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Article

Absolute Configuration of some Dinorlabdanes from the Copaiba Oil

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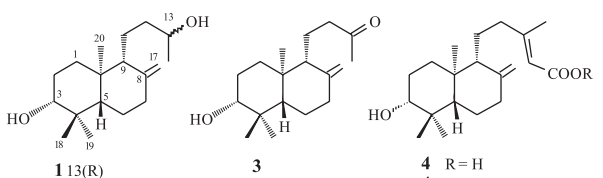
Um novo *ent*-dinorlabdano (–)-13(*R*)-14,15-dinorlabd-8(17)-eno-3,13-diol foi isolado a partir do óleo de copaíba comercial juntamente com dois outros dinorditerpenos conhecidos. A configuração absoluta destes dinorditerpenos foi determinada pela primeira vez através de síntese partindo do ácido (–)-3-hidróxi-copalico isolado do mesmo óleo.

A novel *ent*-dinorlabdane (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol was isolated from commercial copaiba oil along with two known dinorlabdanes. The absolute configuration of these dinorditerpenes was established for the first time through synthesis starting from known (–)-3-hydroxycopalic acid, which was also isolated from the same oleoresin.

Keywords: Copaiba oil, dinorditerpenes, absolute configuration

Introduction

Copaiba oil is a resin exudate obtained from the *Copaifera* sp. tree (*Fabaceae-Caesalpinoideae*) distributed throughout the Amazon basin.[1] This resin is commonly used in folk medicine to treat inflammations and tumors, especially in northern Brazil.[2,3] In early investigations, diterpenes belonging to the clerodane,[4,5] *ent*-labdane,[6] labdane[5,7] and *ent*-kaurane[8,9] skeletons were isolated from copaiba oil and recently, the presence of dinorditerpenes[10-12] was reported. This paper describes the isolation and structural elucidation of three dinorditerpenes, each bearing a small excess of the levorotatory enantiomer. The new (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**) was isolated together with known (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3β,13-diol (**2**) and (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**),[10,11] and additional diterpenes previously described in the literature[6] (Figure 1). The absolute configurations of diols (–)-**1** and (–)-**2** and hydroxyl-ketone (–)-**3** were elucidated through total synthesis beginning from (–)-3-hydroxycopalic acid (**4**). The stereochemistry of the carbinolic carbon at C-13 of **1** and **2** was established through analysis of ^{1}H NMR spectra of (*S*)-α-methoxyphenylacetate derivatives.



1 13(R)
2 13(S)

3

4 R = H
4a R = CH_3

Figure 1. Structures of dinorlabdanes **1**-**3** and (–)-3-hydroxycopalic acid (**4**).

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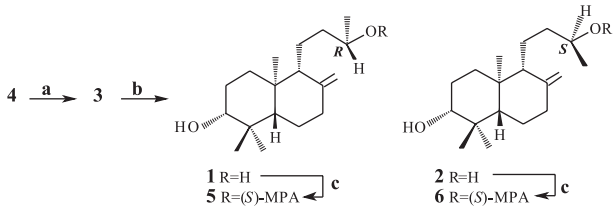
Results and Discussion

The commercial copaiba oleoresin was fractionated as described in the Experimental Section. Successive column chromatography on SiO_2 of the neutral fraction employing a gradient of petroleum ether and Et_2O, furnished two known *ent*-dinorlabdanes. These were characterized as (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**) {oil, $[\alpha]_D^{20}$ −1.3° (*c* 1.6, $CHCl_3$), lit.[10] $[\alpha]_D^{20}$ −1.0° (*c* 1.4, $CHCl_3$)} and (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**) {oil, $[\alpha]_D^{20}$ −1.0° (*c* 1.7, $CHCl_3$), lit.[11] $[\alpha]_D^{20}$ −1.7° (*c* 0.7, $CHCl_3$)}. All other spectral data for both compounds matched those previously reported in the literature.[10,11] A third *ent*-dinorlabdane, identified as the novel (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**), was isolated as colorless crystals, mp 165.0-166.5 °C, $[\alpha]_D^{20}$ −1.3° (*c* 1.1, $CHCl_3$). The HREIMS spectrum indicated a molecular formula of $C_{18}H_{32}O_2$ (*m/z* 281.2484, $[M+H]^+$) and the IR spectrum showed characteristic absorptions of a hydroxyl group at 3333 cm^{-1} and an exocyclic double bond at 2930, 1642, and 885 cm^{-1}. The contour of the ^{1}H NMR spectrum of **1** was nearly superimposable on that of **2** and displayed three methyl group singlets at δ 0.70, 0.78 and 1.00, and one

methyl group doublet at δ 1.18 (J 6.2 Hz). The presence of two characteristic exocyclic methylene hydrogens was also confirmed as singlets at δ 4.56 and 4.85, and two carbinolic hydrogens at δ 3.25 (dd, J 11.5, 4.6 Hz) and δ 3.77 (m) were also present. The ^{13}C NMR spectra displayed resonances for the four methyl groups at δ 14.4, 15.4, 23.7 and 28.3, for the exocyclic methylene carbons at δ 147.9 and 106.9, and for the two carbinolic carbons at δ 68.4 and δ 78.8. Based on these spectroscopic data and considering their similarity with those of compound **2**, structure **1**, a C-13 epimer of **2**, was proposed. To confirm the structure and subsequently elucidate the absolute configuration of any of the natural dinorlabdanes, the synthesis of the dinorlabdanes **1**-**3** was undertaken starting from known (–)-3-hydroxycopalic acid (**4**),[6] isolated from the same oleoresin (Scheme 1).



Scheme 1. a) $KMnO_4$, acetone, 80%; b) $LiAlH_4$, Et_2O, 95%; c) (S)-(+)-methoxyphenylacetic acid, DCC, 85% for **5** and 90% for **6**.

