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# 21-BENZOYL-BARRINGTOGENOL C, A SAPOGENIN FROM *STYRAX OFFICINALIS*

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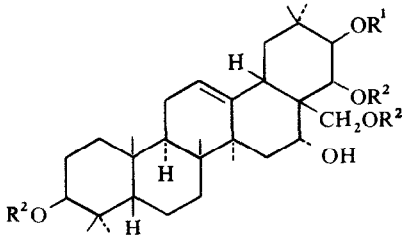
**Key Word Index**—*Styrax officinalis*; Styraceae; saponins; sapogenins; 21-benzoyl barringtogenol C.

## INTRODUCTION

Segal *et al.* [1] isolated a saponin (mp 242°) from the pericarps of *Styrax officinalis* and reported that acid hydrolysis gave a sapogenin of molecular formula $C_{34}H_{48}O_6$ or $C_{34}H_{50}O_6$. We have isolated a saponin (mp 239–242°) from the pericarps of *Styrax officinalis* and now wish to report the structure of its sapogenin as 21-benzoyl-barringtogenol C (**1**).



**1** $R^1$ = Bz; $R^2$ = H
**2** $R^1$ = $R^2$ = H
**3** $R^1$ = $R^2$ = Ac
**4** $R^1$ = $R^2$ = Bz
**5** $R^1$ = Bz; $R^2$ = Ac

## RESULTS AND DISCUSSION

Acid hydrolysis of the saponin gave glucose, galactose, rhamnose and glucouronic acid as well as a sapogenin ($C_{37}H_{54}O_6$, **1**). The IR spectrum of **1** showed a conjugated ester linkage (1715, 1270 $cm^{-1}$). Basic hydrolysis of **1** gave a sapogenol ($C_{30}H_{50}O_5$, **2**) and benzoic acid. Barringtogenol C (theasapogenol B[2]) was found to be identical with **2** by direct comparison by TLC and mmp. The MS and $^1$H NMR spectra of the sapogenol and of its acetate (**3**) and benzoate (**4**) derivatives were also identical with the corresponding spectra of barringtogenol C [3–5].

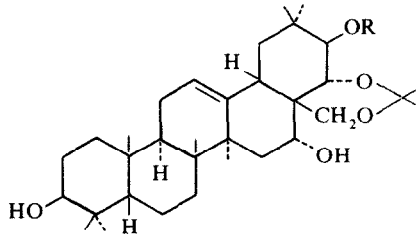
The MS of sapogenin **1** gave peaks at *m/e* 594($M^+$), 386, 368, 264, 246, 215, 207 and 197, which are consistent with the fragmentation pattern of α- and β-amyrin derivatives [3].

Acetylation of **1** gave a triacetate (**5**), $C_{43}H_{60}O_9$, the MS of which showed a molecular ion peak at *m/e* 720. The elemental analysis and MS of both sapogenin **1** and its triacetate (**5**) showed that compound **1** was a monobenzoyl-barringtogenol C.

The signals for the C-16 and C-28 protons in the $^1$H NMR spectra of compounds **3** and **5** had almost identical chemical shifts (Table 1) whereas in the spectrum of compound **4** the signals of the C-28 methylene protons had shifted to δ 4.11 (1H, *d*) and 4.28 (1H, *d*). Also the signal for the C-16 methine proton had shifted to δ 4.68 (1H, *s(br)*). These results indicated that the benzoyl group was esterified to either the C-20 or C-22 hydroxyl groups.

Table 1. $^1$H NMR data of compounds **3–6** (chemical shifts: δ; *J* values: Hz)

| | 12-H | 16β-H | 21α-H, 22β-H | 28-H |
|---|---|---|---|---|
| **3** | 5.44(1H, *m*) | 4.28(1H, *m*) | 5.56(1H, *s*)<br>5.64(1H, *s*) | 3.74(2H, *s(br)*) |
| **4** | 5.54(1H, *s(br)*) | 4.68(1H, *s(br)*) | 6.16(1H, *d*) $J$ = 10<br>6.28(1H, *d*) | 4.14(1H, *d*) $J$ = 12<br>4.28(1H, *d*) |
| **5** | 5.42(1H, *m*) | 4.27(1H, *m*) | 5.60(1H, *d*) $J$ = 10<br>5.84(1H, *d*) | 3.74(2H, *s(br)*) |
| **6** | 5.31(1H, *s(br)*) | 4.84(1H, *s(br)*) | 3.98(1H, *d*) $J$ = 11<br>5.82(1H, *d*) | 3.48(2H, *ABq*) |



**6** R = Bz

The reaction of **1** with 2,2-dimethoxypropane gave an isopropylidene derivative (**6**), $C_{40}H_{58}O_6$. The $^1$H NMR spectrum of **6** showed two doublets for the C-21 and C-22 protons at δ 3.98. (1H, $J$ = 11 Hz) and 5.82 (1H, $J$ = 11 Hz) respectively, which indicated that these protons were *trans*-diaxial. These results showed that the isopropylidene formation involved the primary hydroxyl group. The formation of the isopropylidene derivative and the observation of the large coupling constants ($J$ = 11 Hz) for the C-21 and C-22 protons imply that the secondary hydroxyl group, which was involved in the isopropylidene formation, was bound to C-22 rather than C-21. In order to form a seven-membered isopropylidene ring between C-17 and C-21, a less favoured boat or twist boat conformation of ring E is needed, and in this case a large coupling constant between C-21 and C-22 protons in **6** is not expected [6, 7].

