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TERPENOIDS FROM SEEDS OF *ABIES FIRMA*

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Key Word Index—*Abies firma*; Pinaceae; mono-, sesqui- and diterpenoids; 4α-methoxy-selina-11-ene (kongol methyl ether); 11-hydroxy-4α-methoxy-selinane (cryptomeridiol monomethyl ether).

Abstract—Nine monoterpenoids, 16 sesquiterpenoids including two novel compounds, 12 diterpenoids and sitosterol were identified in seeds of *Abies firma*. Two new selinane-type compounds were isolated and their structures were determined as 4α-methoxy-selina-11-ene and 11-hydroxy-4α-methoxy-selinane on the basis of chemical and spectroscopic evidence.

INTRODUCTION

In continuation of our earlier work on chemical constituents of seeds of some species belonging to the Cupressaceae [1–5], we have investigated those of *Abies firma* Sieb. et Zucc. (Pinaceae). This paper deals with the identification of terpenoids as well as the structural elucidation of two new sesquiterpenoids from the seeds.

RESULTS AND DISCUSSION

The neutral and acidic portions of the ether extract were analysed by GC/MS. Compounds identified were α- and β-pinenes, camphene, β-myrcene, limonene, β-phellandrene, *p*-cymene, α-terpineol, longicyclene, longifolene, caryophyllene, α-humulene, γ-muurolene, γ-cadinene, isopimarinal, isopimaric acid, abietinal, abietic acid, dehydroabietinal and dehydroabietic acid. The neutral fraction was subjected to column chromatography and preparative TLC on silica gel. The following compounds were isolated: bornyl acetate, α-, β- and γ-selinenes, farnesyl acetate, farnesol, farnesal, α- and β-eudesmols, manool, 19-acetoxy-manool, torulosol, isopimarinol, abietinol, dehydroabietinol, sitosterol and two new sesquiterpenes, **1** and **2**. All the isolated compounds except **1** and **2** were identified by direct comparison of their IR, ^{1}H NMR and mass spectra with those of authentic samples.

Compound **1**, $C_{16}H_{28}O$, oil, $[\alpha]_D$ −11.8°, IR; 3080, 1640, 890 (vinylidene), 1100 cm^{-1} (ether); ^{1}H NMR: δ4.63 (2H, *br s*, vinylidene), 3.13 (3H, *s*, methoxy methyl), 1.73 (3H, *s*, vinyl methyl), 1.05, 0.92 (each 3H, *s*, tertiary methyl). Compound **2**, $C_{16}H_{30}O_2$, oil, $[\alpha]_D$ −26.1°, IR: 3400 (hydroxyl), 1100 cm^{-1} (ether); ^{1}H NMR: δ3.14 (3H, *s*, methoxy methyl), 1.20 (6H, *s*, hydroxyisopropyl), 1.08, 0.91 (each 3H, tertiary methyl).

Structures **1** and **2** followed respectively from the above spectral data and comparison of the chemical shift of H-15 in the ^{1}H NMR spectra (**1**, δ0.92; **2** δ0.91) with that of known sesquiterpene alcohols, kongol (δ0.88) and cryptomeridiol (δ0.88) possessing 4eq-OH, neo-intermedeol (δ1.04) and epi-cryptomeridiol (δ1.04) possessing a 4ax-OH. The structures of **1** and **2**, including the absolute configurations, were confirmed by the synthesis, starting from β-eudesmol. According to Brown and Rei Min-Hon [6], β-eudesmol was treated with mercury(II) acetate in methanol and then reduced with sodium borohydride to give 11-hydroxy-4α-methoxy-selinane and its epimer at C-4 in a 7:3 molar ratio. The major product, showing the signal of H-15 at δ0.91 in the ^{1}H NMR spectrum, was identical to **2** in all respects (IR, ^{1}H NMR and $[\alpha]_D$). Dehydration of the compound thus obtained with $SOCl_2$ in pyridine afforded **1**.

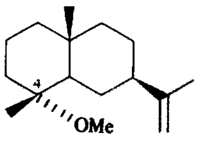
EXPERIMENTAL

^{1}H NMR spectra were recorded with TMS as internal standard in $CDCl_3$. GC/MS was carried out with a 2 m × 3 mm stainless-steel column packed with 10% PEG 20M; temp. programmed 80° to 250° at 5°/min; He 60 ml/min; the mass spectrometer was operated at 20 eV.

Extraction. Seeds (800 g), collected in Chiba Prefecture, Japan, in 1981, were ground and extracted with Et_2O (2 l. × 2). The extract (260 g) was separated into an acidic (10.5 g) and a neutral portion (244 g) in the usual way. The *n*-hexane-soluble part of the neutral fraction (100 g) was chromatographed on silica gel (500 g), eluting successively with hexane, C_6H_6, Et_2O–hexane (1:2), EtOAc and MeOH (each 800 ml).

The hexane eluate (680 mg) was rechromatographed on 5% $AgNO_3$–silica gel (35 g) to give an α- and γ-selinene mixture (23.2 mg) and β-selinene (10.1 mg).