The synthesis began with (–)-3-hydroxycopalic acid (**4**) {colorless crystals, mp 153-155 °C, $[\alpha]_D^{20}$ −38.3° (*c* 0.8, $CHCl_3$), lit.[6] mp 158-160 °C, $[\alpha]_D^{20}$ −38.7° (*c* 3.0, $CHCl_3$)}, which was submitted to an oxidative cleavage of the side chain with $KMnO_4$.[13] After work-up and purification on SiO_2 (hexane:EtOAc, 85:15), keto-alcohol **3** was obtained in 80% yield. All spectroscopic data of **3** were identical with those reported for the natural product, except for the optical rotation, for which a higher value was observed for the synthetic product {$[\alpha]_D^{20}$ −8.8° (*c* 1.5, $CHCl_3$) and $[\alpha]_D^{20}$ −1.3° (*c* 1.6, $CHCl_3$) for the natural product}, [lit.[10] $[\alpha]_D^{20}$ −1.0° (*c* 1.4, $CHCl_3$)]. Next, the reduction of synthetic keto-alcohol **3** with $LiAlH_4$ and purification on SiO_2 (petroleum ether : Et_2O; 9:1) furnished epimeric diols **1** and **2**. The less polar diol was isolated with a 49% yield as colorless crystals, mp 165.0-167.0 °C, $[\alpha]_D^{20}$ −27.0° (*c* 1.1, $CHCl_3$) {natural product proposed as **1**: mp 165.0-166.5 °C, {$[\alpha]_D^{20}$ −1.3° (*c* 1.1, $CHCl_3$)} and the more polar diol (46% yield) was also isolated as colorless crystals, mp 169.5-171.0 °C, $[\alpha]_D^{20}$ −12.0° (*c* 1.7, $CHCl_3$) {natural product identified as **2**: oil, $[\alpha]_D^{20}$ −1.0° (*c* 1.7, $CHCl_3$), lit.[11] $[\alpha]_D^{20}$ −1.7° (*c* 0.7, $CHCl_3$)}. All spectroscopic data for both synthetic diols (**1** and **2**) were in agreement with those observed for the natural products, except for the optical rotation for which a higher value was observed for the synthetic products. Finally, in order to establish the absolute configuration of the carbon at C-13 of diols **1** and **2**, the C-13 (*S*)-(+)-α-methoxyphenylacetate derivatives **5** and **6** were prepared in 90% and 85% yield, respectively, using Trost´s protocol.[14] According to the Trost model, the ^{1}H NMR chemical shift of the methyl group at C-16 of ester **5** was observed at δ 1.12 (upfield) and the C-16 methyl group of ester **6** was observed at δ 1.21 (downfield), indicating the absolute configuration of carbon C-13 for isomer **5** as *R* and for isomer **6** as *S* (Figure 2). No signals corresponding to the diastereoisomeric ester prepared from the possible enantiomer of acid **4** were observed.

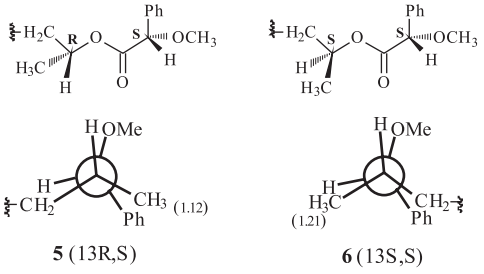


Figure 2. Trost model for the (S)-(+)-α-methoxyphenylacetate derivatives **5** and **6**.

Reduction of a sample containing natural dinorlabdane **3** with $LiAlH_4$ also yielded the C-13-epimeric diols **1** and **2** with the same absolute value for the optical rotation observed for the isolated natural products. Thus, in the present investigation we observed that dinorditerpenes **1**-**3** are present in the resin as a mixture of enantiomers. At this point, the (–)-3-hydroxycopalic acid (**4**)[15] was considered enantiomerically pure since the optical rotation was comparable with that reported for the enantiomer isolated from the leaves of *Metasequoia glyptostroboids*,[16] {mp 157.5-158.5 °C, $[\alpha]_D^{20}$ +40.7° (*c* 2.0, $CHCl_3$)} and for the corresponding methyl ester derivative isolated from the needles of *Pinus pumila*[17] {$[\alpha]_D^{20}$ +36.0° (*c* 13.0, $CHCl_3$); for methyl (–)-3-hydroxycopalate (**4a**), $[\alpha]_D^{25}$ −35.0° (*c* 2.0, $CHCl_3$)}.

Experimental

General

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ solution on an INOVA 500 spectrometer, with δ (ppm), J in Hz, and spectra referred to $CDCl_3$ (δ 7.27 for ^{1}H and 77.0 for ^{13}C) as an internal standard. IR spectra of neat samples or as a KBr disk were measured using a Perkin-Elmer 1600 series FTIR. The mass spectra of purified compounds were recorded with a Hewlett-Packard 5890 GC equipped with a Model 5970 mass-selective

detector. Optical rotations were measured with a Perkin-Elmer photoelectric polarimeter.

Isolation

Commercial copaiba oleoresin (*Copaifera sp.*) (301 g), purchased at "Botica Veado d´ouro", the market in São Paulo, São Paulo State, was dissolved in Et_2O (600 mL) and extracted with 5% KOH (5 × 100 mL). The aqueous layer was acidified with HCl (pH *ca.* 2), and extracted with Et_2O (5 × 100 mL). The combined organic layers were washed with brine until neutral, dried over anhydrous Na_2SO_4, and concentrated under vacuum to afford 244 g (81.1%) of the neutral fraction and 55 g (18.3%) of the acidic fraction. Percolation of the neutral fraction (100 g) on silica gel, eluting with hexane followed by hexane-EtOAc (85:15), furnished 1 g of the more polar fraction. Repeated column chromatography of this material (500 mg) eluted with light petroleum ether:Et_2O (9:1) furnished a fraction containing a mixture of (–)-3-hydroxy-14,15-dinorlabd-8(17)-ene-13-one (**3**) and (+)-7α-acetoxybacchotricuneatin D (300 mg), as previously observed.[10] Continuing the elution with petroleum ether : Et_2O (7:3) furnished fractions containing pure dinorlabdane **1** (20 mg) and dinorlabdane **2** (12 mg). A fraction containing a mixture of dinorlabdane **3** and (+)-7α-acetoxybacchotricuneatin D showed only a slight difference in R_F using TLC impregnated with $AgNO_3$ (15%, hexane-EtOAc, 8:2), and a successive column chromatography using the same conditions as above allowed for the isolation of pure dinorlabdane **3** (7 mg).

*(–)-13(R)-14,15-Dinorlabd-8(17)-ene-3,13-diol (**1**)*

Colorless crystals, mp 165.0-166.5 °C; $[\alpha]_D^{20}$ −1.3° (*c* 1.1, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1}: 3333, 2930, 2851, 1642, 1628, 1033, 885; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.70 (3H, s, H-18), 0.78 (3H, s, H-19), 1.00 (3H, s, H-20), 1.08 (1H, dd, *J* 12.5, 2.9 Hz, H-5), 1.18 (3H, d, *J* 6.2 Hz, H-16), 1.25 (2H, m, H-12), 1.49 (2H, m, H-11), 1.76 (1H, dq, *J* 10.3, 2.9 Hz, H-6β), 1.81 (1H, dt, *J* 13.1, 3.6 Hz, H-1β), 1.96 (1H, ddd, *J* 13.0, 12.5, 2.9 Hz, H-7β), 2.40 (1H, dt, *J* 13.0, 2.9 Hz, H-7α), 3.25 (1H, dd, *J* 11.5, 4.6 Hz, H-3), 3.77 (1H, m, H-13), 4.56 (1H, brs, H-17'), 4.85 (1H, brs, H-17''); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.1 (CH_2, C-1), 27.9 (CH_2, C-2), 78.8 (CH, C-3), 39.1 (C, C-4), 54.6 (CH, C-5), 23.9 (CH_2, C-6), 38.2 (CH_2, C-7), 147.9 (C, C-8), 56.4 (CH, C-9), 39.4 (C, C-10), 19.6 (CH_2, C-11), 38.1 (CH_2, C-12), 68.4 (CH, C-13), 23.7 (CH_3, C-16), 106.9 (CH_2, C-17), 28.3 (CH_3, C-18), 15.4 (CH_3, C-19), 14.4 (CH_3, C-20); HREIMS *m/z* 281.2484 $[M+H]^+$ (calc. for $C_{18}H_{33}O_2$, 281.2481).

