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DITERPENE RESIN ACIDS FROM THE NEEDLE OLEORESIN OF *PINUS STROBUS*

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Key Word Index – *Pinus strobus*; Pinaceae; needles; resin acids; labdanes; anticopalic acid.

Abstract – The resin acid components of *P. strobus* needles were isolated, and the major constituents identified as labdenoic diterpenes. In addition to anticopalic and strobic acids previously reported in the needles, 3-oxoanticopalic, 3β-acetoxyanticopalic, 3β-hydroxyanticopalic acids and the 8α-hydroxy derivative of anticopalic acid were found along with two new compounds. The structures of the two new compounds, a cycloanticopalic acid and an abeoanticopalic acid, were determined by NMR. The composition of the diterpene resin acids was obtained for several samples of *P. strobus* needles from provenance tests.

INTRODUCTION

Preliminary investigation of the resin acids of *P. strobus* L. needle oleoresin indicated the presence of anticopalic acid (**1a**) in a 60–95% range along with small amounts of common tricyclic resin acids [1]. Strobic acid (**2a**), a major resin acid in the cortex oleoresin [2–4], has been found as a minor component in the needle oleoresin [4, 5]. In analyses of needle samples from other sources, 3-oxoanticopalic acid (**3a**) [4], 3β-acetoxyanticopalic (**4a**) [6, 7], and 3β-hydroxyanticopalic acids (**5a**) [6, 7] were tentatively identified. In addition, two minor components were observed [6]: a labdane resin acid postulated as a cycloanticopalic acid, and an unidentified anticopalic acid derivative.

We have now isolated all of the major resin acids of *P. strobus* needle oleoresin, and have characterized the natural product **3a** (as the methyl ester **3b**) by spectroscopic techniques. In addition, we have isolated five minor components: 3β-acetoxyanticopalic (**4a**), 3β-hydroxyanticopalic acid (**5a**), the 8α-hydroxy derivative of anticopalic acid (**8a**), and the two new compounds previously observed. The new compounds have been characterized, as methyl esters, to be **6b** and **7b** by NMR spectroscopic techniques.

RESULTS AND DISCUSSION

Identification of oxygenated resin acids

Needle samples from a wide geographic range of provenance test trees were analysed by GLC. In addition to the previously found compounds **1a** and **2a**, other resin acid components were observed. Gel permeation chromatography provided an enriched fraction of one component which was recrystallized to give a pure resin acid. The IR spectrum (a carbonyl stretch at 1715 cm^{-1} in addition to the ester carbonyl), mass spectrum (m/z = 332), and ^1H NMR spectrum of the methyl ester were consistent with a methyl oxoanticopalate. A 250 MHz ^1H NMR spectrum had resonances for two protons, one at δ2.59 (*dd*, J = 12.4, 6.5 Hz) and the other at 2.66 (*dd*, J = 12.4, 6.5 Hz) (Table 1) clearly isolated from any other resonances. The AA'BB' splitting pattern and *cis*, *gem* coupling constants were in accordance with nonequivalent ring methylene protons coupled to another nonequivalent ring methylene. Sequential addition of Eu(FOD) substantially shifted tertiary methyl resonances at δ1.02 and 1.10 leaving the remaining tertiary methyl at δ0.87 unaffected. The Eu(FOD) experiment also indicated that only one ring methylene group was adjacent to the oxo function. A long range 2-D carbon–proton correlation experiment gave a three bond coupling between the carbonyl carbon resonance at 216 ppm (Table 2) and both H-18 and H-19. This evidence clearly defines the oxo-substitution at C-3, which is consistent with the C-3 oxygenation in two of the other needle resin acids, **4a** and **5a**. The mass spectrum and physical characteristics were in agreement with previous reports [8, 13].

