only been isolated as pure species on rare occasions [10]; they have not been previously reported in the genus *Aristolochia*.

EXPERIMENTAL

GLC, Varian Aerograph Series 2700 (DEGS 5%, 2 m × 1/8″, 150–165°). All analyses were carried out by comparison with synthetic products.

The dried aerial part (without fruits) (5.6 kg) and the dry ground roots (3.5 kg) were extracted with hexane (Soxhlet) to give extracts of 190.4 and 10.1 g, respectively. Both extracts were steam-distilled to separate the volatile components (1.6 and 1.0 g, respectively). 26 g of the hexane extract of the aerial part was chromatographed on silica gel with hexane–Et_2O eluting a mixture of monohydroxylic esters (3.87 g), glycerides (2.21 g), free fatty acids (10.35 g), polyprenols (870 mg) and sitosterol (1.62 g).

Repeated chromatography on silica gel–$AgNO_3$ of 2.10 g of the mixture of monohydroxylic esters, as well as of the mixtures of phytyl-palmitate and -stearate, phytyl-linoleate and -linolenate; and methyl-, ethyl-, isobutyl-palmitate and isobutyl stearate yielded as single species: phytyl palmitate (58 mg), phytyl oleate (82 mg), isobutyl palmitate (306 mg), isobutyl oleate (23 mg), isobutyl linoleate (562 mg) and isobutyl linolenate (202 mg).

The hexane extract of the roots (without essential oil) was fractionated with aq. NaOH (4%) yielding 3.38 g of an acidic fraction. 2.14 g of the neutral fraction was chromatographed on silica gel and silica gel–$AgNO_3$ to give, as well as sitosterol (190 mg) and glycerides (585 mg), ethyl palmitate (56 mg), ethyl oleate (48 mg), ethyl linoleate (92 mg), ethyl linolenate (33 mg), isobutyl esters (103 mg) and traces of methyl palmitate.

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TWO SESQUITERPENE LACTONES FROM *ARTEMISIA* SPECIES

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Key Word Index—*Artemisia feddei*; *A. montana*; Compositae; sesquiterpene lactones; alantolide; guaianolide; himeyoshin; montanone.

Abstract—Two new sesquiterpene lactones, himeyoshin and montanone, were isolated from *Artemisia feddei* and *A. montana*, respectively and identified by chemical and spectral data as 1α,2α-epoxy-3-oxo-5,6-dihydroalantolactone and 1,10-dihydro-11,13-dehydromatricarin.

INTRODUCTION

A previous study of *Artemisia feddei* revealed three sesquiterpene lactones (meridianone, yomogiartemin and yomogin), two coumarins (scopoletin and herniarin) and three steroids (sitosterol, ergosterol and ergosterol-5,8-peroxide) [1]. The present paper reports the isolation and identification of two new sesquiterpene lactones, himeyoshin (**1**) and montanone (**2**) from *Artemisia feddei* and *A. montana*, respectively. In addition, the former plant yielded yomogin, scopoletin, isoscopoletin and sitosterol while the latter yielded yomogin and scopoletin.

RESULTS AND DISCUSSION

The chloroform extract of the aerial parts of *A. feddei* collected in the northern part (Tohoku district) of Japan afforded a new sesquiterpene lactone, **1**, $C_{15}H_{18}O_4$, mp 214–215°. On mass spectral analysis at 70 eV **1** showed *m/z* 262.1206 $[M]^+$ (calculated for $C_{15}H_{18}O_4$: 262.1205) and a diagnostic fragment ion at *m/z* 246 $[M-16]^+$, which indicated the presence of an epoxy group. The UV spectrum exhibited a maximum at 303 nm (ε36) which suggested the presence of a cyclohexanone moiety. The IR spectrum showed characteristic absorptions at 1760 (γ-

lactone), 1705 (cyclohexanone) and 1660 cm^{-1} (exocyclic α-methylene).

