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 λ_{max} nm (95% EtOH): 250, 258, 320. NMR: δ 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 ν_{max}^{KBr} cm^{-1}: 2930, 1720, 1610, 1570, 1500, 1300, 1270.

This was identified as 7,8-dimethoxycoumarin by mmp with an authentic sample.

7,8-*Methylenedioxycoumarin* (*daphnetin methylene ether*) **2**. Colourless needles, mp 180–183° (EtOH, lit. 187–189° [2]), $C_{10}H_6O_4$ (Found: C, 63.4; H, 3.3. Calc. for $C_{10}H_6O_4$ C, 63.2; H, 3.2%). MS (*m/e*): 190 (M^+, base peak); UV λ_{max} nm (95% EtOH): 257, 264, 320. NMR: δ 6.12 (*s*, —O—CH_2—O—), 6.22 and 7.58 (*d*, 3-H and 4-H), 6.76 and 6.98 (*d*, 5-H and 6-H); IR ν_{max}^{KBr} cm^{-1}: 1730, 1715, 1640, 1580, 1500, 1460, 1285, 1050, 930, 840. The mp was not depressed on admixture with authentic 7,8-methylenedioxycoumarin.

7-*Methoxycoumarin* (*herniarin*) **3**. Colourless needles, mp 113–116° (MeOH), $C_{10}H_8O_3$ (Found: C, 67.5; H, 4.3. Calc. for $C_{10}H_8O_3$ C; 68.2; H, 4.6%). MS (*m/e*): 176 (M^+, base peak); UV λ_{max} nm (95% EtOH): 243, 253, 323. NMR: δ 3.88 (*s*, OMe), 6.24 and 7.60 (*d*, 3-H and 4-H), 6.80, 7.32. IR ν_{max}^{KBr} cm^{-1}: 1700, 1620, 1500, 1400, 1350, 1284, 1125. The mp was not depressed on admixture with an authentic 7-methoxycoumarin.

Phytosterols. Colourless needles, mp 136–140° (MeOH). MS (*m/e*): 414 (M^+), 412 (M^+), 400 (M^+). The result of comparison with authentic samples by GLC indicated the presence of campesterol (4.8%), stigmasterol (65.0%) and sitosterol (30.2%).

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A NEW COUMARIN GLUCOSIDE FROM *PRANGOS PABULARIA*

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Key Word Index—*Prangos pabularia*; Umbelliferae; 4-[3-(β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1] benzopyran-7-one; 9-[3-(β-D-glucopyranosyloxy)-2 hydroxy-3-methyl butoxy]-7H Furo [3,2-g] [1] benzopyran-7-one; alloimperatorin methyl ether.

Prangos pabularia Lindl is the only species of the genus found in India in the N.W. Himalayas Range [1]. Earlier workers have shown the presence of some coumarins [2–4]. The residue left after solvent fractionation of the MeOH extract on repeated column chromatography gave a mixture of two compounds BB_1 and BB_2 which could not be separated even by prep. TLC. The mixture was, therefore, subjected to acetylation and on subsequent column chromatography gave BB_1-Ac and BB_2-Ac. Deacetylation of the two gave two compounds, BB_1 and BB_2, mp 250–253° and 196–197°, respectively.

BB_1 analysed for $C_{22}H_{26}O_{11}$, M^+ 466, λ_{max}^{MeOH} 238, 245, 275 and 316 nm. The IR showed bands at 1570, 1600, 1620, 1730 and 3315 cm^{-1}; $[\alpha]_D^{30}$ −30° (H_2O, *c* 0.5). The MS of the compound showed an aglycone fragment ion *m/e* 304 attributable to the loss of a C-3″ *O*-glycosyl moiety. The other prominent fragments were at *m/e* 292, 287, 245, 216, 194 and 145. The compound, on acetylation, formed a pentaacetate indicating the presence of five —OH groups. The IR showed bands at 1725, 1250 and 1550 cm^{-1}. The ^1H NMR ($CDCl_3$) showed signals at δ 1.43 (6H, *s*, side chain *gem* diMe), 2.13 (15H, *m*, 4 acetoxyl groups of sugar moiety and one acetoxyl of the side chain). All the methine and methylene groups of the side chain and the sugar moiety appear as an overlapped complex multiplet between 3.73 and 5.4, 6.31 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 7.1 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.15 (1H, *s*, C_8-H), 7.6 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 8.15 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

The sugar obtained by alcoholic HCl hydrolysis of the glucoside was identified by PC as glucose. Emulsin hydrolysis showed the β-linkage of the sugar moiety and the aglycone. The aglycone which analysed for $C_{16}H_{16}O_6$, mp 134–135° ((±)-oxypeucedanin hydrate, lit. [2, 5] mp 135–135.5°) showed UV fluorescence, λ_{max}^{MeOH} 224, 260, 266 and 310 nm; and IR bands at 3380, 1715, 1580 cm^{-1}, $[\alpha]_D^{30}$ ±0° (MeOH, *c* 1) (lit. [2, 6] $[\alpha]_D^{30}$ ±0° ($CHCl_3$, *c* 2.05). The ^1H NMR ($CDCl_3$) showed signals at δ 1.43 (6H, *s*, C_5-side chain *gem* diMe), 2.53 and 3.2 (2H, *br s*, C_5-sidechain *sec* and *tert* OH, exchangeable with D_2O), 4.03 (1H, *m*, C_5-side chain methine), 4.06 (2H, *m*, C_5-side chain OCH_2), 6.3 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 7.08 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.2 (1H, *s*, C_8-H), 7.7 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H) and 8.35 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

^1H NMR ($CDCl_3$) of the monoacetate of the aglycone showed signals at δ 1.36 (6H, *s*, C_5 *gem* diMe), 2.03 (1H, *br s*, C_5-*tert* OH), 2.1 (3H, *s*, OCOMe of C_5-side chain), 4.65 (2H, *m*, C_5-OCH_2), 5.3 (1H, *m*, C_5-side chain methine), 6.2 (1H, *d*, $J_{3,4}$ = 9 Hz, C_3-H), 6.93 (1H, *d*, $J_{3',2'}$ = 2.2 Hz, $C_{3'}$-H), 7.56 (1H, *d*, $J_{2',3'}$ = 2.2 Hz, $C_{2'}$-H), 7.06 (1H, *s*, C_8-H) and 8 (1H, *d*, $J_{4,3}$ = 9 Hz, C_4-H).

^1H NMR ($CDCl_3$) of the dehydrated product of the monoacetate showed signals at δ 1.9 (3H, *s*, C_5-side chain Me), 2.08 (3H, *s*, C_5-side chain OCOMe), 4.46 (2H, *d*, *J* = 5 Hz, C_5-side chain methylene), 5.1 (2H, *d*, *J* = 5 Hz, C_5-OCH_2), 5.56 (1H, *t*, C_5-side chain methine),