These discussions support both the assumption that the benzoyl group is bound to the C-21 hydroxyl and also the proposed structure of sapogenin **1**.

## EXPERIMENTAL

$^1$H NMR spectra were recorded at 60 MHz in $CDCl_3$ with TMS as internal standard (Table 1). MS were taken at 75 eV. For IR spectra KBr discs were used.

*Isolation of sapogenin* (**1**) *and acetylation to give triacetyl-monobenzoyl-barringtogenol C* (**5**). Air-dried pericarps (400 g) were extracted with 80% EtOH. Evapn of the solvent under red. pres. gave a dark mass (36 g) which was chromatographed on a Si gel column ($CHCl_3$–MeOH–$H_2O$, 65:35:10, lower phase) yielding the saponin in pure state (4.82 g). The saponin (900 mg) was hydrolysed in a mixture of 30 ml 2 N HCl, 10 ml dioxan and 25 ml $C_6H_6$ for 6 hr. The $C_6H_6$ phase was separated and the aq. layer was extracted with $CHCl_3$–MeOH (4:1). The combined organic phases were evapd and the residue was fractionated on a Si gel column ($CHCl_3$–MeOH, 20:1) to give 154 mg of sapogenin (**1**), mp 254–257° (from EtOH); $[\alpha]_D$ + 29.4° (*c*, 0.6 in $CHCl_3$). Found: C, 74.58; H, 9.16. Calc. for $C_{37}H_{54}O_6$: C, 74.71; H, 9.15%). Acetylation of **1** (100 mg) with $Ac_2O$ in Py at room temp. gave an acetate **5** (94 mg), mp 290°–292° (from EtOH); $[\alpha]_D$ + 77.1° (*c*, 0.42 in $CHCl_3$). (Found: C, 71.80; H, 8.30. Calc. for $C_{43}H_{60}O_9$: C, 71.64; H, 8.39%).

*Isopropylidene derivative of sapogenin* (**5**). The sapogenin **1** (100 mg) was dissolved in DMF (6 ml) and 2,2-dimethoxypropane (2 ml) and a few mg of *p*-toluene sulphonic acid were added. The mixture was stirred at room temp. for 24 hr and then diluted with $H_2O$. The product was extracted from this soln with $CHCl_3$. After removal of the solvent the product was purified by PLC ($C_6H_6$–$Me_2CO$, 5:1), 86 mg, mp 182–184° (from MeOH); $[\alpha]_D$ + 9.6° (*c*, 0.72 in $CHCl_3$). (Found: C, 75.48; H, 9.26. Calc. for $C_{40}H_{58}O_6$: C, 75.67; H, 9.20%).

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# COUMARINS FROM *ARTEMISIA APIACEA**

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**Key Word Index**—*Artemisia apiacea*; Compositae; coumarins; 7,8-dimethoxycoumarin; 7,8-methylenedioxycoumarin; 7-methoxycoumarin; phytosterols.

*Artemisia apiacea* Hance (Compositae) is a winter annual plant growing on waste land or on river beaches in Japan. The volatile constituents from the roots of the plant have been isolated by Yano [1]. We now report the isolation of three coumarins and phytosterols obtained from flower heads of the plant. The coumarins are 7,8-dimethoxycoumarin (daphnetin dimethyl ether, **1**), 7,8-methylenedioxycoumarin (daphnetin methylene ether, **2**), 7-methoxycoumarin (herniarin, **3**). The identity of each of the above coumarins was established by direct comparison (mmp, IR and NMR) with synthetic authentic samples [2, 3]. So far, **1** has not been reported as a naturally occurring coumarin.

The results of the comparison with authentic samples by GLC suggested that the phytosterols are campesterol, stigmasterol and sitosterol.

* Part 1 in the series "The Chemical Components of *Artemisia apiacea*".

## EXPERIMENTAL

All mps are uncorr. NMR spectra were recorded at 100 MHz in $CDCl_3$ with TMS as internal standard. GLC was carried out on OV-101, at 240°.

*Plant.* Spikes of *A. apiacea* were collected in Noda, Chiba prefecture, on 29 August, 1976 and dried at room temp. Afterwards, they were divided into flower heads and other parts.

*Extraction and isolation.* Flower heads (1.3 kg) were extracted with hot EtOH (22 l.). The extract, after removal of the solvent, was extracted with *n*-hexane, $Et_2O$ and EtOAc, successively. Each extract was chromatographed on Si gel with *n*-hexane–EtOAc system. Coumarins **1** (3.6 g), **2** (21 mg) and **3** (26 mg) were isolated from the EtOAc extract and phytosterols (75 mg) were isolated from the *n*-hexane extract.

*7,8-Dimethoxycoumarin* (*daephnetin dimethyl ether*) **1**. Colourless needles, mp 114–116° (*n*-hexane–EtOAc), $C_{11}H_{10}O_4$ (Found: C, 64.2; H, 4.9. Calc. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.9%). UV $\lambda_{max}$ nm (95% EtOH): 250, 258, 320. NMR: $\delta$ 3.94 and 3.98 (*s*, 2 OMe), 6.24 and 7.62 (*d*, 3-H and 4-H), 6.86 and 7.18 (*d*, 5-H and 6-H). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2930, 1720, 1610, 1570, 1500, 1300, 1270.