3200, 2860, 1680, 1580, 1480; MS *m/z* (%): 164 $[M]^+$ ($C_9H_8O_3$), 149 (100), 147 (8), 135 (18), 121 (15), 93 (33); ^1H NMR (400 MHz, $CDCl_3$): see text.

4-*Hydroxy*-3-(3′-*hydroxyisopentyl*)*acetophenone* (**2**). Colourless needles, mp 100–102° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3360, 3140, 1650, 1600, 1650, 1600, 1580, 1430; MS *m/z* (%): 222 $[M]^+$ ($C_{13}H_{18}O_3$), 207 (9), 205 (6), 189 (54), 161 (17), 149 (76), 133 (28), 43 (100); ^1H NMR (400 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (20 MHz, $CDCl_3$): δ24.82 (*t*, C-2′), 26.19 (*q*, C-4′, C-5′) 29.40 (*q*, Me–CO), 42.85 (*t*, C-1′), 71.98 (*s*, C-3′), 116.02 (*d*, C-5), 129.01 (*d*, C-6), 129.78 (*s*, C-1, C-3), 130.95 (*d*, C-2), 159.48 (*s*, C-4) 184.57 (*s*, Me–CO).

4-*Acetoxy*-3-(3′-*hydroxyisopentyl*)*acetophenone* (**3**). Colourless oil IR ν_{max}^{film} cm^{-1}: 3450, 1760, 1680, 1370, 1210; ^1H NMR (60 MHz, $CDCl_3$): see Table 1.

4-*Acetoxy*-3-(3′-*acetoxyisopentyl*)*acetophenone* (**4**). Colourless oil. IR ν_{max}^{film} cm^{-1}: 1760, 1680, 1580, 1370; ^1H NMR (60 MHz, $CDCl_3$): see Table 1.

Acknowledgements—We thank Professor C. Marticorena of the University of Concepción for botanical classification and F. Bohlmann for 400 MHz ^1H NMR determinations. Financial help from DICYT-BOO3 (Universidad de Antofagasta) is acknowledged.

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TERPENOIDS FROM THE SEED OF *PLATYCLADUS ORIENTALIS*

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Key Word Index—*Platycladus orientalis*; Cupressaceae; diterpenoids; pinusolide; 15,16-bisnor-13-oxo-8(17)-labden-19-oic acid; 15,16-bisnor-13-oxo-8(17),11*E*-labdadien-19-oic acid; 14,15,16-trisnor-8(17)-labdene-13,19-dioic acid; 12*R*,13*RS*-dihydroxycommunic acid.

Abstract—Four labdane-type diterpenoids have been isolated from the seed of *Platycladus orientalis*. Their structures have been elucidated by spectroscopic and chemical methods.

INTRODUCTION

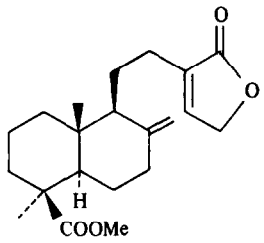
Platycladus is a monotypic genus. The heartwood constituents of *Platycladus orientalis* (L.) Franco (= *Biota orientalis* Endl.) have been extensively investigated [1–5]. We have now investigated the terpenoid components of the seed of this species, from which we have isolated and identified several diterpenoids. This paper deals with the isolation and structural elucidation of these compounds.

RESULTS AND DISCUSSION

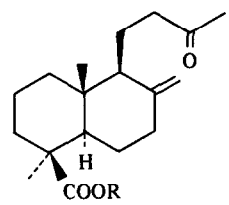
The ethyl acetate extract was fractionated into an acidic and a neutral fraction. The neutral fraction from which acylglycerols had been removed was analysed by GC/MS. The mass spectra revealed the presence of cedrol, sitosterol and pinusolide (**1**), the latter of which was also isolated from the fraction by CC.

The acidic fraction gave two bisnor diterpenoids (A and B), one trisnorditerpenoid (C) and a communic acid derivative (D), as well as *trans*-communic, sandaracopimaric and isopimaric acids.