Gel permeation chromatographic fractions eluting prior to **3b** gave a mixture of acids, which by silica gel chromatography (of the methyl esters) yielded methyl 3β-acetoxyanticopalate (**4b**). The ^1H NMR and ^{13}C NMR spectra of **4b** were in agreement with those reported by Braun and Breitenbach [13]. The corresponding hydroxy acid was purified by silica gel chromatography of a gel permeation fraction, yielding **5a** after recrystallization from methyl *t*-butyl ether–diethyl ether (9:1). The ^1H NMR and mp agreed with the previous report [13]. Since completion of our work, Raldugin *et al.* [8] have reported **3a** in the needle oleoresin of *P. pumila* (Pall.) Regel.; identification was by spectral and physical comparison with the product of Jones oxidation of **5b**. The 3β-

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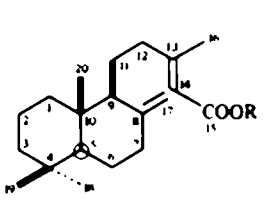

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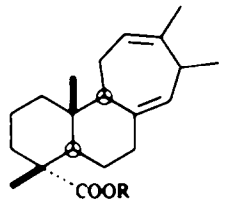
1b R = CH_3



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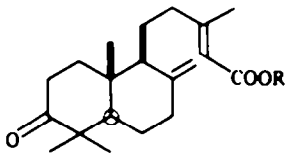

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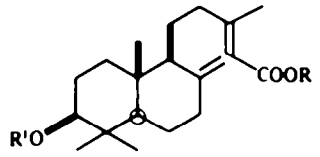
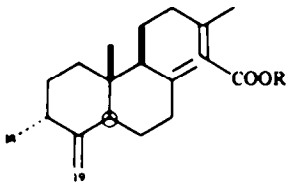
3b R = CH_3



4a R = H, R' = OAc
4b R = CH_3, R' = OAc
5a R, R' = H
5b R = CH_3, R' = H



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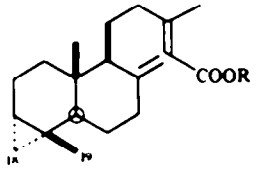
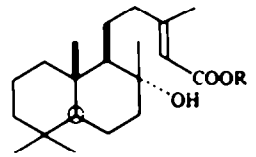
6b R = CH_3



7a R = H
7b R = CH_3



8a R = H
8b R = CH_3

acetoxyanticopalic and 3β-hydroxyanticopalic acids have also been reported in the xylem [14] and foliage [8] of *P. pumila*.

A minor resin acid component (*ca* 1%) of the needle oleoresin (see footnote in Table 3) matched the GLC retention characteristics of a component also observed in cortical oleoresin in the 3–8% range. The compound was isolated from the cortex as the methyl ester by chromatography on $AgNO_3$–silica gel. The physical and spectral characteristics were in agreement with those reported for the methyl ester of a sclareol oxidation product, identified as the 8α-hydroxy derivative of methyl anticopalate, **8b** [16, 17]. We have oxidized sclareol and isolated the corresponding reaction product to confirm this identification. This is the first report of **8a** as a natural product from the genus *Pinus*. It has been reported previously in the trunk resin of the Amazonian leguminous species *Hymenaea courbaril* L. [18]. However, the reported physical and spectral data are not consistent with our results or with those of others (for details, see Experimental).

Identification of two new resin acids

Two unidentified minor components were observed [6] in the needle oleoresin of *P. strobus* and subsequently labelled Unknowns 1 and 2 [7]. On the basis of its molecular weight (M^+ at *m/z* 316 by GCMS), Unknown 2 was postulated to be a cycloanticopalic acid derivative; Unknown 1 was also presumed to be an anticopalic acid derivative.