*(–)-13(S)-14,15-Dinorlabd-8(17)-ene-3,13-diol (**2**)*

Colorless oil, $[\alpha]_D^{20}$ −1.0° (*c* 1.7, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1}: 3400, 2934, 2851, 1642, 1627, 1033, 885; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.70 (3H, s, H-18), 0.78 (3H, s, H-19), 1.00 (3H, s, H-20), 1.08 (1H, dd, *J* 12.5, 2.9 Hz, H-5), 1.20 (3H, d, *J* 6.2 Hz, H-16), 1.25 (2H, m, H-12), 1.49 (2H, m, H-11), 1.76 (1H, dq, *J* 10.3, 2.9 Hz, H-6β), 1.81 (1H, dt, *J* 13.1, 3.6 Hz, H-1β), 1.97 (1H, ddd, *J* 13.0, 12.5, 2.9 Hz, H7β), 2.40 (1H, dt, *J* 13.0, 2.9 Hz, H-7α), 3.25 (1H, dd, *J* 11.5, 4.6 Hz, H-3), 3.77 (1H, m, H-13), 4.56 (1H, brs, H-17'), 4.85 (1H, brs, H-17''); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.1 (CH_2, C-1), 27.9 (CH_2, C-2), 78.8 (CH, C-3), 39.1 (C, C-4), 54.6 (CH, C-5), 24.0 (CH_2, C-6), 38.1 (CH_2, C-7), 148.1 (C, C-8), 56.7 (CH, C-9), 39.4 (C, C-10), 20.0 (CH_2, C-11), 38.4 CH_2, C-12), 68.8 (CH, C-13), 23.5 (CH_3, C-16), 106.7 (CH_2, C-17), 28.3 (CH_3, C-18), 15.4 (CH_3, C-19), 14.4 (CH_3, C-20); HREIMS *m/z* 281.2486 $[M+H]^+$ (calc. for $C_{18}H_{33}O_2$, 281.2481).

*(–)-3-Hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**)*

Colorless oil, $[\alpha]_D^{20}$ −1.3° (*c* 1.6, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1}: 3436, 2937, 2873, 1713, 1640, 1460, 1380, 735; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.70 (3H, s, H-20), 0.78 (3H, s, H-18), 1.00 (3H, s, H-19), 1.08 (1H, dd, *J* 12.5, 2.9 Hz, H-5), 1.78 (1H, dq, *J* 13.0, 2.9 Hz, H-6β), 1.94 (1H, ddd, *J* 13.0, 12.5, 2.9 Hz, H-7β), 2.40 (1H, dt, *J* 13.0, 2.9 Hz, H-7α), 2.58 (1H, ddd, *J* 17.8, 9.0, 4.0 Hz, H-12''), 3.24 (1H, dd, *J* 11.5, 4.6 Hz, H-3), 4.46 (1H, brs, H-17'), 4.85 (1H, brs, H-17''); ^{13}C NMR ($CDCl_3$, 125 MHz,) δ 37.0 (CH_2, C-1), 28.0 (CH_2, C-2), 78.8 (CH, C-3), 39.2 (C, C-4), 54.6 (CH, C-5), 24.0 (CH_2, C-6), 38.1 (CH_2, C-7), 147.6 (C, C-8), 56.0 (CH, C-9), 39.5 (C, C-10), 17.6 (CH_2, C-11), 42.7 CH_2, C-12), 209.0 (C, C-13), 30.1 (CH_3, C-16), 106.6 (CH_2, C-17), 28.2 (CH_3, C-18), 15.3 (CH_3, C-19), 14.3 (CH_3, C-20).

*Synthesis of (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**)*

(−)-3-Hydroxycopalic acid (**4**) (300 mg), isolated from the same copaiba oleoresin as previously described,[13] was dissolved in acetone (5 mL). $KMnO_4$ (200 mg) was then added in small portions over a period of 7 h at 0 °C. The excess of $KMnO_4$ was destroyed by adding isopropanol and the solvent was removed under reduced pressure. The residue was suspended in EtOAc (60 mL), washed with brine (3 × 30 mL) and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the crude product on SiO_2 (hexane-EtOAc, 9:1) provided ketone **3** (209.1 mg, 80%) of as an oil, $[\alpha]_D^{20}$ −8.8° (*c* 1.7, $CHCl_3$).

*Syntheses of dinorlabdane alcohols **1** and **2***

To a suspension of $LiAlH_4$ (50 mg, 1.32 mmol) in anhydrous Et_2O (3 mL) was added a solution of hydroxyl-ketone **3** (150 mg, 0.54 mmol) in Et_2O (5 mL). The reaction mixture was refluxed for 2 h and then the excess of $LiAlH_4$ was destroyed by adding an aqueous solution of 0.1 mol L^{-1} NaOH. The solution was filtered and dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product on SiO_2 (petroleum ether : Et_2O, 7:3) furnished (−)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**) (74 mg, 49%) as colorless crystals, mp 165.0−167.0 ºC, $[\alpha]_D^{20}$ −27.0º (*c* 1.1, $CHCl_3$) and (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**) (70 mg, 46%) as colorless crystals, mp 169.5-171.0 ºC, $[\alpha]_D^{20}$ −12.0º (*c* 1.7, $CHCl_3$).

*Synthesis of (S)-(+)-α-methoxyphenylacetate ester **5***

DMAP (17.7 mg, 0.143 mmol) was added in one portion to a solution of **1** (40 mg, 0.143 mmol), (*S*)-(+)-α-methoxyphenylacetic acid (24.1 mg, 0.143 mmol) and of DCC (40 mg, 0.143 mmol) in CH_2Cl_2 (5 mL). After stirring for 2 h at room temperature, the dicyclohexylurea was removed by filtration and washed with hexane (10 mL), and the combined filtrates were washed with cold 1.0 mol L^{-1} aq. HCl (2 × 10 mL), saturated $NaHCO_3$ (10 mL), and brine (10 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was purified on SiO_2 (hexane-EtOAc, 8:2) to afford ester **5** (59.4 mg, 85%) as a colorless oil. IR (KBr) ν_{max}/cm^{-1}: 3330, 2930, 2850, 1744, 1623, 1452, 1177, 1113, 737, 699; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.62 (3H, s, H-20), 0.77 (3H, s, H-19), 1.00 (3H, s, H-18), 1.12 (3H, d, *J* 6.2 Hz, H-16), 3.25 (1H, dd, *J* 11.5, 4.6 Hz, H-3), 4.43 and 4.82 (each 1H, H-17), 4.75 (1H, s, ArC<u>H</u>(OCH_3)CO), 7.29-7.39 (3H, m, Ar), 7.43-7.48 (2H, m, Ar); EIMS 70 eV, *m/z* (rel. int. %): 262 [M^+- $C_9H_{10}O_3$] (2), (5), 244 (4), 220 (7), 201 (6), 159 (8), 135 (15), 121 (100), 105 (14), 91 (20).

