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Short Report

New Triterpene and Antibacterial Labdenoic Acid Derivatives from *Moldenhawera nutans*

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Um novo triterpeno (22β-hidroxilupeol) foi isolado do extrato em metanol do caule de *Moldenhawera nutans* (Leguminosae) além de diterpenos derivados do ácido labdenóico de ocorrência comum nesta espécie. A partir do ácido labd-8(17)-en-15-óico foram preparados derivados com atividade *in vitro* discreta frente à *Staphylococcus aureus, Pseudomonas aeruginosa*, *Escherichia coli*, *Salmonella cholerasuis* e *Vibrio parahaemolyticus.*

A new triterpene derivative (22β-hydroxylupeol) was isolated from the MeOH extract of stems of *Moldenhawera nutans* (Leguminosae) together with labdenoic acid derivatives of common occurrence in this species. From the labd-8(17)-en-15-oic acid were prepared simple derivatives, which exhibited *in vitro* weak activity against *Staphylococcus aureus, Pseudomonas aeruginosa*, *Escherichia coli*, *Salmonella cholerasuis*, and *Vibrio parahaemolyticus*.

Keywords: *Moldenhawera nutans,* Leguminosae, antibacterial labdene derivatives, 22β-hydroxylupeol

Introduction

Genus *Moldenhawera* Schrard. (Leguminosae: Caesalpinoideae), endemic to Northeast Brazil, is represented by approximately ten species.[1] Previous phytochemical study of *M. nutans* resulted in the isolation of four known labdene diterpenes besides a new bis-diterpene named moldenin.[2] The present work describes the results of the fractionation of the hexane phase obtained from the MeOH extract of *M. nutans*. Besides the known diterpenes previously isolated, it was also obtained the 3-oxo-labd-8(17)-en-15-oic acid (**1**) as a methyl derivative (**1a)**, and three triterpenes, lupeol, betulin, and the new lupane derivative (**2**). The labd-8(17)-en-15-oic acid (**3**) was the predominant compound in this extract. From this compound, derivatives (**4-8**) were prepared and some of them were submitted to *in vitro* antibacterial assays.

Results and Discussion

The structural elucidation of **1a** (Figure 1) was based on MS, IR, and NMR data analyses. Comparison of NMR data of the methyl ester derivative with moldenin,[2] methyl *ent*-3-oxo-labd-8(17)-en-15-oate[3] and literature data[4] allowed establishing the labdanic structure. The normal series of this compound was confirmed by positive optical rotation.

The HREIMS of **2** exhibited a molecular ion signal at *m/z* 442.3829, indicating the molecular formula $C_{30}H_{50}O_2$ (requires 442.3811). The ^{1}H NMR data (Experimental section) showed characteristic signals of lupane triterpene, seven methyl groups, one isopropenyl (δ 4.61, 4.71, and 1.70) and two signals of oxymethine hydrogens (δ 3.68 and 3.20). The ^{13}C NMR spectra (BB and DEPT 135°) displayed 30 signals and confirmed the data above through the resonances displayed at δ 19.3, 109.8, 150.3, as well as at δ 78.0 and 79.7 for the isopropenyl and two oxymethine groups, respectively. The presence of an additional oxymethine signal indicated that **2** is a hydroxylated lupeol derivative. The localization of the hydroxyl group at C-22 of the lupane framework was proposed by comparison with ^{13}C NMR data (Table 1) of 16-hydroxylupeol[5] and the correlations observed in the long range HETCOR of H-22 (δ 3.68) and C-28 (δ 12.2), C-19 (δ 45.9) and C-18 (δ 45.1) as well as by the carbon shifts observed in the diacetyl derivative (**2a**) (Table 1). Thus, the NMR spectra of **2a** showed a shielding effect at C-21 ($\Delta\delta$ = -3.5 ppm), which is indicative that C-22 bears a hydroxyl group. The

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insignificant effect observed at C-19 in the NMR spectra of **2a** together with the coupling constants observed in the ^{1}H NMR suggested that the hydroxyl group is in equatorial position. The ^{1}HNMR nOe difference spectra of this compound permitted to corroborate the proposition. When the H-22 was irradiated it was possible to assign increments in Hα-21 (25%), H-29 (3%) and, H-19 (10%). These findings are indicative that all the affected protons were in the same plane. The fragmentation pattern observed in the MS of **2** was also indicative of a hydroxyl group in C-22 of the cyclopentyl ring, especially by mass fragments of **2** at *m/z* 374 and **2a** at *m/z* 458 (Figure 2).

Since labd-8(17)-en-15-oic acid (**3**) showed antibacterial activity (Table 2), some of its simple chemical derivatives were prepared and also evaluated. Derivative **3** was refluxed with MeOH/HCl to obtain the isomeric methyl esters **4a** and

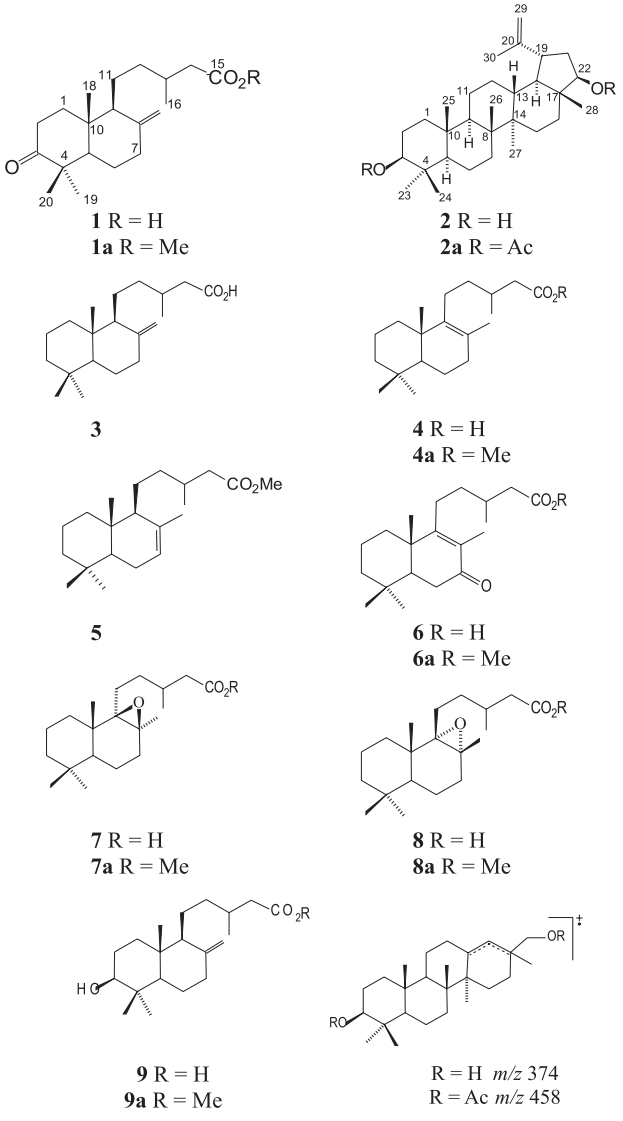

Figure 1. Isolated compounds from *Moldenhawera nutans,* their derivatives and mass fragments of **2** and **2a**.