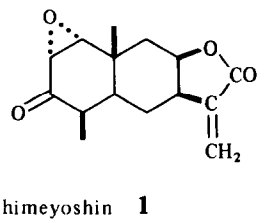
The ^1H NMR spectrum showed: δ 1.08 (3H, *s*, H-15), 1.12 (3H, *d*, *J* = 6 Hz, H-14), 4.60 (1H, *ddd*, *J* = 2, 4.5 and 6 Hz, H-8, alantolide skeleton), 3.26 and 3.36 (each 1 H, *d*, *J* = 4 Hz, AB-system; the chemical shifts of H-1 and H-2, and coupling constant, suggested the presence of a 1,2-epoxide), 5.64 and 6.18 (each 1H, *d*, *J* = 1.5 Hz, H-13 and H-13'). The ^{13}C NMR spectrum showed: δ 63.89 (*d*, C-1) and 56.23 (*d*, C-2) which suggested an epoxy group. Signals at δ 204.67 (C-3) and 76.09 (*d*, C-8) suggested a carbonyl function and the alantolide skeleton, respectively.

Treatment of **1** with NaI, NaOAc and excess Zn afforded 3-oxo-tetrahydroalantolactone, $C_{15}H_{22}O_3$, mp 179–180°, which was in agreement with hydrogenated yomogin [2–4]. Finally, the ORD curve showed a positive Cotton effect, thus indicating that the epoxy group which is attached at C-1 and C-2 has the α-configuration [5].

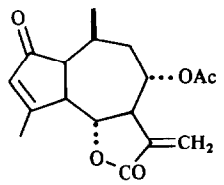
The second new sesquiterpene lactone **2** was isolated by column chromatography from the crude extract of *A. montana*. This compound, **2**, $C_{17}H_{20}O_5$, a colourless gum, on mass spectral analysis at 20 eV showed *m/z* 304 $[M]^+$, and a diagnostic fragment ion (70 eV) at *m/z* 244.1108 $[M - HOAc]^+$ (calculated for $C_{15}H_{16}O_3$: 244.1109) which suggested the molecular formula and the presence of an acetyl group. The IR spectrum showed characteristic bands at 1780 (γ-lactone), 1750 (acetyl νC=O), 1720 (cyclopentenone), 1665 and 1640 cm^{-1} (exocyclic α-methylene and a second double bond). The ^1H NMR spectrum showed: δ 1.29 (3H, *d*, *J* = 6 Hz, H-15), 1.90 (3H, *s*, H-14), 2.18 (3H, *s*, OAc), 3.92 (1H, *t*, *J* = 10 Hz, H-6, guaianolide skeleton), 5.2 (1H, *m*, $W_{1/2}$ = 20 Hz, quasi-axial H-8, an acetyl group fused quasi-equatorial), 5.38 (1H, *s*, H-3, olefine), 5.65 and 6.21 (each 1H, *d*, *J* = 3 Hz, H-13 and H-13', exocyclic α-methylene). Hydrogenation of **2** afforded tetrahydromatricarin, $C_{17}H_{24}O_5$, mp 181–183°, colourless needles [7]. Thus **2** is 1,10-dihydro-11,13-dehydromatricarin.

EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr. UV and ORD spectra were recorded in $CHCl_3$ and MeOH, respectively. NMR spectra were determined at 60 MHz, using TMS as internal standard.



himeyoshin **1**



montanone **2**

The air-dried aerial parts (*ca* 20 kg) of *A. feddei* ('himeyomogi' in Japanese), collected in the northern part (Tohoku district) of Japan, were extracted with $CHCl_3$ and treated in the usual way. The crude extract (70 g) was column-chromatographed (silica gel) and each fraction was collected (100 ml) and checked by TLC in $CHCl_3$–Me_2CO (4:1). Fractions 20–50 gave a gum and crystallized from Et_2O as colourless needles of sitosterol, (10 mg). Fractions 187–189 gave a gum and crystallized from EtOAc as colourless orthorhombic plates, yomogin, (77 mg). Fractions 193–196 were re-chromatographed on a silica gel column with 5% Me_2CO in $CHCl_3$; fractions 1–3 were combined and crystallized from Et_2O as colourless needles, **1**, 25 mg. Fractions 207–209 were combined and crystallized from Et_2O as colourless needles of scopoletin, 10 mg. Fractions 220–233 were combined and crystallized from Et_2O as colourless needles of isoscopoletin, 200 mg. The known compounds agreed in spectral properties, mmp and TLC with authentic samples.