*Synthesis of (S)-(+)-α-methoxyphenylacetate ester **6***

DMAP (17.7 mg, 0.143 mmol) was added in one portion to a solution of 2 (40 mg, 0.143 mmol), (*S*)-(+)-α-methoxyphenylacetic acid (24 mg, 0.143 mmol), and DCC (30.3 mg, 0.143 mmol) in CH_2Cl_2 (5 mL). Following the same work-up and purification procedure as described previously, ester **6** (62.9 mg, 90%) was obtained as a colorless oil. IR (KBr) ν_{max}/cm^{-1}: 3412, 2930, 2851, 1744, 1623, 1454, 1177, 1100, 737, 696; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.45 (3H, s, H-20), 0.73 (3H, s, H-19), 0.96 (3H, s, H-18), 1.21 (3H, d, *J* 6.2 Hz, H-16), 3.18 (1H, dd, *J* 11.5, 4.6 Hz, H-3), 4.20 and 4.58 (each 1H, bs, H-17), 3.41 (3H, s, OCH_3), 4.73 (1H, s, ArC<u>H</u>(OCH_3)CO), 7.29-7.39 (3H, m, Ar), 7.43−7.48 (2H, m, Ar); EIMS 70 eV, *m/z* (rel.int. %): 262 [M^+- $C_9H_{10}O_3$) (2), (5), 244 (5), 220 (7), 201 (7), 159 (8), 135 (15), 121 (100), 105 (14), 91 (20).

*Reduction of natural (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**)*

To a suspension of $LiAlH_4$ (40 mg, 1.06 mmol) in anhydrous Et_2O (10 mL) was added a solution of **3** (20 mg) in Et_2O (3 mL). The reaction mixture was heated to reflux for 2 h. Work-up and purification on SiO_2 (petroleum ether : Et_2O, 7:3) afforded alcohol **1** (5 mg, 25%) {$[\alpha]_D^{20}$ −1.2º (*c* 0.5, $CHCl_3$)} and **2** (5 mg, 25%) {$[\alpha]_D^{20}$ −1.0º (*c* 0.5, $CHCl_3$)}.

Acknowledgments

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Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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Absolute Configuration of some Dinorlabdanes from the Copaiba Oil

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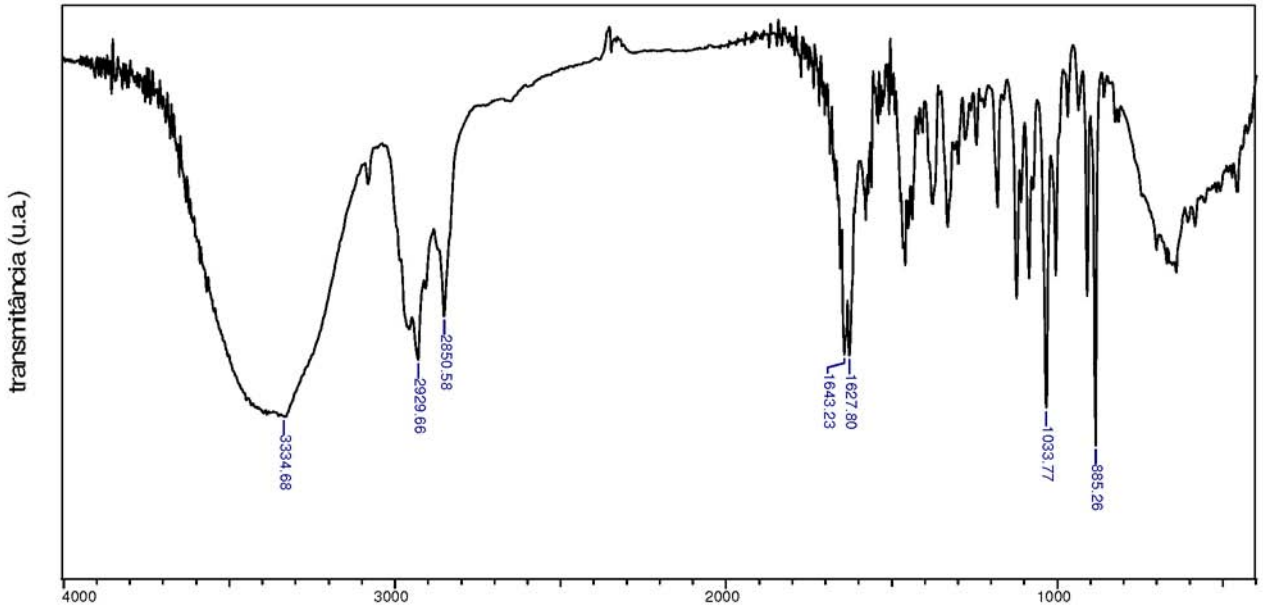

Figure S1. IR spectrum of (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**).

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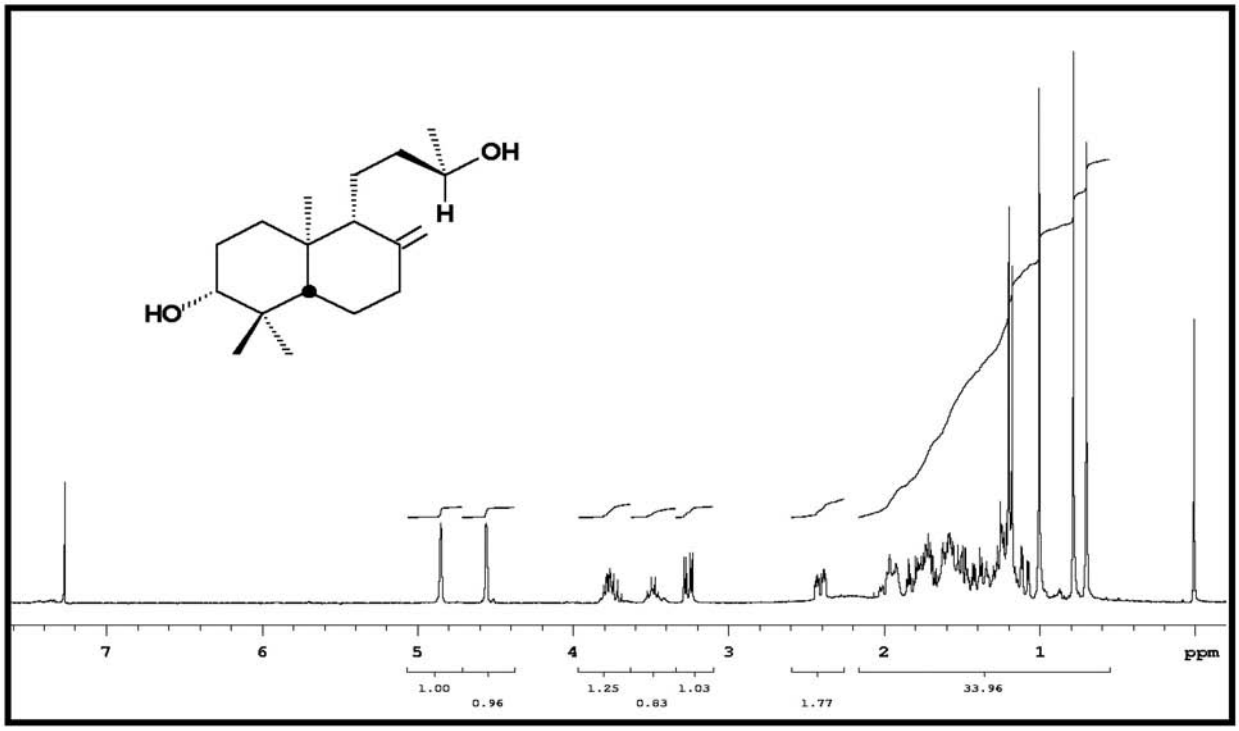

