**) *acetate.* A soln of SeO_2 (2.0 g) in 96% AcOH (40 ml) was added to a soln of **8a**-acetate (1.0 g) in glacial AcOH (286 ml) and mixture refluxed for 4 hr. After the usual work-up and argentation TLC, **10a**-acetate was obtained (0.8 g, RR_t. GC, 1.27). UV λ_{max} nm: 234, 242, 251 (^{1}H NMR: Table 2). MS *m/z* (relative intensity): 468.3959 $[M]^+$ ($C_{32}H_{52}O_2$, 95, requires 468.3964), 453 (18), 408 (10), 393 (26), 365 (2), 355 (8), 313 (25), 295 (13), 253 (50), 239 (13), 43 (100).

24α-Ethyl-5α-cholestan-3α-ol (**5g**). Alkaline hydrolysis of **5g**-acetate (1.2 mg) gave free sterol **5g** (0.5 mg). MS *m/z* (rel. int.): 416 $[M]^+$ (19), 401 (8), 398 (3), 383 (9), 355 (1), 257 (6), 234 (27), 233 (37), 216 (13), 215 (65), 43 (100). (^{1}H NMR: Table 4).

The MS data of the acetates of **3c**, **3g**, **5g**, **7k** and **10e** isolated from *N. sericea* in this study, are given below

Mixture of both C-24 *epimers of* 14α,24-*dimethyl-5α-cholest-9(11)-en-3β-yl* (**3c**) *acetate.* MS *m/z* (rel. int.): 456 $[M]^+$ (14), 441 (85), 396 (3), 381 (23), 329 (3), 287 (6), 273 (6), 269 (6), 227 (8), 213 (7), 43 (100).

14α-*Methyl*-24α-*ethyl-5α-cholest-9(11)-en-3β-yl* (**3g**) *acetate.* MS *m/z* (rel. int.): 470 $[M]^+$ (19), 455 (81), 410 (2), 395 (24), 329 (3), 287 (5), 273 (6), 269 (5), 227 (8), 213 (8), 43 (100).

24α-*Ethyl-5α-cholestan-3α-yl* (**5g**) *acetate.* MS *m/z* (rel. int.): 458.4095 $[M]^+$ ($C_{31}H_{54}O_2$, 12, req. 458.4120), 443.3931 ($C_{30}H_{51}O_2$, 1), 398.3922 ($C_{29}H_{50}$, 64), 383.3675 ($C_{28}H_{47}$, 23),

Table 3. Composition (%), chromatographic data and mp of sterols from *Neolitsea sericea*

Sterols	Composition (%)	Acetate		
		RR_t^* on GC	RR_t^* on HPLC	Mp
24-Methylcholesterol (**1c**)	10.4	1.31	1.14	140–142°
Sitosterol (24α-ethylcholesterol, **1g**)	72.1	1.63	1.29	124–126°
Stigmasterol (24α-ethyl-22-dehydrocholesterol, **1h**)	12.3	1.43	1.10	144–145°
24β-Methyl-22-dehydrolathosterol (**2d**)	0.3	1.36	0.93	170–174°
14α,24-Dimethylcholest-9(11)-enol (**3c**)	0.1	1.50	0.96	84–86°
14α-Methyl-24α-ethylcholest-9(11)-enol (**3g**)	0.1	1.85	0.89	97–98°
24α-Ethylcholestan-3β-ol (**6g**)	2.8	1.65	1.48	130–133°
Others, unidentified	1.9	—	—	—

*RR_t in GC and HPLC were expressed relative to cholesteryl acetate.

Table 4. ^{1}H NMR data of some sterols from *Neolitsea sericea* (400 MHz, $CDCl_3$; TMS as int. standard)*

Protons	Acetate		
	5a‡	**5g**	**5g**†
H_3-18 (*s*)	0.652	0.654	0.651
H_3-19 (*s*)	0.787	0.787	0.777
OAc-3α (*s*)	2.052	2.052	—
H-3β (*br s*)	5.007	5.008	4.038
H_3-21 (*d*)	0.902 (6.6)	0.910 (6.6)	0.908 (6.6)
H_3-26 (*d*)	0.866 (6.6)	0.835 (6.9)	0.834 (6.9)
H_3-27 (*d*)	0.862 (6.6)	0.814 (6.9)	0.813 (6.9)
H_3-24″ (*t*)	—	0.845 (7.5)	0.844 (7.5)

*Given as δ values. Figures in parentheses denote *J* values (Hz).

†Free sterol.

‡Reference compound.

355.3406 ($C_{26}H_{43}$, 1), 344.3466 ($C_{25}H_{44}$, 3), 276.2031 ($C_{18}H_{28}O_2$, 12), 275.1979 ($C_{18}H_{27}O_2$, 12), 257.2260 ($C_{19}H_{29}$, 7), 216.1875 ($C_{16}H_{24}$, 34), 215.1832 ($C_{16}H_{23}$, 65), 203.1774 ($C_{15}H_{23}$, 4), 43.0551 (C_3H_7, 100).

24-Methylene-25-methylcycloartanyl (**7k**) *acetate.* MS *m/z* (rel. int.): 496.4253 $[M]^+$ ($C_{34}H_{56}O_2$, 5, req. 496.4277), 481.4072 ($C_{33}H_{53}O_2$, 4), 436.4032 ($C_{32}H_{52}$, 31), 421.3865 ($C_{31}H_{49}$, 16), 379.3347 ($C_{26}H_{40}O_2$, 2), 357.2802 ($C_{24}H_{37}O_2$, 1), 338.3017 ($C_{25}H_{38}$, 2), 314.2596 ($C_{23}H_{38}$, 9), 297.2581 ($C_{22}H_{33}$, 2), 255.2087 ($C_{19}H_{27}$, 3), 241.1948 ($C_{18}H_{25}$, 2), 43.0173 ($C_2H_3O_1$, 100).

24-Methylene-5α-lanosta-7,9(11)-dien-3β-yl (**10e**) *acetate.* MS *m/z* (rel. int.): 480 $[M]^+$ (60), 465 (6), 437 (2), 420 (3), 405 (8), 377 (3), 355 (6), 313 (9), 295 (4), 253 (19), 239 (7), 43 (100).

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