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DIARYLHEPTANOIDS, FLAVONOIDS, STILBENOIDS, SESQUITERPENOIDS AND A PHENANTHRENE FROM *ALNUS MAXIMOWICZII*

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Key Word Index—*Alnus maximowiczii*; Betulaceae; diarylheptanoid; flavonoid; stilbenoid; eudesmane-type sesquiterpenoid; elemane-type sesquiterpenoid; trimethoxyphenanthrene.

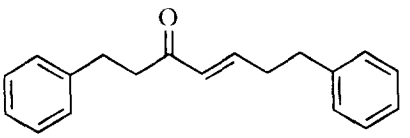
Abstract—The chemical constituents of *Alnus maximowiczii* have been investigated to yield a new diarylheptanoid and a trimethoxyphenanthrene as well as previously known diarylheptanoids, flavonoids and sesquiterpenoid acetates. The new compounds are 1,7-diphenylhept-3-en-5-one and 2,3,4-trimethoxyphenanthrene.

INTRODUCTION

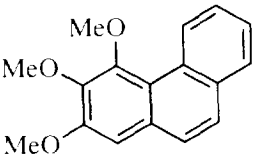
Betulaceae and Zingiberaceae plants are well known to produce a variety of diarylheptanoids, which frequently show significant biological activities [1–23]. Among these, yashabushiketol and dihydroyashabushiketol from *Alnus sieboldiana* are the first examples of this class of compounds [1–4, 6] and received attention of many synthetic chemists [24–28]. We have previously isolated five more compounds, yashabushidiols A and B, yashabushiketodiols A and B and yashabushitriol from *A. sieboldiana* [14]. In a continuation of the chemical study of this plant family, we had a chance to collect *A. maximowiczii* and investigate the constituents of the flowers, buds and leaves. Quite recently a report of isolation of 1,7-diphenylheptane-3,5-dione from *Alpinia conchigera* has appeared [29] and it prompted us to report structures of a new diarylheptanoid, **1**, and a new phenanthrene **2** from *A. maximowiczii*.

RESULTS AND DISCUSSION

The benzene extract of *Alnus maximowiczii* was separated by a combination of silica gel column chromatography, preparative TLC and HPLC to afford 12 compounds. Compound **1** showed a molecular ion peak at *m/z* 264 and the molecular formula was determined to be $C_{19}H_{20}O$ by HRMS. The ^{1}H NMR and IR spectra showed the presence of an α,β-unsaturated carbonyl group (1690, 1680 and 1625 cm^{-1}; δ6.10 (1H, *d*, J = 16 Hz, 4-H), 6.86 (1H, *dt*, J = 16, 6.8 Hz, 5-H)) as well as two phenyl groups (δ7.15–7.29 (10H, *m*)). The structure was determined to be 1,7-diphenylhept-3-en-5-one, which was reported to be obtained by dehydration of dihydroyashabushiketol [6].



1



2

Compound **2** was an aromatic substance. It showed the presence of three methoxyl groups (δ4.02, 4.03, 4.04). The molecular formula was revealed as $C_{17}H_{16}O_3$ by HRMS. These spectral features suggest that this is a phenanthrene derivative. In order to determine the position of the methoxyl group the NOE experiment was performed. When the signal at δ4.02 was irradiated, a significant NOE was observed into a signal at δ7.10. A NOE was also observed for the signal at δ9.50 on irradiation of δ4.03. Aromatic protons were analyzed by decoupling experiments to assign all the signals (see Experimental). Thus **2** was established as 2,3,4-trimethoxyphenanthrene. Although this has been known as a synthetic product [30], this is the first example of isolation from Nature to the best of our knowledge.