Table 1. ^{13}C NMR data for compounds **2**, **2a** and the model compound 16-hydroxylupeol[5] [75 MHz, δ (ppm)]

C	**2**	**2a**	16-hydroxylupeol
1	38.8	38.2	38.9
2	27.5	23.5	27.4
3	79.7	81.2	78.8
4	39.1	37.7	38.9
5	55.5	55.2	55.4
6	18.4	18.0	18.3
7	34.3	34.0	34.3
8	40.7	40.7	41.0
9	50.4	50.1	50.0
10	37.1	36.9	37.1
11	20.7	20.7	20.9
12	25.2	24.7	24.9
13	37.7	37.3	37.3*
14	42.6	42.5	44.1
15	27.2	26.3	36.9*
16	33.7	33.3	76.9
17	45.3	44.5	48.6
18	45.1	44.7	47.7
19	45.9	45.8	47.6
20	150.3	149.1	149.8
21	38.9	35.4	30.0
22	78.0	80.8	37.8
23	28.3	27.8	28.0
24	16.0*	16.0	15.4
25	16.1*	16.4	16.1
26	15.9	15.8	16.1
27	14.3	14.3	16.1
28	12.2	12.6	11.8
29	109.8	110.4	109.6
30	19.3	19.1	19.4
OAc		170.9, 171.0	
OAc		21.1, 21.2	
OMe			

*values may be interchangeable.

5. Next, **4a** was submitted to allylic oxidation by *t*-butyl chromate[6] and furnished **6a**. It was also prepared the epoxy derivatives **7a** and **8a** from **4a** by reaction with MCPBA. The derivatives **7a** and **8a** are new and they were characterized by spectrometric analyses data. Compounds **1a**, **2**, **4a**, and **6a-8a** were submitted to antibacterial evaluation and none of them was active; while the acid derivatives (**1**, **4, 6-8**) obtained after saponification, together with **9**, a labdane previously obtained from this plant, showed moderate antibacterial activity at 90 μg *per* disc (Table 2). These results indicate the need of the presence of an acid group for the antibacterial activity and also that structural features contribute to the inhibition area as well.

Experimental

General procedures

The ^{1}H and ^{13}C NMR, DEPT, COSY, and HETEROCOSY (*J* 140 and 9 Hz) spectra were obtained

Table 2. Diameter of inhibition zones of compounds **1**, **3**, **4**, **6-9** from *M. nutans* in agar diffusion test in mg *per* disk

Sample	ϕ / mm				
	EC	SA	SC	VP	PA
1	7	-	10	8	-
3	8	-	15	15	13
4	20	20	8	35	6
6	15	-	-	12	13
7 + **8***	15	-	-	12	-
9	-	-	13	-	-
Penicillin	35	-	31	-	25
Tetracycline	35	15	36	34	30
Chloramphenicol	22	-	26	34	23

EC = *Escherichia coli*; SA = *Staphylococus aureus*; SC = *Salmonella cholerasuis*; VP = *Vibrio parahaemolyticus*; PA = *Pseudomonas aeruginosa.* *evaluation performed in mixture.

on a Varian Gemini 2000 instrument employing $CDCl_3$ as both solvent and reference. The FTIR spectrum was recorded on a JASCO spectrophotometer Mod. Valor III. MS was recorded on a Micromass Autospec spectrometer (HRMS) and an HP model 5973 spectrometer (EIMS). Melting points were measured on a Microquímica MIAPF 301 apparatus and are uncorrected. Column chromatography was carried out on silica gel 60 and, silica gel TLC was used to monitor the fraction employing iodine fumes, Liberman-Buchard spray reagent, and UV light (254/366 nm).

Plant material

The plant material of *M. nutans* were collected at sandy soil of Reserva do Parque da Lagoa do Abaeté, Salvador, BA, Brazil in the spring of 1997 and identified by Prof. Maria L. S. Guedes of Herbarium Alexandre Leal Costa, where a voucher (#029057) is deposited.

Extraction and isolation

The powdered stem (4 kg) of *Moldenhawera nutans* was extracted with MeOH. The methanol extract (153 g) was partitioned with hexane, furnishing 73.2 g of extract. The hexane phase was purified through CC over silica gel with mixtures of hexane/EtOAc as eluents. The fraction eluted with 5% of EtOAc furnished the labd-8(17)-en-15-oic acid (**3**, 42 g). All the fractions eluted from the main CC (7.3 g) with hexane:EtOAc (8:2) were submitted to methylation using an ether solution of N-methyl-N-nitroso-*p*-toluenesulfonamide (Diazald®). The product of this reaction was then subjected to silica gel CC and from the fraction eluted with hexane:EtOAc (9:1) afforded 39.9 mg of **1a** (methyl 3-oxo-labd-8(17)-en-15-oate), lupeol (10.5 mg), and 22β-hydroxylupeol (**2**, 70.3 mg). The fraction eluted with hexane:EtOAc led to the isolation of 25.4 mg of betulin[7] and methyl 3-hydroxy-labd-8(17)-en-15-oate (**9a**, 102 mg).

*Methyl 3-oxo-labd-8(17)-en-15-oate (**1a**)*

Pale yellow oil. $[\alpha]_D^{25}$ 33.4° (*c* 0.1, $CHCl_3$), IR(film) ν_{max}/cm^{-1}: 3080, 2950, 1737, 1706, 1643, 1385, 1160, 1008, 890; $C_{21}H_{34}O_3$ (Found: C, 75.1; H, 10.5%. Requires: C, 75.4; H, 10.2%), EIMS: 70 eV (rel. int.) *m/z*: 334 [M^+] (18), 319 (4), 303 (7), 233 (51), 220 (15), 205 (48), 177 (16), 163 (22), 137 (34), 135 (100), 123 (68), 109 (68); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.88 (sl, 1H, H-17a), 4.55 (sl, 1H, H-17b), 3.64 (s, 3H, OCH_3), 1.08 (s, 3H, Me-19), 1.01 (s, 3H, Me-18), 0.93 (d, *J* 6.6 Hz, 3H, Me-16), 0.85 (s, 3H, Me-20); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.3 (C-1), 34.4 (C-2), 216.2 (C-3), 47.4 (C-4), 54.8 (C-5), 24.8 (C-6), 37.6 (C-7), 146.9 (C-8), 55.6 (C-9), 39.0 (C-10), 21.1 (C-11), 37.3 (C-12), 30.5 (C-13), 41.5 (C-14), 173.2 (C-15), 21.4 (C-16), 107.2 (C-17), 19.3 (C-18), 25.6 (C-19), 13.8 (C-20), 51.0 (OCH_3).

*22β-Hydroxylupeol (**2**)*

White amorphous powder; mp 158-160 °C. $[\alpha]_D^{25}$ 71.2° (*c* 0.1, $CHCl_3$); IR(film) ν_{max}/cm^{-1}: 3401, 2934, 2868, 1643, 1455, 1385, 880; HREIMS: *m/z* 442.3829 ($C_{30}H_{50}O_2$ requires 442.3811), EIMS: 70 eV (rel. int.) *m/z:* 442 [M^+] (12), 427 (4), 374 (100), 291 (6), 273 (57), 247 (14), 234 (12), 219 (8), 207 (23), 189 (31), 175 (14), 161 (13), 147 (16), 135 (35), 121 (24), 107 (26); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.71 (m, 1H, H-29b), 4.61 (m, 1H, H-29a), 3.68 (t, *J* 8.8 Hz, 1H, H-22), 3.20 (dd, *J* 10.7 and 5.6 Hz, 1H, H-3), 2.46 (m, 1H, H-19), 1.70 (s, 3H, Me-30), 1.60 (m, 1H, H-5), 1.06 (s, 3H, Me-23), 0.98 (s, 3H, Me-24), 0.94 (s, 3H, Me-26), 0.85 and 0.84 (s, 3H each, Me-28 or Me-27), 0.79 (s, 3H, Me-25); ^{13}C NMR (75 MHz, $CDCl_3$): see Table 1.