A crude sample of *P. strobus* needle resin acids was fractionated by gel permeation chromatography. One fraction was methylated and chromatographed on Ag–sulphonic acid resin to yield an enriched fraction of Unknown 1, which was subsequently isolated in high purity by preparative GLC. The ^1H NMR spectrum of Unknown 1 (Table 1, **6b**) contained two exocyclic methylene resonances at δ4.39 and 4.77 in addition to those expected for an 8(17)-labdene. Homodecoupling experiments indicated coupling between an isolated broad 'quintet' (actually a doublet of a quartet) at δ2.54 (J = 7 Hz, 1H), a secondary methyl at δ1.10 (*d*, J = 7.2 Hz), and a partially resolved resonance at *ca* δ1.68. Irradiation at 1.68 ppm gave a doublet of a quartet at δ2.54 (J = 7, 2 Hz); irradiation of the secondary methyl (δ1.10) yielded a broad doublet at δ2.54 (J = 5 Hz, $W_{1/2}$ = 2 Hz). The splitting and broadening of the AM_3XX' pattern indicated that the allylic (A) proton at δ2.54 was coupled to a ring methylene of nonequivalent protons (XX') in addition to the secondary methyl (M_3). The assignment of an α-configuration to the secondary methyl was de-

Table 1. ^{1}H NMR spectral data of compounds **3b**, **6b** and **7b**

	3b*	6b	7b
H-2	2.59 *dd* (12.4, 6.5)	*ca* 1.68	†
	2.66 *dd* (12.4, 6.5)		†
H-3	—	2.54 *br dq* (7, 2)‡	*ca* 0.56 *m*
H-5	*ca* 1.6¶	*ca* 2.1‖	*ca* 1.20 *d* (3)‖
H-6	†	*ca* 1.4‖	*ca* 1.8‖
	†	*ca* 1.8‖	*ca* 1.9‖
H-14	5.65 *q* (1.1)	5.67 *q* (1.2)	5.64 *q* (1.2)
H-16	2.15 *d* (1.2)	2.17 *d* (1.2)	2.14 *d* (1.2)
H-17	4.59 *br s*	4.54 *br s*	4.53 *br s*
	4.93 *br s*	4.91 *br s*	4.88 *br s*
H-18	1.02 *s*¶	1.10 *d* (7.2)	0.04 *dd* (6, 4) αH**
			0.42 *dd* (9, 4) βH
H-19	1.10 *s*¶	4.39 *t* (1.8)	0.92 *s*
		4.77 *t* (1.6)	
H-20	0.87 *s*	0.52 *s*	0.65 *s*
H-21	3.69 *s*	3.69 *s*	3.68 *s*

cf. in CCl_4, ref. [8]
†Shifts are unresolved.
‡Appears as a quintet.
‖Assigned by short range 2-D carbon–proton correlation.
¶Assigned by long range 2-D carbon–proton correlation.
**A supplemental spectrum without TMS ($CHCl_3$ as internal standard) was used to observe the splitting pattern.

termined by NOE difference spectroscopy [19]. Irradiation of an exocyclic methylene proton (4.77 ppm) showed a clear NOE on the allylic proton resonance (δ2.54), with no effect observed on the resonance of the secondary methyl (δ1.10). It follows that the secondary methyl is in an axial (α) configuration. The substitution position of the exocyclic methylene was determined as follows. Irradiation of the other exocyclic proton at 4.39 ppm showed effects of *equal* intensity at *ca* δ1.4 and 1.8 (determined by 2-D carbon–proton correlation to be hydrogens of one ring methylene). The exocyclic methylene must be at C-4 since it is only at this position that the $=CH_2$ plane bisects a neighbouring ring H–C–H bond angle (at C-6) allowing for equal NOE on both ring methylene protons. The structure of methylated Unknown 1, thus, is **6b**. ^{13}C NMR assignments are given in Table 2.