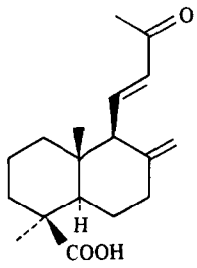
Compound A (**2**) was purified as its methyl ester, after methylation with diazomethane. The methyl ester (**2a**), $C_{19}H_{30}O_3$, $[\alpha]_D^{30}$ +60.6°, MS *m/z*: 306 $[M]^+$ showed IR absorptions at 3080, 1640, 890 (>C=CH_2), 1710 and 1155 cm^{-1} (–COOMe). The ^1H NMR spectrum (Table 1) indicated the presence of two tertiary methyl groups, a methyl ketone group, a methoxycarbonyl group and an exomethylene group. These spectral data suggested that **2** was a bisnor diterpenoid identical with a labdane isolated



1



2 R = H
2a R = Me



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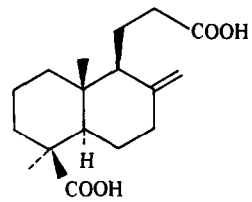

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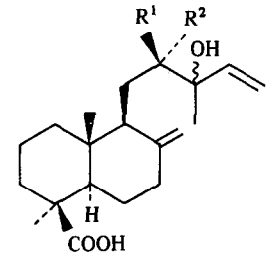

5a R^1 = OH R^2 = H
5b R^1 = H R^2 = OH

from berries of *Juniperus thurifera* by De Pascual Teresa *et al.* [6]. This conclusion was confirmed by its synthesis from (+)-isocupressic acid by epoxidation followed by oxidation with periodic acid. The methyl ester obtained was identical with that of **2** (IR, NMR, $[\alpha]_D$).

Compound B (**3**), oil, $C_{18}H_{26}O_3$, MS *m/z*: 290 $[M]^+$, showed a UV absorption at 226 nm (log ε4.02) and IR absorptions at 3500–2400 (COOH), 1680 (α,β-unsaturated ketone) and 890 cm^{-1} ($>C=CH_2$). The ^1H NMR spectrum (Table 1) indicated the presence of two tertiary methyl groups, a methyl ketone group, an exomethylene group and a *trans*-disubstituted double bond. These data showed that compound B was 15,16-bisnor-13-oxo-8(17),11*E*-labdadien-19-oic acid (**3**).

Compound C (**4**), $C_{17}H_{26}O_4$, MS *m/z*: 294 $[M]^+$, showed IR absorptions at 3500–2400, 1695 (COOH) and 890 cm^{-1} ($>C=CH_2$). The ^1H NMR spectrum (Table 1) indicated the presence of two tertiary methyl groups and an exomethylene group. In the ^{13}C NMR spectrum, the signals at δ179.6 and 183.3 were assigned to two carboxylic groups. The methyl ester prepared by methylation with diazomethane, $C_{19}H_{30}O_4$, MS *m/z* 322 $[M]^+$, $[\alpha]_D$ + 59.3° showed IR absorptions at 1730 and 1160 cm^{-1} (COOMe). The ^1H NMR spectrum indicated the presence of two methoxycarbonyl groups. These spectral data indicated that compound C is 14,15,16-trisnor-8(17)-labdene-13,19-dioic acid (**4**). Oxidation of **2** with sodium iodate afforded a dicarboxylic acid, identical with **4** (MS, ^1H NMR, ^{13}C NMR).