Preparation of derivatives

*Acetylation of 22β-hydroxylupeol (**2**)*

Compound **2** (15.0 mg) was added to a solution of pyridine (0.5 mL) and acetic anhydride (2.0 mL) and the mixture was left at room temperature for 24 h. Cold H_2O was added and the diacetyl derivative (**2a**, 14.3 mg) was extracted with $CHCl_3$.

*3β,22β-Diacetoxylup-20(29)-ene (**2a**)*

Oil, EIMS: 70 eV (rel. int.) *m/z:* 526 [M^+] (35), 466 (42), 458 (50), 416 (46), 398 (10), 289 (21), 276 (39), 249

(19), 216 (38), 201 (50), 189 (95), 161 (27), 135 (58), 107 (42); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.70 (sl, 1H, H-29b), 4.60 (sl, 1H, H-29a), 4.65 (t, *J* 8.9 Hz, 1H, H-22), 4.46 (dd, *J* 10.9 and 5.8 Hz, 1H, H-3), 2.48 (m, 1H, H-19), 2.04 (s, 3H), 2.03 (s, 3H), 1.69 (sl, 3H, Me-30), 1.03 (s, 3H, Me-23), 0.92 (s, 3H, Me-24 and Me-26), 0.85, 0.84 and 0.83 (s, 3H each, Me-28 or Me-27 or Me-25); ^{13}C NMR (75 MHz, $CDCl_3$): see Table 1.

*Preparation of derivatives of labd-8(17)-en-15-oic acid (**3**)*

Compound **3** (1.0 g) was refluxed with 36 mL of an acidic methanolic solution (HCl 0.048 N) under stirring for 4.5 h. Sequentially, water was added and the solution was extracted with $CHCl_3$. The product was submitted to Si gel with $AgNO_3$ CC and eluted with hexane:EtOAc (9:1). This procedure furnished 489.4 mg of methyl labd-8-en-15-oate[8] (**4a**, 49%) and 210 mg of methyl labd-7-en-15-oate[9] (**5a**, 21%). Methyl labd-8-en-15-oate (**4a**, 480 mg) was diluted to 11 mL of CCl_4 and sequentially added with 3.5 mL of acetic acid, 2.0 mL of acetic anhydride, and 4.5 mL of solution of *terc*-butyl chromate freshly prepared by established procedures.[6] The system was refluxed for 90 minutes followed by the addition of 21 mL of an oxalic acid (5 %) aqueous solution. The mixture was stirred until two layers were produced and next it was extracted with $CHCl_3$. The organic phase was recovered and washed with a 10% solution of Na_2CO_3 and yielded 243.1 mg of methyl 7-oxo-labd-8-en-15-oate[10] (**6a**, 50%). In parallel, to a solution of 100 mg of **4a** in 4 mL of CH_2Cl_2 was added another solution of 80 mg MCPBA in 4 mL of dichloromethane and the mixture was stirred for 30 minutes. Next, purification of the mixture reaction product through CC over Al_2O_3 with hexane/EtOAc (7:3) as an eluent, furnished compounds **7a** (24.3 mg) and **8a** (15.8 mg).

*Methyl labd-8-en-15-oate (**4a**)*

Oil. $[\alpha]_D^{25}$ 60.2° (*c* 0.8, $CHCl_3$); IR(film) ν_{max}/cm^{-1}: 2947, 2926, 1741, 1643, 1459, 1154, 887; $C_{21}H_{36}O_2$, EIMS: 70 eV (rel. int.) *m/z:* 320 [M$^+$] (13), 305 (24), 264 (5), 196 (10), 191 (100), 177 (13), 163 (15), 149 (28), 135 (33), 121 (53), 109 (47); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 3H, OCH_3), 1.54 (s, 3H, Me-17), 0.97 (d, *J* 6.4 Hz, 3H, Me-16), 0.87 (s, 3H, Me-19), 0.83 (s, 3H, Me-18) and 0.79 (s, 3H, Me-20); ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.6 (C-1), 19.1 (C-2), 39.5 (C-3), 33.3 (C-4), 51.8 (C-5), 25.4 (C-6), 36.9 (C-7), 125.4 (C-8), 140.4 (C-9), 38.9 (C-10), 19,0 (C-11), 41.4 (C-12), 31.5 (C-13), 37.3 (C-14), 173.6 (C-15), 19.0 (C-16), 20.1 (C-17), 21.7 (C-18), 33.3 (C-19), 19.6 (C-20), 51.9 (OCH_3).

*Methyl labd-7-en-15-oate (**5a**)*

Oil. $[\alpha]_D^{25}$ 30.2° (*c* 0.2, $CHCl_3$), $C_{21}H_{36}O_2$, EIMS: 70 eV (rel. int.) *m/z:* 320 [M$^+$] (9), 305 (15), 196 (12), 191 (52), 177 (6), 163 (10), 149 (15), 135 (20), 122 (100), 109 (84); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.39 (sl, 1H, H-7), 3.66 (s, 3H, OCH_3), 1.68 (s, 3H, Me-17), 0.97 (d, *J* 6.5 Hz, 3H, Me-16), 0.84 (s, 3H, Me-19), 0.81 (s, 3H, Me-18) and 0.78 (s, 3H, Me-20); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.2 (C-1), 19.0 (C-2), 42.2 (C-3), 32.7 (C-4), 54.7 (C-5), 23.8 (C-6), 122.1 (C-7), 135.1 (C-8), 49.8 (C-9), 36.6 (C-10), 25.3 (C-11), 37.1 (C-12), 30.8 (C-13), 41.7 (C-14), 172.9 (C-15), 18.5 (C-16), 22.2 (C-17), 21.7 (C-18), 33.1 (C-19), 13.5 (C-20), 51.7 (OCH_3).

*Methyl 7-oxo-labd-8-en-15-oate (**6a**)*

Oil. $[\alpha]_D^{25}$ 41.1° (*c* 1.0, $CHCl_3$); IR(film) ν_{max}/cm^{-1}: 2953, 1736, 1661, 1605, 1461, 1437, 1156, 1080, 1007; $C_{21}H_{34}O_3$, EIMS: 70 eV (rel. int.) *m/z:* 334 [M$^+$] (30), 303 (7), 233 (52), 220 (15), 205 (44), 177 (10), 163 (10), 149 (13), 135 (100), 123 (48), 109 (56); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.56 (s, 3H, OCH_3), 1.62 (s, 3H, Me-17), 0.90 (d, *J* 6.4 Hz, 3H, Me-16), 0.96 (s, 3H, Me-19), 0.80 (s, 3H, Me-18) and 0.76 (s, 3H, Me-20); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.7* (C-1), 18.5 (C-2), 41.2$^\#$ (C-3), 33.0 (C-4), 50.1 (C-5), 35.2* (C-6), 200.0 (C-7), 129.7 (C-8), 168.0 (C-9), 40.8 (C-10), 26.9 (C-11), 35.1 (C-12), 31.3 (C-13), 41.0$^\#$ (C-14), 173.1 (C-15), 19.4 (C-16), 11.2 (C-17), 21.2 (C-18), 32.4 (C-19), 18.1 (C-20), 51.3 (OCH_3), $^{*,\#}$ values may be interchangeable.