Table 2. ^{13}C NMR spectral data of compounds **1b**, **3b**, **6b** and **7b**

	1b*	3b†	6b†	7b†
C-1	39.3	37.7	33.4	33.1
C-2	19.5	34.7	29.4‡	20.1
C-3	42.3	216.0	38.4	19.3
C-4	33.6	47.8	154.6	16.6
C-5	55.7	26.2	45.9	51.6
C-6	24.6	25.3	27.2‡	28.5
C-7	38.5	38.0	37.7	38.4
C-8	148.4	147.1	148.0	148.8
C-9	56.5	55.4	54.4	52.9
C-10	40.0	39.4	42.2	38.9
C-11	21.8	22.2	22.5	22.6
C-12	40.0	39.7	40.0	40.0
C-13	160.8	160.1	160.6	160.7
C-14	115.2	115.4	115.4	115.1
C-15	167.2	167.1	167.2	167.2
C-16	18.9	18.9	18.9	18.8
C-17	106.4	107.6	107.2	106.9
C-18	33.6	26.2	106.4	21.9
C-19	21.8	21.7	19.9	23.9
C-20	14.6	14.1	11.9	11.7
OMe	50.6	50.7	50.6	50.6

*Assignments of refs [9, 10].
†DEPT [11] and 2-D carbon–proton correlations [12] were used to aid in assignments.
‡Assignments may be interchanged.

A gel permeation chromatographic fraction consisting mainly of Unknown 2 and anticopalic acid (**1a**) was methylated and chromatographed on silica gel to remove small amounts of more polar components. Preparative GLC was subsequently used to isolate Unknown 2 in high purity. The ^{1}H NMR spectrum of Unknown 2 (Table 1) gave two resonances, at δ0.04 (*dd*, J = 6.4, 4 Hz; α-methylene H) and at δ0.42 (*dd*, J = 9, 4 Hz; β-methylene H), and a signal at *ca* δ0.56 (*m*, 1H), all indicative of cyclopropyl hydrogens (*cf.* the related 3,18-cyclopimarane, ref. [20]. A clear NOE between the cyclopropyl α-methylene proton at δ0.04 and H-5 confirmed a 3,18 rather than 3,19 cyclization for Unknown 2 (**7b**); the chemical shift of H-5 (*ca* δ1.20) was determined by 2-D carbon-proton correlation. Cyclization in **1a** between the equatorial C-18 methyl with C-3 is as expected on steric considerations. A-Ring annelated cyclopropyl systems are rare in natural products; only one 3,18-cyclization has been reported previously [20].

Resin acid composition in P. strobus *needles*

In a limited survey of *P. strobus*, several samples of needles were obtained from provenance studies to provide

Table 3. Composition and retention characteristics of resin acids in the needle oleoresin of Eastern white pine

Source*	Resin acid† (% of total)														
	Sand	Comm	Levo	Palu	AbAC	Isop	ACop	Stro	CAC	Abie	Deab	Neo	OAC	HAC	AAC
3407-Va.	1.8	0.3	7.5	3.8	1.8	2.7	22.4	6.4	8.6	0.4	0.2	3.9	37.6	1.0	0.4
3414-N.C.	1.0	0.1	1.4	3.2	2.7	3.9	44.7	0.6	9.6	0.4	0.4	2.5	32.1	0.4	2.7
3420-Tenn.	0.8	0.2	5.1	5.2		3.9	78.1	1.3	-	0.3	0.3	3.4	0.5	tr	tr
3449-Ky.	1.0	0.2	3.0	6.1	2.4	2.0	29.8	1.9	9.3	0.3	0.3	1.6	38.0	1.2	0.8
3458-W.Va.	0.8	0.3	2.8	6.2	1.2	2.6	27.8	0.9	4.9	0.5	0.3	3.1	47.5	1.4	1.4
3481-Md.	1.2	0.3	2.1	2.3	3.1	0.8	34.7	4.1	9.8	0.3	0.2	0.6	33.0	1.0	5.5
1301-Ga.	0.8	0.5	2.3	5.9	2.0	3.6	19.4	1.5	7.0	0.6	0.2	3.5	46.7	2.4	1.7
1313-Mass.	0.8	0.4	0.2	1.8	3.9	1.6	32.5	0.6	12.3	0.4	0.4	1.7	37.0	0.7	5.3
1328-Minn.	0.7	0.2	2.2	2.1	2.1	1.6	25.0	1.6	7.7	0.5	0.2	2.3	47.6	2.1	3.0
1329-Mich.	0.7	0.2	1.7	2.1	tr	0.5	90.5	6.8	1.9	0.4	tr	1.0	0.6	tr	tr
Retention characteristics (r_{para})															
DB-1 (170°)	1.065	1.095	1.282	1.302	1.313	1.230	1.316	1.446	1.460	1.698	1.429	2.027	2.718	3.127	4.750
(190°)	1.057	1.057	1.237	1.237	1.148	1.202	1.249	1.390	1.373	1.596	1.355	1.890	2.435	2.750	3.974
BDS (190°)	1.119	1.291	1.349	1.396	1.482	1.471	1.479	1.697	1.859	2.186	2.285	2.505	9.96	13.40	10.70