Figure S2. ^{1}H NMR spectrum of (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**) (300 MHz, $CDCl_3$).

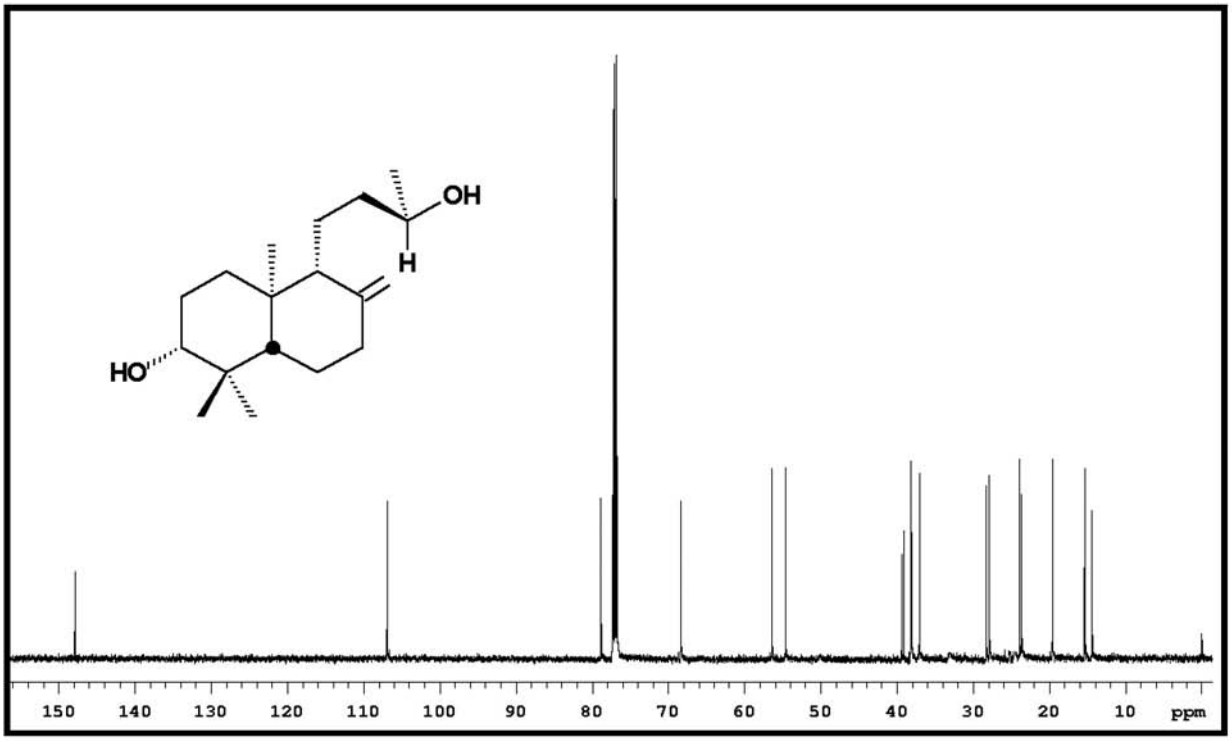

Figure S3. ^{13}C NMR spectrum of (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**) (75.5 MHz, $CDCl_3$).

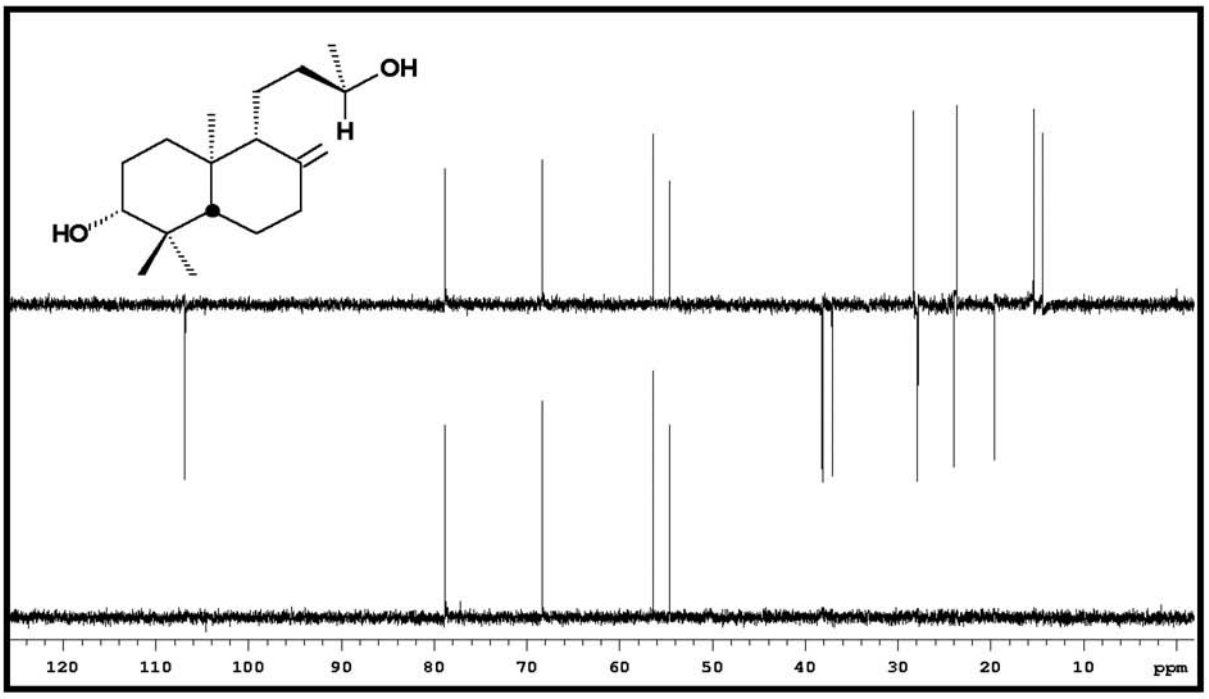

Figure S4. ^{13}C NMR spectrum (DEPT 135 and 90) of (–)-13(*R*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**1**), (75.5 MHz, $CDCl_3$).