*Methyl 8β,9β-epoxy-labd-8-en-15-oate (**7a**)*

Oil. $[\alpha]_D^{25}$ 38.2° (*c* 0.8, $CHCl_3$), $C_{21}H_{36}O_3$, EIMS: 70 eV (rel. int.) *m/z:* 336 [M$^+$] (14), 321 (10), 305 (7), 278 (15), 264 (20), 253 (25), 251 (23), 235 (20), 207 (100), 177 (18), 163 (25), 149 (58), 125 (57), 121 (35), 109 (47); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 3H, OCH_3), 1.13 (s, 3H, Me-17), 0.89 (d, *J* 6.4 Hz, 3H, Me-16), 0.96, 0.78 (s, 3H, Me-19 and Me-18) and 0.76 (*s*, 3H, Me-20); ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.2 (C-1), 17.2 (C-2), 41.5 (C-3), 32.8 (C-4), 42.3 (C-5), 23.9 (C-6), 43.5 (C-7), 62.2 (C-8), 72.2 (C-9), 38.5 (C-10), 18.4 (C-11), 41.4 (C-12), 31.0 (C-13), 35.1 (C-14), 173.5 (C-15), 19.6 (C-16), 21.2 (C-17), 21.9 (C-18), 33.5 (C-19), 17.2 (C-20), 51.3 (OCH_3).

*Methyl 8α,9α-epoxy-labd-8-en-15-oate (**8a**)*

Oil. $C_{21}H_{36}O_3$. $[\alpha]_D^{25}$ 42.2° (*c* 0.6, $CHCl_3$), EIMS: 70 eV (rel. int.) *m/z:* 336 [M$^+$] (15), 321 (13), 305 (6), 278 (15), 264 (23), 253 (26), 251 (26), 235 (18), 207 (100), 177 (18), 163 (22), 149 (62), 125 (59), 121 (36), 109 (52);

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 3H, OCH_3), 1.24 (s, 3H, Me-17), 0.90 (d, *J* 6.4 Hz, 3H, Me-16), 1.00, 0.80 (s, 3H, Me-19 and Me-18) and 0.74 (s, 3H, Me-20); ^{13}C NMR (75MHz, $CDCl_3$): δ 33.4 (C-1), 16.7 (C-2), 41.4 (C-3), 33.6 (C-4), 53.8 (C-5), 29.2 (C-6), 29.0 (C-7), 64.7 (C-8), 72.5 (C-9), 38.7 (C-10), 19.7 (C-11), 41.4 (C-12), 31.4 (C-13), 37.0 (C-14), 173.5 (C-15), 19.5 (C-16), 21.4 (C-17), 21.9 (C-18), 33.2 (C-19), 16.5 (C-20), 51.3 (OCH_3).

Hydrolyses of the ester derivatives

All the methyl ester derivatives were submitted to hydrolysis by adding 1.5 mL of a solution of 10 mg NaOH in H_2O/EtOH (1:1) to 10 mg of each compound for 30 minutes. After this time, the reaction medium was saturated with 3 mL of brine and the produced ppted was acidified with 4 mL of an aqueous solution of H_2SO_4 and extracted with $CHCl_3$. The organic phase was washed and dried over $NaSO_4$, yielding acid compounds.

Antibacterial assays

This assay was performed by disc diffusion method using the established protocol.[11] The antibacterial activity using paper disk with ϕ 9 mm was determined through the microorganism growth inhibition halo for *Staphylococcus aureus* (ATCC 10708)*, Pseudomonas aeruginosa* (ATTCC 15442), *Escherichia coli* (ATCC 112229), *Salmonella cholerasuis* (ATCC 10708), and *Vibrio parahaemolyticus* (ATCC 17802) under the action of test substances (90 mg). Penicillin (10 mg), tetracycline (30 mg) and chloramphenicol (30 mg) were used as positive controls.

Supplementary Information

Supplementary data of **1a**, **2**, **2a**, **4a** and **6a** as ^{13}C and ^{1}H NMR spectra are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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New Triterpene and Antibacterial Labdenoic Acid Derivatives from *Moldenhawera nutans*

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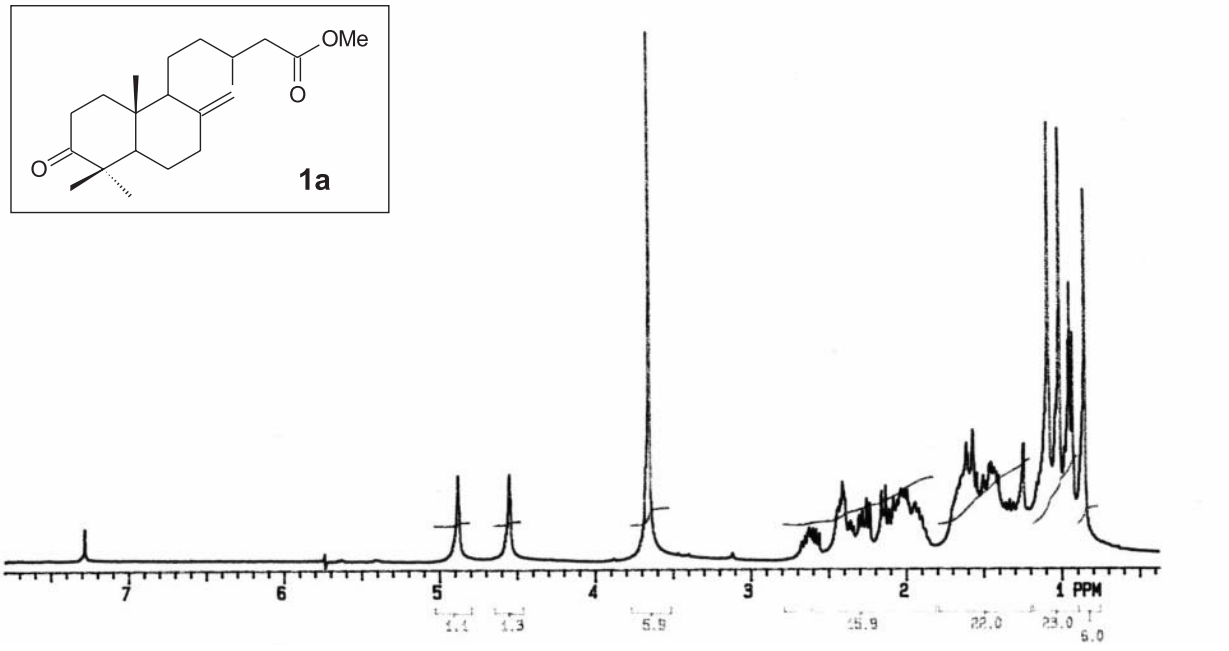

Figure S1. ^{1}H NMR of compound **1a** [300 MHz, $CDCl_3$, δ (ppm)].

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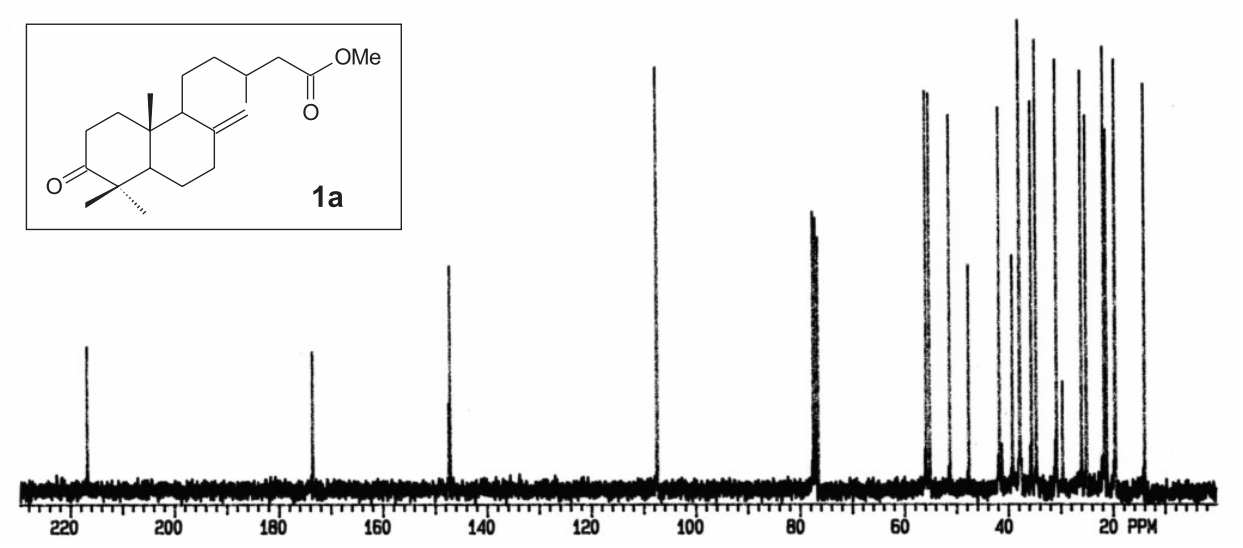