Himeyoshin, **1**, $C_{15}H_{18}O_4$, mp 214–215°, EIMS (probe) 70 eV *m/z* (rel. int.): 262.1206 $[M]^+$ (78.4), 247 $[M-15]^+$ (10.0), 246 (13.1), 233 (93.8), and 219 (100). The ^{13}C NMR ($CDCl_3$) showed: δ 63.89 (*d*, C-1), 56.23 (*d*, C-2), 204.67 (C-3), 37.92 (C-4), 39.99 (C-5), 28.11 (C-6), 43.23 (C-7), 76.09 (C-8), 33.11 (C-9), 37.14 (C-10), 137.31 (C-11), 185.46 (C-12), 121.03 (C-13), 15.52 (C-14) and 16.75 (C-15). ORD (MeOH, *c* 7.63×10^{-3} mol/l., 24.5) data showed positive Cotton effect $[\Psi]_{335}$ +4520 (shoulder), $[\Psi]_{324}^{peak}$ +4847, $[\Psi]_{277}^{trough}$ −2751.

Treatment of **1** (15 mg) with NaI (200 mg), NaOAc (67 mg) and excess Zn (200 mg) at room temp. for 4 hr in the usual manner afforded 3-oxo-tetrahydroalantolactone, $C_{15}H_{22}O_3$, colourless orthorhombic plates, mp 179–180°, 5 mg [2–4]. IR ν_{max}^{KBr} cm^{-1}: 1756 (lactone), 1706 (cyclohexanone). ^1H NMR (60 MHz, $CDCl_3$): δ 1.15 (3H, *d*, *J* = 7 Hz, H-15), 1.16 (3H, *s*, H-14), 1.25 (3H, *d*, *J* = 7 Hz, H-13), 4.48 (1H, *m*, H-8). ^{13}C NMR ($CDCl_3$): δ 214.72, 191.22, 77.59, 48.83, 43.63, 41.56, 40.78, 40.45, 34.35, 32.21, 23.18, 20.13, 13.38 and 9.28.

Hydrogenation of yomogin. A soln of yomogin (50 mg) in EtOAc (30 ml) was hydrogenated on PtO_2 (24 mg) at room temp. After 3 hr the catalyst was filtered and treated in the usual way, and yielded 3-oxo- (10 mg), and 3β-hydroxy-tetrahydroalantolactone, $C_{15}H_{24}O_3$, mp 164–165° (from Et_2O, colourless needles), 20 mg; EIMS (70 eV) *m/z* (rel. unt.): 252 $[M]^+$ (16.9), 234 (17.9), 219 (20.0), 208 (100); IR ν_{max}^{KBr} cm^{-1}: 3500 (νOH), 1740 (lactone); ^1H NMR ($CDCl_3$): δ 0.88 (3H, *d*, *J* = 7 Hz, H-15), 0.98 (3H, *s*, H-14), 1.21 [C_6D_6: 0.98] (3H, *d*, *J* = 7 Hz, H-13), 3.70 (1H, *m*, H-7) and 4.42 (1H, *m*, H-8); ^{13}C NMR ($CDCl_3$): δ 2.3.75, 78.11, 73.83, 44.74, 43.18, 41.56, 40.97, 39.80, 32.33, 25.78, 24.41, 21.33, 9.28 and 8.12; and tetrahydroalantolactone, $C_{15}H_{24}O_2$, mp 143–144°, 5 mg. IR ν_{max}^{KBr} cm^{-1}: 1760 (lactone); ^1H NMR ($CDCl_3$): δ 0.87 (3H, *d*, *J* = 7 Hz, H-15), 0.98 (3H, *s*, H-14), 1.18 (3H, *d*, *J* = 7 Hz, H-13), 2.70 (1H, *m*, H-7), 4.39 (1H, *m*, H-8); (C_6D_6: 1.01, H-13, $\delta_{CDCl_3} - \delta_{C_6D_6}$ = 0.17, quasi-equatorial, hence α-configuration of C-13 bonded methyl group (C-13) [3, 4, 6].

Lactone **2** was isolated by the same method as for **1**, from *A. montana* ('yamayomogi' in Japanese). *A. montana* was collected in the northern part (Tohoku district) of Japan. Montanone, **2**, $C_{17}H_{20}O_5$, colourless gum, EIMS (probe) 20 eV, *m/z* (rel. int.): 304 $[M]^+$ (5), 289 (4), 286 (5) and the diagnostic fragment ion (70 eV) at *m/z* 244.1108 (62). IR ν_{max}^{KBr} cm^{-1}: 1780 (lactoneε), 1750 (acetyl), 1720 (cyclopentenone), 1665 and 1640 (exocyclic α-methylene and second double bond). ^1H NMR ($CDCl_3$): δ 1.29 (3H, *d*, *J* = 6 Hz, H-15), 1.90 (3H, *s*, H-14), 2.18 (3H, *s*, OAc), 3.92 (1H, *t*, *J* = 10 Hz, H-6, guaianolide), 5.2 (1H, *m*, $W_{1/2}$ = 20 Hz, quasi-axial H-8), 5.38 (1H, *s*, H-3), 5.65 and 6.21 (each 1H, *d*, *J* = 3 Hz, H-13 and H-13'). Hydrogenation of **2** with PtO_2 in