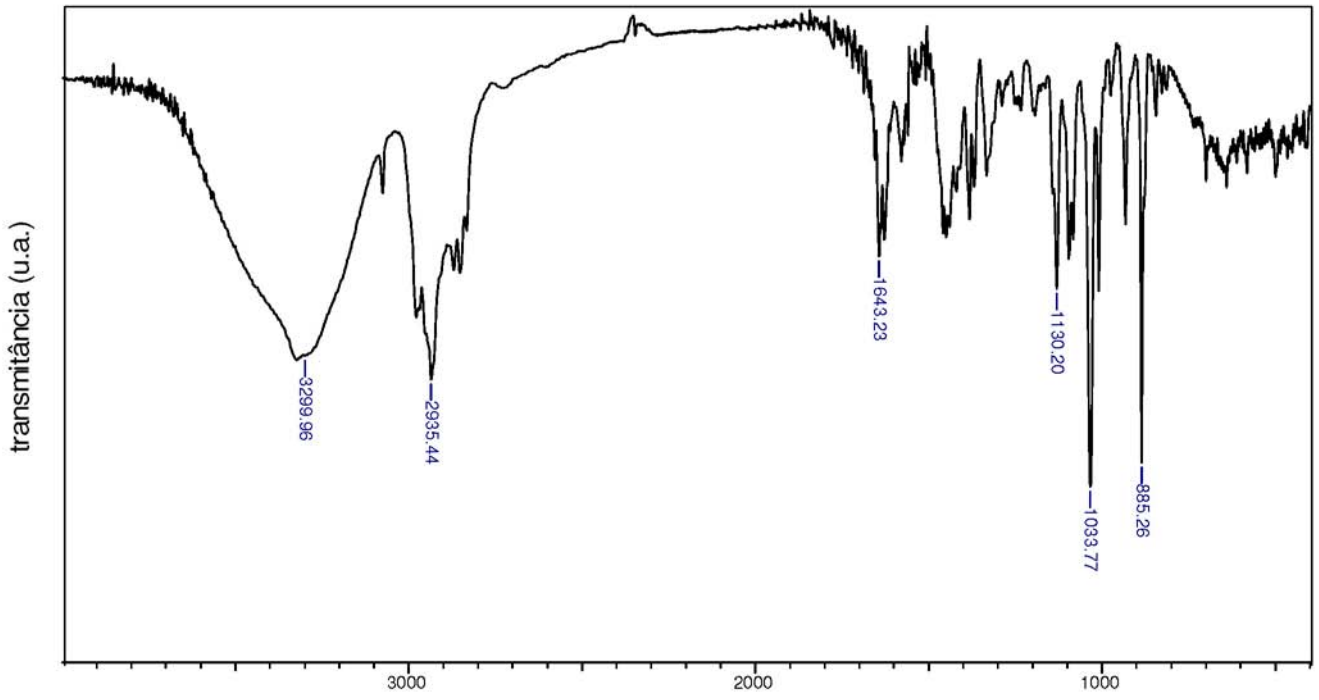

Figure S5. IR spectrum of (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**).

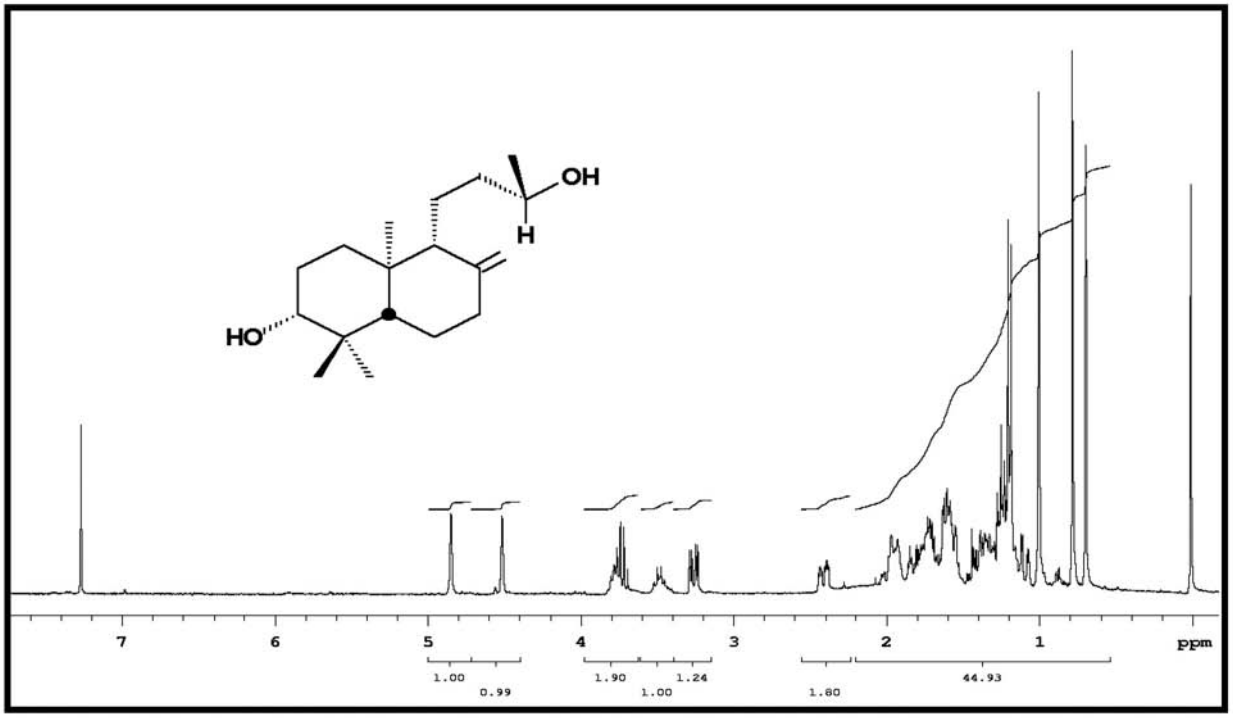

Figure S6. ^{1}H NMR spectrum of (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**) (300 MHz, $CDCl_3$/TMS).