Figure S2. ^{13}C NMR of compound **1a** [75 MHz, $CDCl_3$, δ (ppm)].

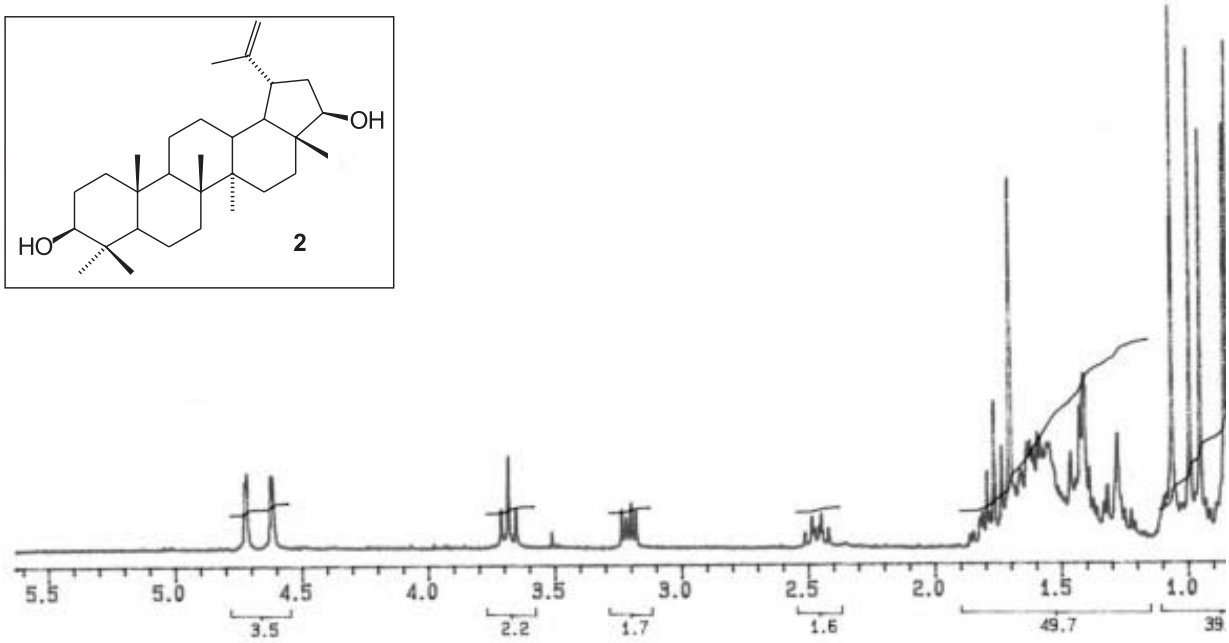

Figure S3. ^{1}H NMR of compound **2** [300 MHz, $CDCl_3$, δ (ppm)].

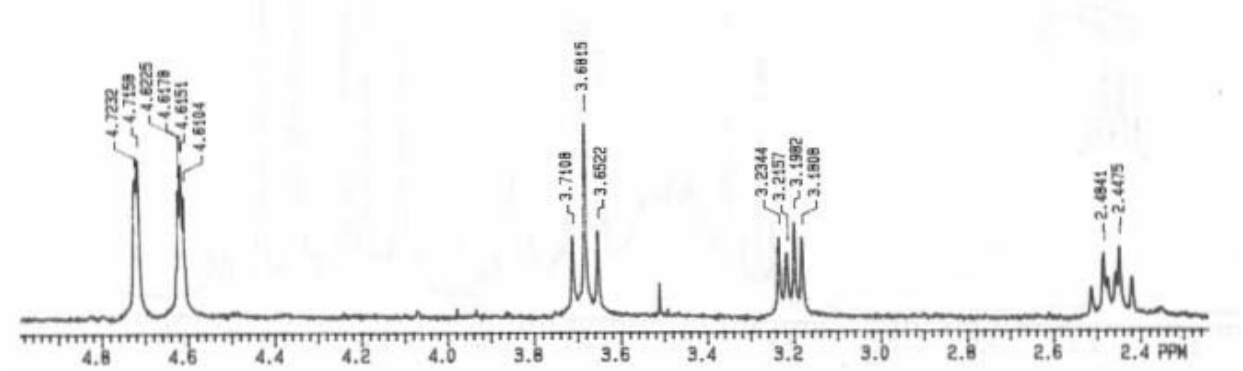

Figure S4. ^{1}H NMR of compound **2** [300 MHz, $CDCl_3$, δ (ppm)].