* Mature 1985 needles were obtained in December from provenance test trees located in the Michigan State University Kellogg Forest near Augusta, Mich., U.S.A.

† By GLC of methyl esters on DB-1 (methyl silicone) capillary column (170°) with supplementary data from a BDS capillary column (190°), *cf.* ref. [15]. Retention characteristics are for the corresponding methyl ester relative to methyl pimarate. Sand = sandaracopimaric, Comm = communic, Levo = levopimaric, Palu = palustric, AbAC = abeoanticopalic, Isop = isopimaric, ACop = anticopalic, Stro = strobic, CAC = cycloanticopalic, Abie = abietic, Deab = dehydroabietic, Neo = neoabietic, OAC = 3-oxoanticopalic, HAC = 3β-hydroxyanticopalic, and AAC = 3β-acetoxyanticopalic acid. Several components at the *ca* 1% level were also observed. One of these has retention characteristics corresponding to the 8α-hydroxy derivative of methyl anticopalate isolated from the cortex; r_{para} DB-1 (170°) 2.514; (190°) 2.269; BDS 7.887.

some representation of the range of the species (Table 3). The provenance samples appear to fall into one of two chemotypes: (1) an anticopalic or (2) an anticopalic/3-oxoanticopalic type. The proportion of C-3 oxygenated anticopalic acids has been reported [7] to increase during the growing season, resulting in an increase of **5a** (subsequently **4a**) and **3a**. The sequence of oxidation is postulated as **1a** → **5a** → **3a**. As minor components, both **6a** and **7a** may represent side products of the enzymatic oxidation at C-3. Anticopalic acid oxygenation at C-8 also occurs in the needles at *ca* 1% (**8a**; see footnote in Table 3). This compound may be the precursor to the cyclolabdane, strobic acid (**2a**), since both **8a** and **2a** are found in much higher relative proportions in the cortical oleoresin of *P. strobus*. Although the data are not sufficient to provide population/composition correlations, they do indicate the potential for resin acid composition in chemosystematic and genetic studies, particularly with the development of a rapid method for determination of resin acid composition for needles [21].

EXPERIMENTAL

Needle samples were obtained from Michigan State University's W. K. Kellogg Forest near Augusta, Mich. For the isolation sequence, the 3481-Md needles were cut, extracted with Et_2O, and the acids separated by DEAE-Sephadex [22, 23]. Methylations were carried out with CH_2N_2 in Et_2O MeOH (9:1) according to Nestler and Zinkel [24]. Preparative GLC was done with a Hewlett Parkard model 5750 equipped with TCD using a 1/4 in. × 12 ft. (3.7 m) packed column (3% OV-17 on 60/80 mesh chromosorb) under isothermal conditions. For the GLC analysis of resin acid composition in provenance samples (Table 3), the resin acids were first separated from the neutrals of the needle oleoresin by a micro DEAE-Sephadex method [21]. ^{1}H NMR and ^{13}C NMR were obtained with a Bruker spectrometer, controlled by an ASPECT 2000A minicomputer, at 250 and 62.87 MHz, respectively ($CDCl_3$ soln, TMS as internal standard unless otherwise noted). Standard Bruker DISN86 microprograms were utilized for the NOE difference, DEPT and the 2-D carbon proton correlation experiments (XHCORR, short range; COLOC, long range). EIMS (CIMS supplementary) were run on Finnegan model 4510 at 70 and 40 eV.