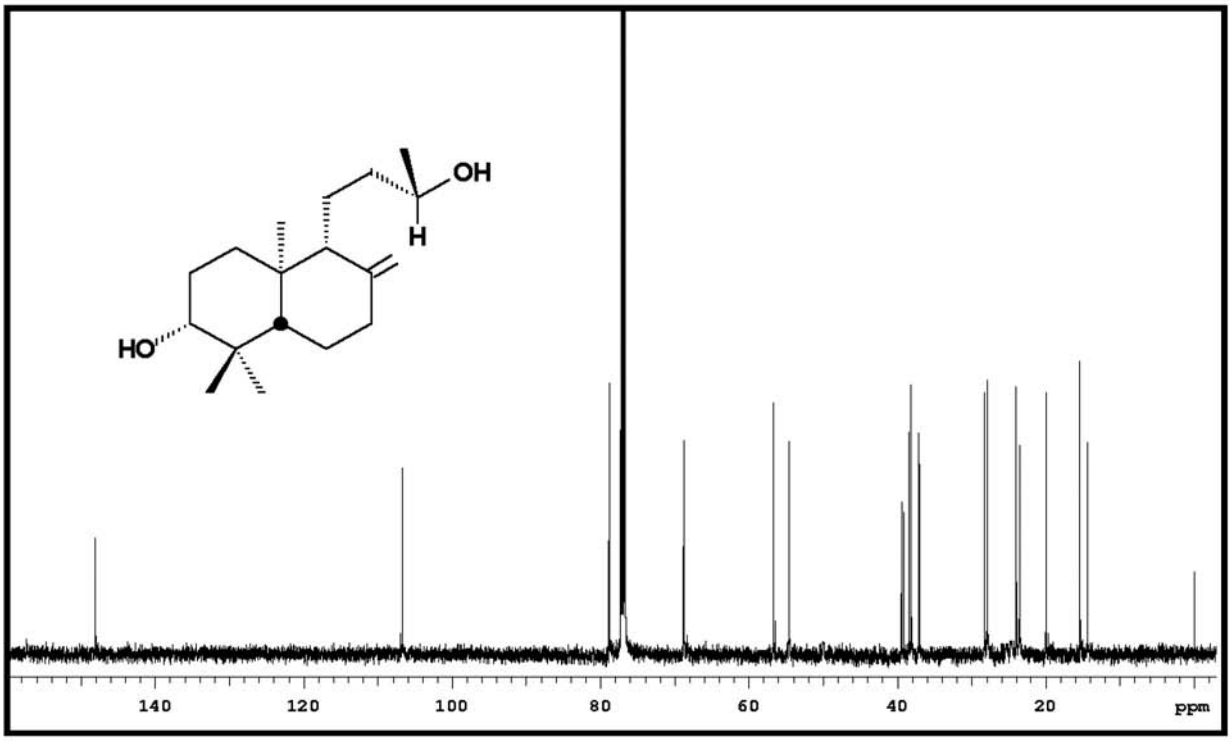

Figure S7. ^{13}C NMR spectrum of (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**) (75.5 MHz, $CDCl_3$).

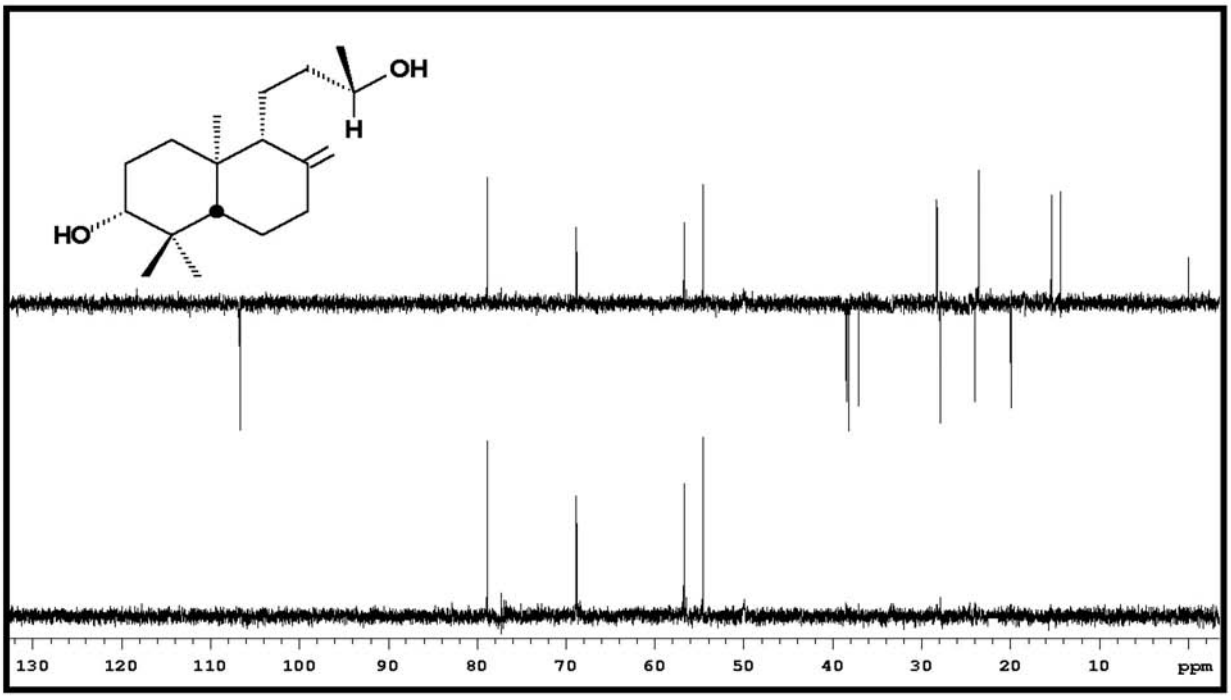

Figure S8. ^{13}C NMR spectrum (DEPT 135 and 90) of (–)-13(*S*)-14,15-dinorlabd-8(17)-ene-3,13-diol (**2**), (75.5 MHz, $CDCl_3$).

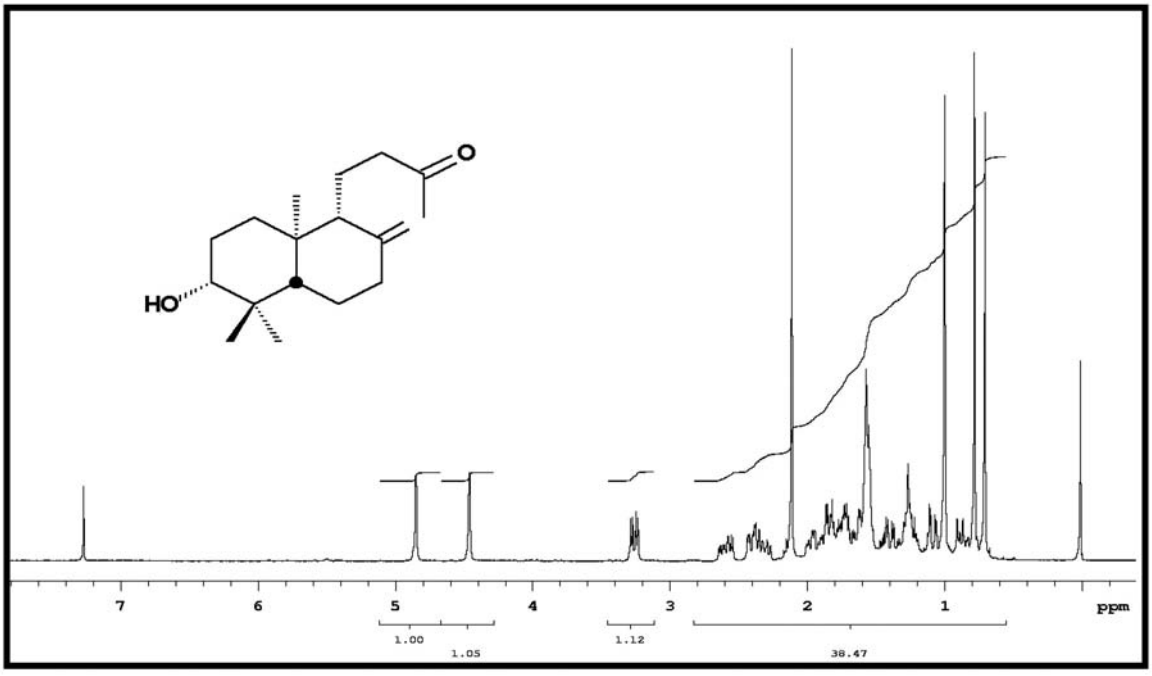

Figure S9. ^{1}H NMR spectrum of (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**) (300 MHz, $CDCl_3$/TMS).