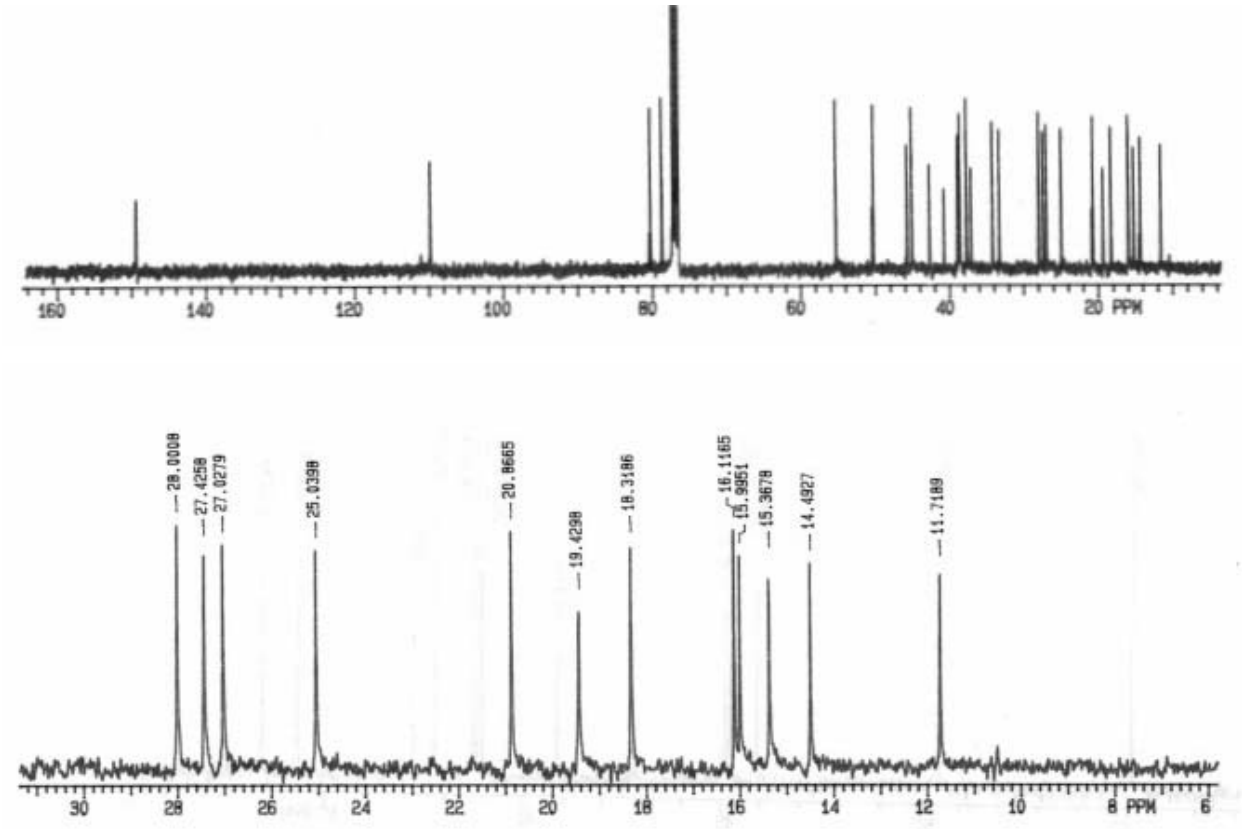

Figure S5. ^{13}C NMR of compound **2** [75 MHz, $CDCl_3$, δ (ppm)].

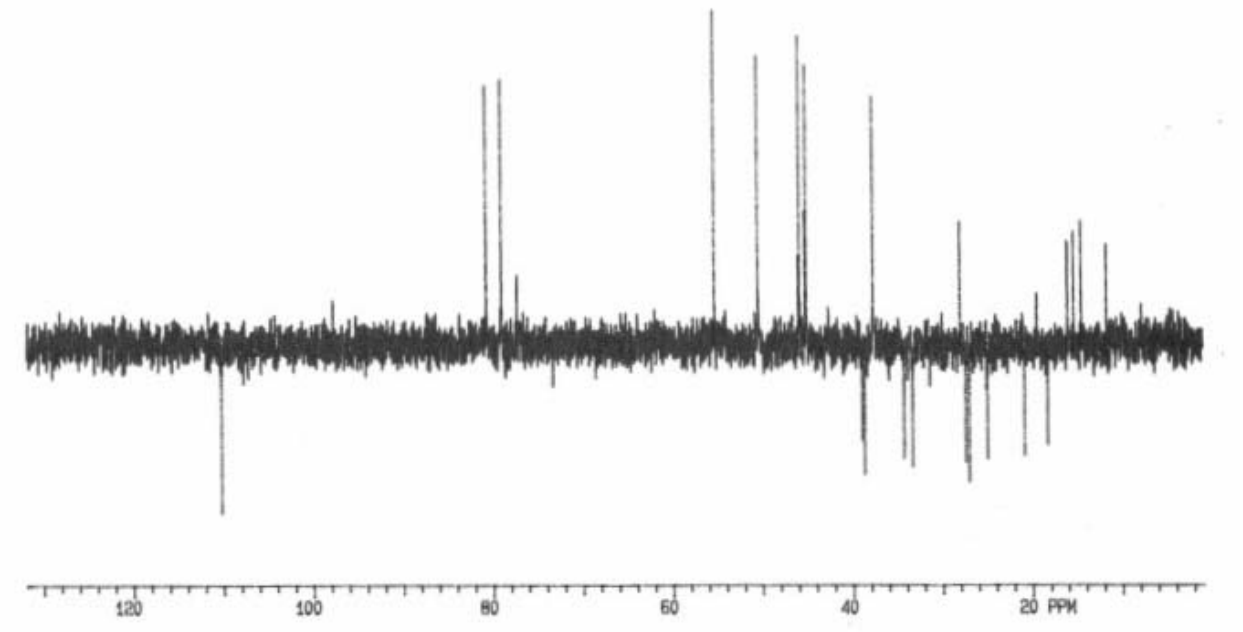

Figure S6. DEPT 135 NMR spectra of compound **2** [75 MHz, $CDCl_3$, δ (ppm)].

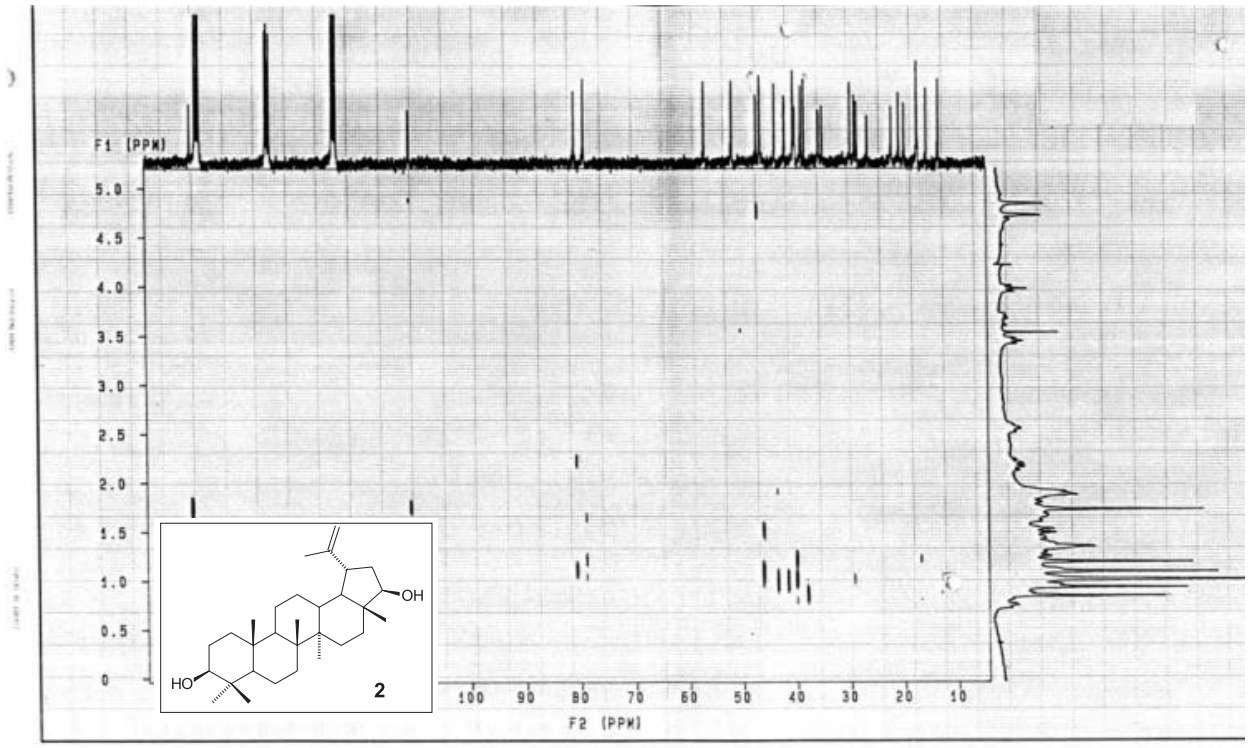

Figure S7. ^{13}C x ^{1}H COSY (*J* 140 Hz) of compound **2** $CDCl_3$.