3-Oxoanticopalic acid [*3-oxo*-8(17),E-13-*labdadiene*-15-*oic acid*, **3a**]. The resin acids from the needle extract were separated by gel permeation chromatography (styragel) [25] with Et_2O to yield **3a** in good purity. After recrystallization from MeOH and heptane, mp 90.8 91.5° (lit. [13] 86 88.5° for synthesized **3a**); $[\alpha]_D^{20}$ + 41.8° ($CHCl_3$; *c* 1.1), lit. [8] + 34.4° ($CHCl_3$; *c* 5.2). Compound **3a** was converted to the Me ester (**3b**). MS (*cf.* with acid in ref. [13]) *m/z* (rel. int.): 332 (32), 317 (31), 301 (24), 285 (22), 258 (92), 243 (27), 215 (13), 201 (28), 191 (12), 187 (12), 175 (18), 173 (17), 163 (24), 150 (26), 133 (46), 125 (33), 121 (52), 114 (74), 109 (43), 107 (50), 105 (35), 95 (59), 55 (100), 53 (38); IR ν_{max}^{film} cm^{-1} (*cf.* ref. [8]): 2955, 2865, 1718 *br* (two bands at 1725 and 1715 in CCl_4), 1652, 1229, 1150, 895. CD: (*c* 0.003, $CHCl_3$) $[\theta]_{345}$ 0°, $[\theta]_{313.5}$ −714°, $[\theta]_{307\,sh}$ −632°, $[\theta]_{283}$ 0°, $[\theta]_{277.5}$ +62°, $[\theta]_{265}$ 0°; ^{1}H NMR and ^{13}C NMR: see Tables 1 and 2.

3β-Hydroxyanticopalic acid [*3β-hydroxy*-8(17),*E*-13-*labdadien*-15-*oic acid*, **5a**]. A fraction eluting prior to the bulk of **3a** contained **5a** as a major component with a mixture of **2a**, **3a** and **4a** eluting simultaneously. Recrystallization from Me *t*-butyl ether–Et_2O (9:1) yielded **5a** (4 mg, 97% by GLC), mp 155.5–156° (evac. cap.; lit. [13] mp 157.5–158.5°); ^{1}H NMR of **5a** and MS of **5b** were identical to lit. [13]. ^{1}H NMR of **5b**: δ0.69 (Me-20), 0.77 and 1.00 (Me-18 and Me-19), 2.15 (*d*, *J* = 1.2 Hz, Me-16), 3.25 (*dd*, *J* = 11, 5 Hz, H-3), 3.69 (OMe), 4.51 and 4.86 (exocyclic $=CH_2$), 5.64 (*d*, *J* = 1 Hz, H-14).

Methyl 3β-acetoxyanticopalate [*methyl 3β-acetoxy*-8(17),E-13-*labdadien*-15-*oate*, **4b**]. A gel permeation chromatographic fraction containing a mixture of **1a**, **4a** and **7a** was methylated and chromatographed on silica gel yielding impure mixtures of **1b** and **7b**, and a purified fraction of **4b** (28 mg, 98% by GLC). MS (GC) *m/z* (rel. int.): 376 (4), 361 (4), 345 (1), 316 (20), 301 (40), 285 (5), 273 (5), 260 (2), 241 (10), 225 (8), 203 (30), 187 (12), 175 (20), 159 (15), 147 (20), 135 (100), 114 (30), 107 (40), 93 (30), 81 (30), 69 (30), 55 (38); ^{1}H NMR and ^{13}C NMR were consistent with those reported for the acid [13].