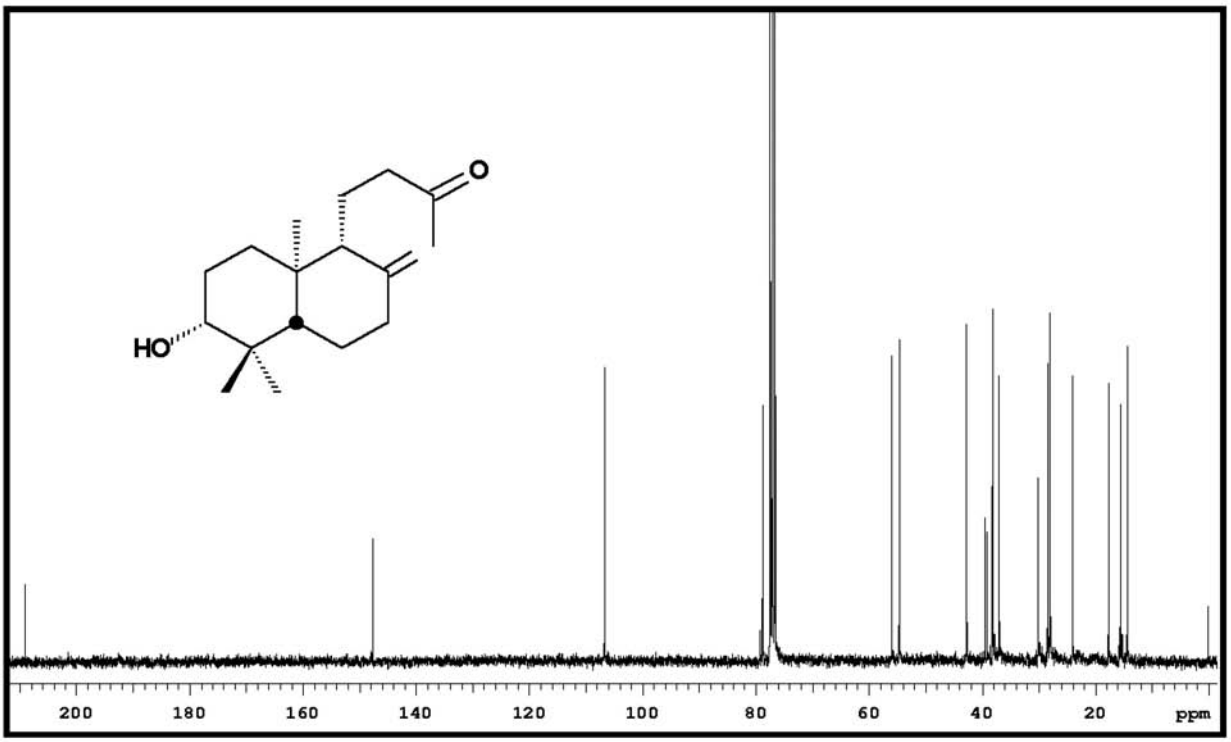

Figure S10. ^{13}C NMR spectrum of (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**) (75.5 MHz, $CDCl_3$).

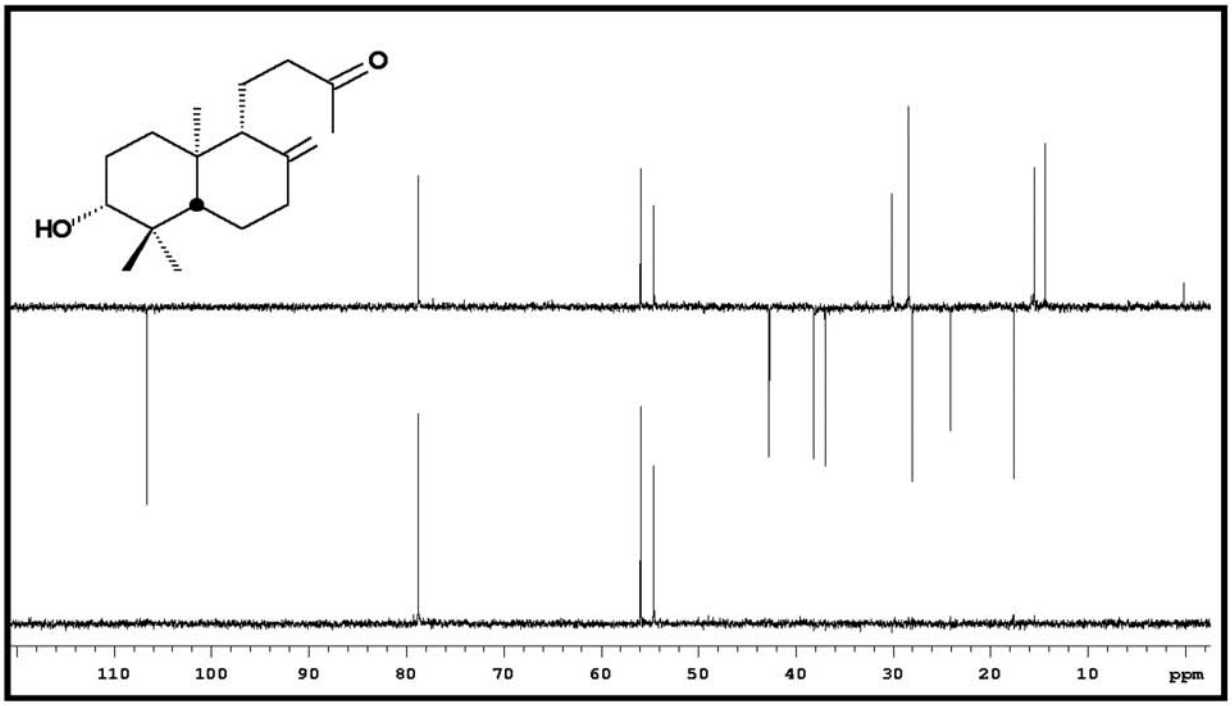

Figure S11. ^{13}C NMR spectrum (DEPT 135 and 90) of (–)-3-hydroxy-14,15-dinorlabd-8(17)-en-13-one (**3**) (75.5 MHz, $CDCl_3$).