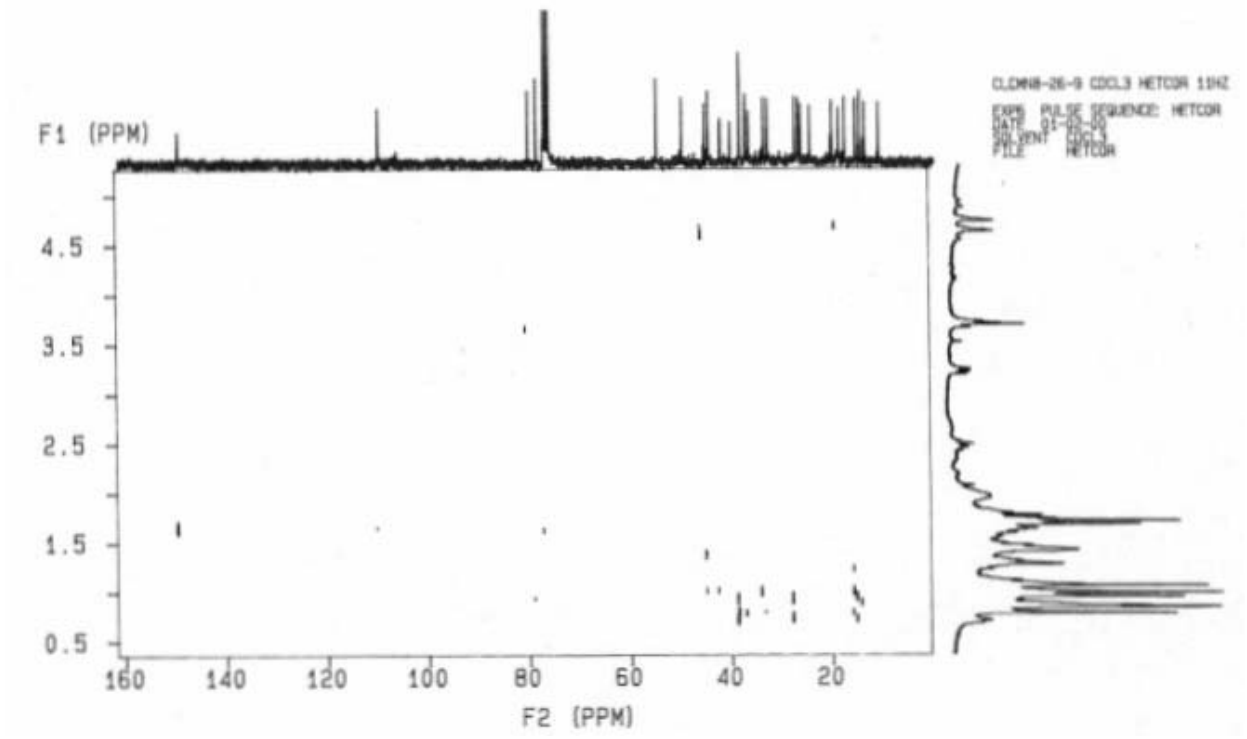

Figure S8. ^{13}C x ^{1}H COSY (*J* 11 Hz) of compound **2** $CDCl_3$.

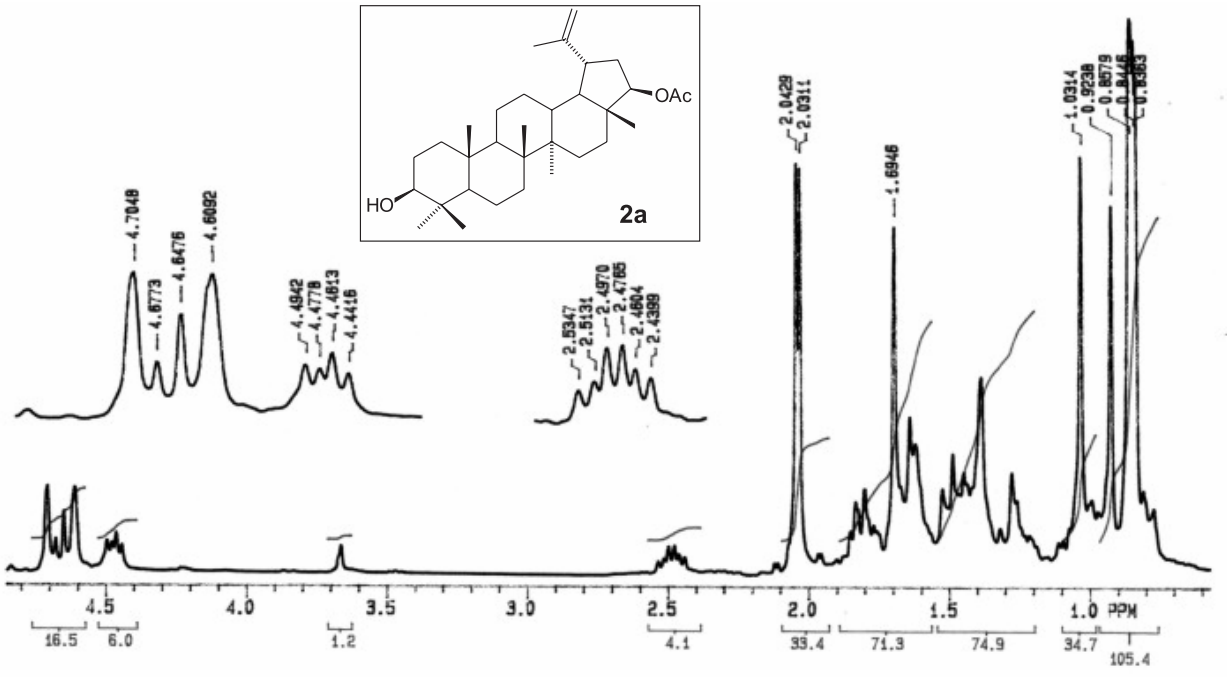

Figure S9. [1]H NMR of compound **2a** [300 MHz, $CDCl_3$, δ (ppm)].

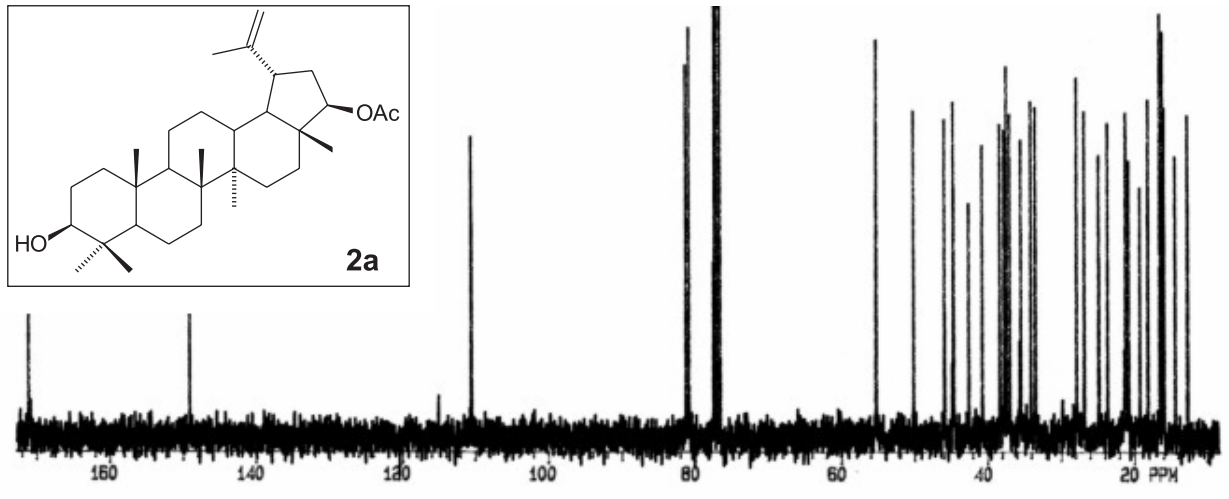

Figure S10. [13]C NMR of compound **2a** [75 MHz, $CDCl_3$, δ (ppm)].