Methyl abeoanticopalate [*methyl* 18(4 → 3R)-*abeolabda*-4(19),8(17),E-13-*trien*-15-*oate*, **6b**]. An acidic gel permeation chromatographic fraction containing a mixture of **1a**, **5a**, **6a** and **7a** was methylated and chromatographed on Ag-sulphonic acid resin [26] with acetone to yield a **5b**/**6b** mixture, *ca* 1:1 ratio. The **5b**/**6b** mixture was submitted to preparative GLC (OV-17, 250°; t'_R of **6b** = 7 min), and a total of 15 mg of pure **6b** (99% by capillary GC) collected from several runs. $[\alpha]_D^{20}$ + 41.5° ($CHCl_3$; *c* 1.3); MS *m/z* (rel. int.): 316 (35), 301 (70), 285 (10), 269 (12), 242 (70), 227 (20), 215 (5), 203 (35), 187 (23), 175 (53), 161 (32), 147 (47), 135 (40), 119 (38), 114 (60), 107 (60), 93 (100), 79 (58), 67 (52), 55 (68); IR ν_{max}^{film} cm^{-1}: 3080, 2930, 2881, 2850, 1740, 1642, 1435, 1225, 1146, 889, 862; ^{1}H NMR and ^{13}C NMR: see Tables 1 and 2.

Methyl cycloanticopalate [*methyl* 3*S*,18-*cyclolabda*-8(17),E-13-*dien*-15-*oate*, **7b**]. A fraction containing a mixture of **1a**, **4**–**7a** was methylated and chromatographed on silica gel with petrol–Et_2O (99:1) to yield a **1b**/**7b** mixture, which in turn was separated by gas chromatography (OV-17, 240°, t'_R of **7b** = 10 min). A total of 8 mg of 99% **7b** was collected from repeated runs. $[\alpha]_D^{20}$ + 87.5° ($CHCl_3$; *c* 1.4); MS *m/z* (rel. int.): 316 (10), 301 (30), 287 (10), 274 (8), 261 (30), 242 (30), 215 (10), 203 (25), 187 (18), 274 (12), 261 (30), 242 (35), 227 (10), 215 (10), 203 (25), 187 (20), 175 (25), 161 (25), 147 (38), 135 (55), 114 (68), 107 (93), 93 (100), 79 (65), 67 (67), 55 (82); IR ν_{max}^{film} cm^{-1}: 3086 (w); 3055 (w); 2985, 2950, 2869, 1720, 1645, 1225, 1145; ^{1}H NMR and ^{13}C NMR: see Tables 1 and 2.

8α-hydroxy derivative of methyl anticopalate [*methyl* 8α-*hydroxy*-E-13-*labden*-15-*oate*, **8b**]. Cortex oleoresin was fractionated by DEAE-Sephadex to give 190 mg resin acids. The acids were methylated and chromatographed on silica gel with a stepwise gradient of Et_2O–petrol (1:200, increasing to 1:5). A homogeneous fraction by GLC (r_{pim} 2.514 (170°) and 2.269 (190°) on DB-1 and r_{pim} 7.887 (190°) on BDS capillary columns, ref. [15]) eluted in the 1:5 step and was recrystallized from *n*-pentane to give **8b** in high purity, mp 100.6–101.9° (evac. cap. corr.); $[\alpha]_D^{20}$ + 9.6° ($CHCl_3$; *c* 6.0); ^{1}H NMR: δ0.80 (Me-18 and Me-20), 0.87 (Me-19), 1.16 (Me-17), 2.17 (*d*, *J* = 1.3 Hz, Me-16), 3.68 (OMe), 5.69 (*q*, *J* = 1.2 Hz, H-14). For comparison, we isolated both **8a** and its *Z* isomer (mp 130.8 131.8°; $[\alpha]_D^{20}$ + 42.6°; δ1.18 for Me-16 [17]) from the sclareol oxidation [27] product. Our data for the *E* and *Z* isomers are in accordance with those reported by Vlad and Xuan [16] and, with the exception of our larger optical rotation for the *E* isomer, also with that of Bory *et al.* [17, 28]. The + 42° rotation in combination with the ^{1}H NMR resonance for Me-16 at δ2.18 reported [18] for the compound isolated from *H. courbaril* conflict with the above.

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