Compound D (**5a**) was purified as the methyl ester after methylation with diazomethane. The methyl ester, $C_{21}H_{34}O_4$, MS *m/z* 350 $[M]^+$, $[\alpha]_D$ + 46.8°, showed IR absorptions at 3450 (OH), 1725, 1160 (COOMe), 995, 925 ($>CH=CH_2$) and 895 cm^{-1} ($>C=CH_2$). The ^1H NMR

Table 1. ^1H NMR spectral data of **2**–**4** and **5a**

H No.	2	3	4	5a
11	—	6.81 *dd* (16, 10)	—	—
12	2.3 *m*	6.04 *d* (16)	2.4 *m*	3.5 *m*
14	2.10 *s*	2.26 *s*	—	5.91 *dd* (10, 17)
15	—	—	—	5.19 *dd* (10, 15)
				5.3 *dd* (17, 15)
16	—	—	—	1.27 *s*
				1.33 *s*
17	4.43 *br s*	4.41 *br s*	4.48 *br s*	4.42 *br s*
	4.83 *br s*	4.79 *br s*	4.84 *br s*	4.81 *br s*
18	1.17 *s*	1.27 *s*	1.24 *s*	1.19 *s*
20	0.50 *s*	0.80 *s*	0.62 *s*	0.50 *s*
MeOC(=O)–	3.61 *s*	—	—	—

Coupling constants (Hz) are given in parentheses.

spectrum (Table 1) indicated the presence of two tertiary methyl groups, a methoxycarbonyl group, an exomethylene group, a vinyl group (ABX system, δ5.19, 5.3 and 5.91) and a secondary alcohol methine group. Additional signals at δ1.27 and 1.33 showed that **5a** was an epimeric mixture at C-13, since the relative intensities of these signals were about 1:1.5 the intensity of the signals at δ0.5 and 1.19 due to methyl groups at C-10 and C-4, respectively. Compound D was assigned the structure 12ξ,13*RS*-dihydroxycommunic acid on the basis of these spectral data. To confirm this structure and to determine the chirality at C-12, conversion of *trans*-communic acid into 12,13-dihydroxycommunic acid via 12,13-epoxycommunic acid was carried out. As a result, two stereoisomers at C-12 were obtained, one of which was identical with D in all respects (IR, ^{1}H NMR, mass spectra).

Recently, the syntheses of methyl (12*S*)- and (12*R*)-12-hydroxylabd-8(17)-en-19-oates have been reported by Bell *et al.* [7], who pointed out the effect of a hydroxyl group at C-12 on the vinylic proton, H-17, in the ^{1}H NMR spectrum; the (12*S*)-isomer showed the vinylic proton signal, H-17, at δ4.72, while the (12*R*)-isomer showed the corresponding proton signal at δ4.40. As the signal of the vinylic proton in **5a** was observed at δ4.42, the chirality at C-12 of **5a** was concluded to be *R*.

The fact that **5a** was isolated as an epimeric mixture at C-13 suggests that compound D might be an artefact derived from 12,13-epoxycommunic acid, although the latter was not detected in the extracts.

EXPERIMENTAL

^{1}H NMR (60 and 100 MHz) and ^{13}C NMR (25.1 MHz): $CDCl_3$, TMS as int. standard; GC/MS: stainless steel column (2 m × 3 mm) packed with 5% OV-17 on Uniport; temp. programmed from 150° to 350° at 5°/min; He gas 60 ml/min; MS: 20 eV.

Extraction and fractionation. Seeds (450 g), imported from the U.S.A. in 1981, were ground and extracted with EtOAc. The extract (89 g) was separated into acidic (7.6 g) and neutral (81 g) portions in the usual way.

The neutral fraction (1.1 g), from which acylglycerols had been removed by treating with cold MeOH, was chromatographed on silica gel, eluting with hexane–Et_2O (1:2) and then Et_2O. The Et_2O eluate afforded pinusolide (21 mg): $[\alpha]_D^{20}$ +66.3° ($CHCl_3$; *c* 0.94), by repeated chromatography on silica gel and prep. TLC.