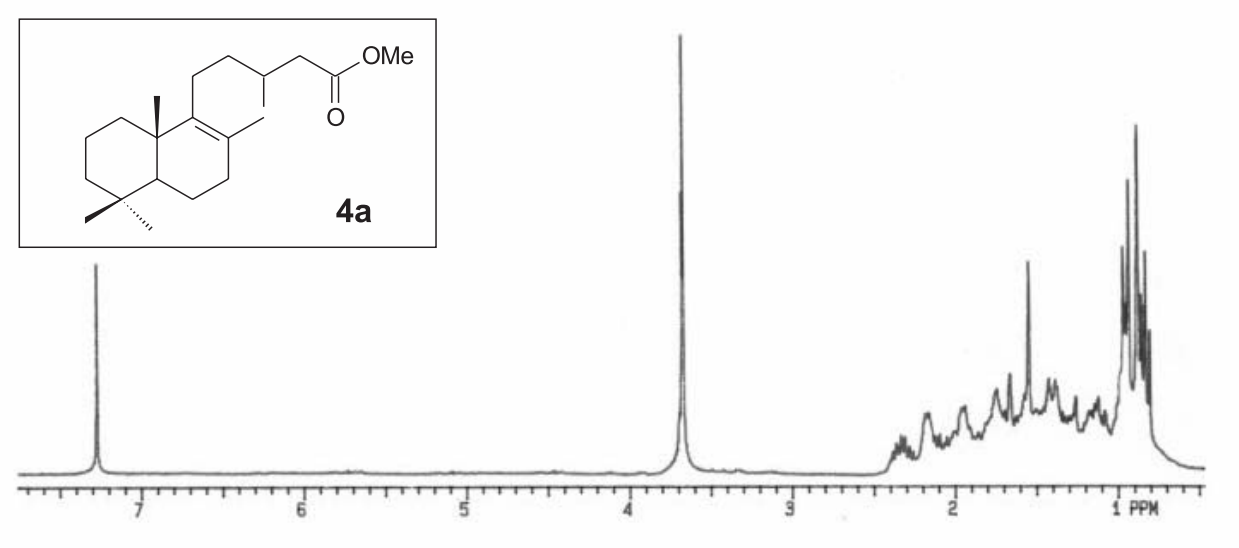

Figure S11. ^{1}H NMR of compound **4a** [300 MHz, $CDCl_3$, δ (ppm)].

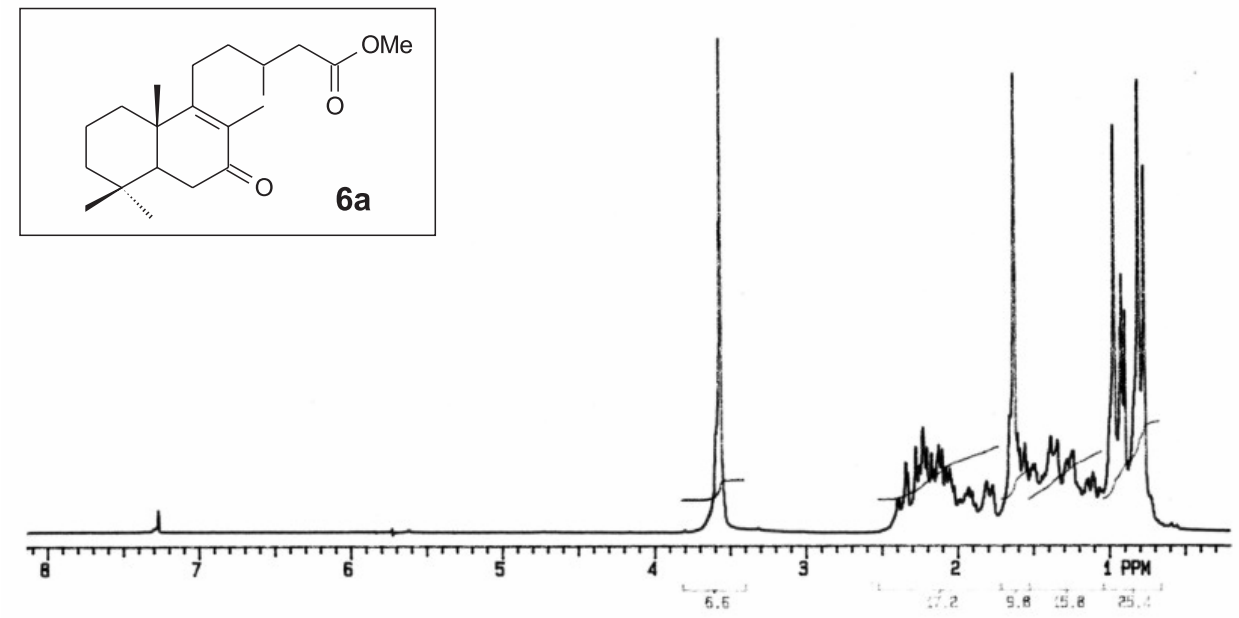

Figure S12. ^{1}H NMR of compound **6a** [300 MHz, $CDCl_3$, δ (ppm)].

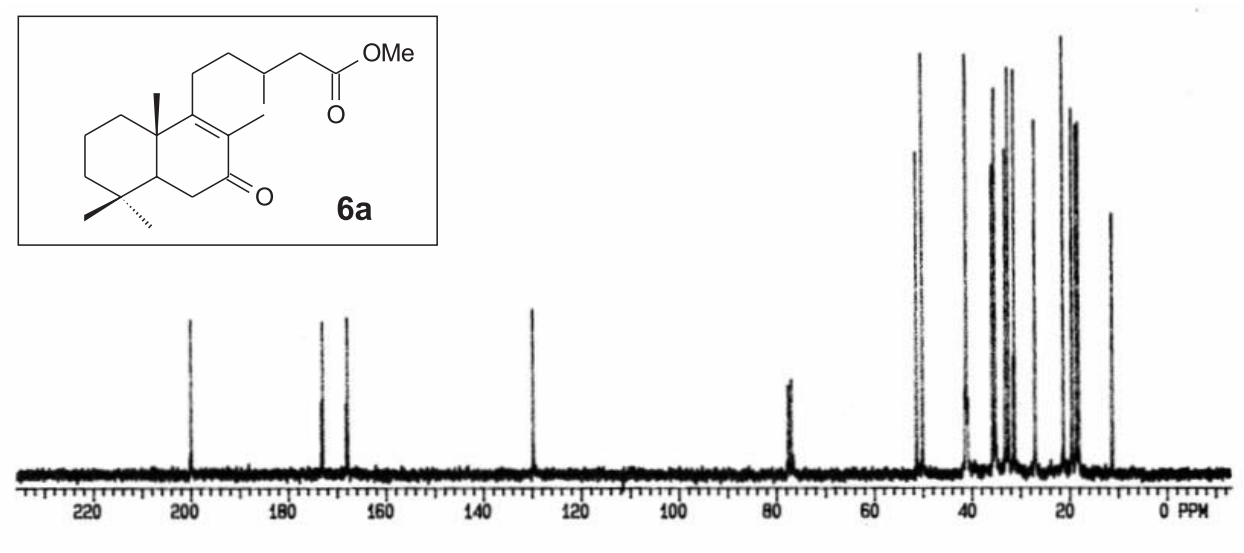

Figure S13. ^{13}C NMR of compound **6a** [75 MHz, $CDCl_3$, δ (ppm)].