Other constituents were identified as dihydroyashabushiketol [1–4, 6], 1,7-diphenyl-hept-1-ene-3,5-dione [11], 1,7-diphenylheptane-3,5-dione [29], pinosylvin monomethyl ether [5], pinosylvin dimethyl ether [5], pinocembrin [5], alnustinol [5], cryptomeridiol 11-*O*-monoacetate [31], β-eudesmol acetate [31] and elemol acetate [31]. It is interesting to note that this plant

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produces specifically sesquiterpenoid acetates and diarylheptanoids. Yashabushiketol found in *A. sieboldiana* has not been detected in *A. maximowiczii*.

EXPERIMENTAL

General. ^{1}H NMR: 400 or 600 MHz. ^{13}C NMR: 100 MHz (in $CDCl_3$ soln. TMS as int. stand.). CC: Silica gel 60 (70–230 mesh, Merck). TLC: silica gel 60 F_{254} plates (Merck).

Plant material. Alnus maximowiczii Call. (Betulaceae) was collected in Shizuoka Prefecture in 1983. The voucher specimen was deposited in Faculty of Pharmaceutical Sciences (Tokushima Bunri University). Aerial part (66.5 g) of *A. maximowiczii* (leaf, flower, bud) was extracted with benzene to afford an extract (7.6 g), which was separated by silica gel column chromatography (hexane–PhH = 1:1, PhH–EtOAc = 19:1, EtOAc and MeOH), preparative TLC and HPLC (Nucleosil Si 50-5, hexane–EtOAc) to give 1,7-diphenylhept-4-en-3-one (**1**) (32 mg), dihydroyashabushiketol (23 mg), 1,7-diphenylhept-1-ene-3,5-dione (5.8 mg), 1,7-diphenylheptane-3,5-dione (13 mg), pinosylvin monomethyl ether (4.5 mg), pinosylvin dimethyl ether (12 mg), pinocembrin (14 mg), alnustinol (9 mg), cryptomeridiol monoacetate (5 mg), β-eudesmol acetate (4 mg), elemol acetate (1 mg) and 2,3,4-trimethoxyphenanthrene (**2**) (4.2 mg).

1,7-Diphenylhept-4-en-3-one (**1**). HRMS: Obs. *m/z* 264.1510 [M^+]. $C_{19}H_{20}O$ requires M 264.1513; *m/z* 264 [M^+], 159, 131, 105 and 91 (base); ν_{max} (CCl_4)/cm^{-1}: 3050, 3010, 1690, 1680, 1625, 1600, 1490, 1450 and 690; ^{1}H NMR ($CDCl_3$, 400 MHz) δ2.50–2.94 (8H, *m*), 6.10 (1H, *d*, *J* = 16 Hz, 4-H), 6.86 (1H, *dt*, *J* = 16, 6.8 Hz, 5-H), 7.15–7.29 (10H, *m*).

2,3,4-Trimethoxyphenanthrene (**2**). HRMS: Obs. *m/z* 268.1135 [M^+]. $C_{17}H_{16}O_3$ requires M 268.1100; *m/z* 268 [M^+], 253, 210, 159, 139 and 91; ν_{max} ($CHCl_3$)/cm^{-1}: 1595, 1460, 1125 and 1080; ^{1}H NMR ($CDCl_3$, 400 MHz) δ4.02 (3H, *s*, OMe), 4.03 (3H, *s*, OMe), 4.04 (3H, *s*, OMe), 7.10 (1H, *s*, 1-H), 7.54 (1H, *ddd*, *J* = 8.0, 7.0, 1.2 Hz, 7-H), 7.62 (1H, *ddd*, *J* = 8.4, 7.0, 1.5 Hz, 6-H), 7.60 (1H, *d*, *J* = 8.8 Hz, 9-H), 7.62 (1H, *ddd*, *J* = 8.4, 7.0, 1.5, 6-H), 7.66 (1H, *d*, *J* = 8.8 Hz, 10-H), 7.84 (1H, *dd*, *J* = 8.0, 1.5 Hz, 8-H), 9.50 (1H, *dd*, *J* = 8.4, 1.2 Hz, 5-H).

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