The C_6H_6 eluate (67 g) was shaken with MeOH (100 ml × 2) to remove acylglycerols. The MeOH-soluble fraction (9.1 g) was chromatographed on silica gel (120 g), eluting with $CHCl_3$–hexane (1:3, 400 ml) and C_6H_6 (200 ml) to give three fractions, A, B and C. Fraction A (1.9 g), after saponification with 2 N KOH–EtOH, was purified by prep. TLC (0.7 mm) on silica



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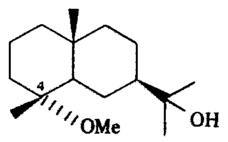

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gel (C_6H_6–hexane, 1:2) to give **1** (7.3 mg); MS m/z (rel. int.): 236 $[M]^+$ (17.2), 204 (23.7), 152 (100), 109 (37.1), 85 (37.1), 75 (47.8). Fractions B and C gave, on repeated chromatography on silica gel, bornyl acetate (11.5 mg) and farnesyl acetate (74 mg), respectively.

The Et_2O–hexane (1:2) eluate (12 g), on chromatography, followed by prep. TLC on silica gel gave farnesol (4.3 g), farnesal (0.5 g), manool (72.4 mg), α- and β-eudesmols (17.4 mg) and a resinous material which, after acetylation with Ac_2O in pyridine, was rechromatographed on silica gel to give acetates of abietinol (20.3 mg), dehydroabietinol (5.3 mg) and isopimarinol (9.9 mg).

The EtOAc eluate (2.6 g) was rechromatographed on silica gel (52 g), to give sitosterol (77 mg) and a resinous material which was subjected to HPLC (LiChroprep RP-8, H_2O–MeOH, 1:9), to give **2** (6.9 mg), 19-acetoxy-manool (9.5 mg) and torulosol (6.5 mg)

Syntheses of **1** *and* **2**. To a soln of β-eudesmol (222 mg) in MeOH (1 ml) was added $Hg(OAc)_2$ (319 mg) with stirring at room temp. After 90 min, 3 M NaOH (1 ml) and 0.5 M $NaBH_4$ in 3 M NaOH (1 ml) were added and stirred for 90 min. The reaction mixture was extracted with Et_2O (10 ml), and the Et_2O extract was washed with brine, dried and evapd, to give a crude product, which was chromatographed on silica gel (4.4 g, EtOAc–C_6H_6, 1:4) to give **2** (77.9 mg) and its epimer (32.0 mg). The synthesized **2** (25.2 mg) was dehydrated with $SOCl_2$ (0.1 ml) in C_6H_6 (5 ml) and pyridine (0.5 ml). The reaction mixture was washed with 5% HCl, brine and dried to give, on chromatography on 5% $AgNO_3$–silica gel (1 g, C_6H_6–hexane, 2:1), **1** (10.4 mg) and 4α-methoxy-selina-7-ene (3.2 mg).

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SESQUITERPENE LACTONES OF *CICHORIUM INTYBUS* AND *LEONTODON AUTUMNALIS**

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Key Word Index—*Cichorium intybus*; *Leontodon autumnalis*; *Sonchus oleraceus*; *S. arvensis*; *Hieracium pilosella*; Compositae; guaianolides; triterpenoids; Zimmermann rule.

Abstract—8-Deoxylactucin, lactucin and lactupicrin were isolated from *Cichorium intybus*. 8-Deoxylactucin and jacquilenin were isolated from *Leontodon autumnalis* and were found in particular abundance in flowers of the latter species. Flowers of *L. autumnalis* do not produce pentacyclic triterpenoid diols. Thus this species is the first noted exception to the Zimmermann rule, which correlates the co-occurrence of triterpenoid diols and carotenoids in flowers of Compositae plants.

Three closely related guaianolides, jacquilenin (**2a**), 8-deoxylactucin (**1a**) and lactucin (**3a**), were isolated as constituents of plants belonging to the tribe Cichorieae of the Compositae [1–4]. 8-Deoxylactucin is relatively active in the HeLa test (ED_{50} 0.26 μg/ml) especially when compared to lactucin, which shows much less activity (7.56 μg/ml) [5].

Cichorium intybus L., already known to produce lactucin [6] and lactupicrin [7], and *Leontodon autumnalis* L. were analysed and 8-deoxylactucin (**1a**) was isolated from both species. *L. autumnalis* contains only 8-deoxylactucin and jacquilenin, other lactones not being detected. Flowers of the latter species contain these lactones at ten-fold the concentration of that in leaves and roots.

The extracts of *Sonchus oleraceus* L., *S. arvensis* L. and *Hieracium pilosella* L. (all collected in the Warsaw area,

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*Part 13 in the series "Terpenes of Compositae Plants"; presented at EUCHEM conference, Lago di Como, Italy (1977). For Part 12 see Pyrek, J. St. (1984) *J. Nat. Prod.* **47** (in press).