The acidic fraction (5 g) was chromatographed on charcoal, eluting with H_2O–Me_2CO. The 90% Me_2CO eluate (970 mg), on methylation with CH_2N_2 followed by prep. TLC, gave **2** (4.0 mg): MS *m/z* (rel. int.): 306 $[M]^+$ (12), 246 (39), 121 (100), 43 (24). The 80% Me_2CO eluate (270 mg) gave **3**, **4** and **5a** (76, 76 and 9 mg), respectively, by repeated chromatography on silica gel and prep. TLC. Compound **3**: MS *m/z* (rel. int.): 290 $[M]^+$ (58), 275 (14), 247 (16), 221 (21), 121 (100), 43 (70). Compound **4**: MS *m/z* (rel. int.): 294 $[M]^+$ (23), 248 (73), 221 (47), 167 (62), 121 (100). Methyl ester of **4**: MS *m/z* (rel. int.): 322 $[M]^+$ (11), 262 (47), 181 (15), 121 (100). Compound **5a** was purified as its Me ester: MS *m/z* (rel. int.): 350 $[M]^+$ (11), 314 (4), 279 (24), 236 (37), 201 (46), 181 (17), 121 (100).

Synthesis of **2**. To a soln of (+)-isocupressic acid (218 mg) in $CHCl_3$ (10 ml) was added *m*-chloroperbenzoic acid (153 mg) in small portions. The reaction mixture was stirred at −15° for 140 min and then the product was extracted with Et_2O. The Et_2O extract, after purification by prep. TLC on silica gel (EtOAc–C_6H_6, 3:7), gave 13,14-epoxyisocupressic acid (155 mg) in 68% yield as a colourless oil: ^{1}H NMR (60 MHz): δ3.0 (1H, *t*, *J* = 5 Hz), 1.30 (3H, *s*), 3.73 (2H, *m*). The epoxy acid was treated with NaIO (342 mg) in aq. dioxane at room temp. for 1 hr. After usual work-up, the crude product (134 mg) was subjected to prep. TLC on silica gel (*n*-hexane–Et_2O, 1:1) to give **2** (72 mg) in 58% yield: $[\alpha]_D^{30}$ +52.6° ($CHCl_3$; *c* 1.54); IR ν_{max}^{neat} cm^{-1}: 2400–3500, 1715, 1690, 890. The Me ester of synthetic **2** was identical with natural **2** (IR, ^{1}H NMR, $[\alpha]_D$).

Synthesis of **4**. A soln of **2** (53 mg) in dioxane–H_2O (1:1) (8 ml) was mixed with an alkaline soln of NaOI (12 ml) and stirred at 60° for 90 min. After usual work-up, the crude product (51 mg) was purified by chromatography on silica gel (*n*-hexane–Et_2O, 1:3) to give a dicarboxylic acid (24 mg) in 46% yield: $[\alpha]_D$ +48.0° ($CHCl_3$; *c* 4.69); ^{13}C NMR (25.1 MHz, $CDCl_3$): δ12.7 (*q*, C-20), 19.0 (*t*, C-11), 19.8 (*t*, C-2), 26.0 (*t*, C-6), 29.0 (*q*, C-18), 33.0 (*t*, C-12), 37.8 (*t*, C-3), 38.5, 38.9 (each *t*, C-7 or C-1), 40.4 (*s*, C-10), 44.2 (*s*, C-4), 55.3 (*d*, C-9), 56.2 (*d*, C-5), 106.6 (*t*, C-17), 147.1 (*s*, C-8), 180.7 (*s*, C-19), 184.4 (*s*, C-13). The compound obtained was identical with **4** (MS, ^{1}H NMR, ^{13}C NMR).

Synthesis of **5a**. Methyl *trans*-communate (200 mg) was epoxidized with *m*-chloroperbenzoic acid (148 mg) by the same method as described above to give a mixture of methyl (12*R*,13*R*)- and (12*S*,13*S*)-12,13-epoxycommunates, which were separated from each other by prep. TLC on silica gel (*n*-hexane–Et_2O, 12:1). On treatment with HOAc, the two stereoisomers afforded Me (12*R*,13*RS*)- (**5a**) and (12*S*,13*RS*)-12,13-dihydroxycommunate (**5b**), respectively. The synthetic **5a** was identical with natural **5a**.

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