EtOAc at room temp. was carried out in the usual way, and afforded tetrahydromatricarin, $C_{17}H_{24}O_5$, mp 181–183°, colourless needles, IR ν_{max}^{KBr} cm^{-1}: 1770 (lactone), 1740 (cyclopentanone and acetyl) [7].

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TOMEXANTHIN, AN OXEPANE DITERPENE FROM *MONTANOA TOMENTOSA**

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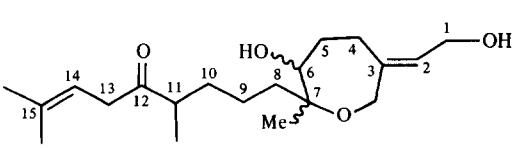
Key Word Index—*Montanoa tomentosa*; Compositae; Heliantheae; oxepane; diterpene.

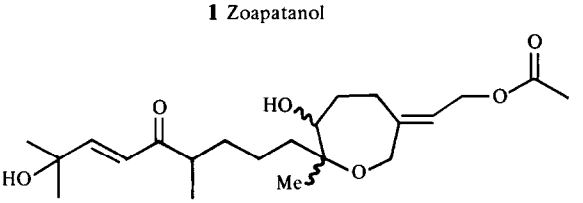
Abstract—Chemical analysis of *Montanoa tomentosa* yielded an oxepane diterpene, tomexanthin, which was characterized by spectral comparison with the previously established zoapatanol.

In continuation of our biochemical systematic analysis of *Montanoa*, the terpenes of *Montanoa tomentosa* Cerv. subsp. *xanthiifolia* (Schultz Bip. in C. Koch) Funk were characterized. In addition to novel sesquiterpene lactones, an oxepane diterpene was isolated which was similar to the known zoapatanol (**1**) a compound of established X-ray structure [1]. Tomexanthin (**2**) differs from **1** by the presence of: (a) an acetyl group at the allylic C-1 position instead of a hydroxyl function, (b) a C-13 double bond instead of one at C-14 and (c) a tertiary hydroxyl group at C-15. The ^1H NMR spectrum of **2** showed the following differences from that of **1**. The two vinyl methyl singlets (δ1.62 and 1.75) of **1** are replaced by a pair of overlapping singlets at δ1.4. A pair of downfield doublets (δ6.38 and 6.92, J = 15.5 Hz) which are characteristic of a *trans*-α,β-unsaturated carbonyl system appear instead of the two signals for H-13 (δ3.12) and H-14 (δ5.47) of **1**. The only other significant difference results from the presence of an acetyl function at C-1 in **2**. Instead of the two-proton doublet (δ4.14) due to H-1a and b of **1** in compound **2** a more downfield absorption at δ4.60 (J = 7 Hz) together with an acetate methyl singlet (δ2.04) appears.

High resolution MS did not yield a molecular ion, but the empirical formula ($C_{22}H_{36}O_6$) was confirmed from the $[M-H_2O]^+$ (378), $[M-C_2H_4O_2]^+$ (336) and $[M-C_2H_4O_2-H_2O]^+$ values. CIMS of **2** confirmed that the molecular weight is 396 ($C_{22}H_{36}O_6$; $[M+1]^+$ = 397). Other significant CIMS peaks occurred at 379 $[M+1-H_2O]^+$, 355 $[M+1-CH_2CO]^+$, 337 $[M+1-AcOH]^+$ and 319 $[M+1-AcOH-H_2O]^+$. Low resolution EIMS produced no molecular ion, but $[M-H_2O]^+$ (378), $[M-CH_2CO]^+$ (354) and $[M-AcOH-H_2O]^+$ (318) characterized the high mass region of the



1 Zoapatanol



2 Tomexanthin

*Part 1 in the series "*Montanoa* Terpenes".