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Article

Dammarane Triterpenoids from Carnauba, *Copernicia prunifera* (Miller) H. E. Moore (Arecaceae), Wax

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Phytochemical investigation from carnauba (*Copernicia prunifera*) wax led to the identification of sixteen dammarane–type triterpenes, including thirteen new characterized as: (24*R**)-methyldammara-20,25-dien-3α-ol and a mixture of alkyl (24*R**)-methyldammar-25-en-20-ol-3β-carboxylates, together with three previously described triterpenes: carnaubadiol, (24*R**)-methyldammara-20,25-dien-3β-ol and (24*R**)-24-methyldammara-20,25-dien-3-one. Moreover, four fatty alcohols (eicosanol, docosanol, tetracosanol and hexacosanol) as well as four sterols (cholesterol, campesterol, stigmasterol, and sitosterol) were also obtained. These compounds were isolated using classical chromatographic methods and their structures were determined by spectroscopic and chemical methods.

Keywords: carnauba wax, *Copernicia prunifera*, Arecaceae, dammarane-type triterpenoids

Introduction

Copernicia genus (Arecaceae) comprises thirteen species being *C. prunifera* and *C. alba* native to Brazil.[1-3] *C. prunifera* (syn. *C. cerifera*) is known as carnauba. Its occurrence has been described in several states of Brazilian Northeast region, mainly Piauí, Ceará and Rio Grande do Norte, where it is a source of an exudate from their leaves, known as carnauba wax.[4] This plant material is commercially classified as types 1, 3 and 4. Type 1 occurs as a pale yellow material exuded from young leaves while type 4, frequently found as a dark color material, is obtained from old leaves. Type 3 is prepared from type 4 wax, after clarification with H_2O_2.[4,5] Chemically, these exudates are composed by hydrocarbons, fatty acids, esters, long-chain alcohols, triterpenoids, and cinnamic acid derivatives.[6-10]

As part of our ongoing project involving the phytochemistry of Brazilian plant species, mainly those of Northwest region,[11-14] the present work was aimed to identify secondary metabolites of carnauba wax (types 1 and 4). As a result, thirteen new dammarane-type triterpenoids containing an unusual methyl group on the side chain (**3a**-**3l** and **5**) were characterized, together with three previously described triterpenes (**1**, **2** and **4**), four fatty alcohols (**6-9**) and four sterols (**10-13**).

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Experimental

General experimental procedures

Infrared (IR) spectra were recorded on a Spectrum 100 spectrometer (PerkinElmer, Waltham, USA) using KBr pellets. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Inova 500 (Varian, Palo Alto, USA) and DRX-500 (Bruker Avance, Billerica, USA) spectrometers, operating at 500 MHz (^{1}H) and 125 MHz (^{13}C), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Column chromatography procedures (CC) were performed using silica gel 60 (70-230 mesh; Across Organic) or Sephadex LH-20 (Pharmacia Biotech). Flash CC procedures were conducted using silica gel (40-60 μm, 12 × 150 mm) coupled to a B-688 pump containing 6-way valves with

loop (BÜCHI Laboratory Equipment AG, Switzerland). Analyses by gas chromatography - low resolution electron ionization mass spectrometry (GC-LREIMS) were conducted using a 7890A gas chromatograph (Agilent, Santa Clara, USA) coupled to a VLMSD mass spectrometer (Agilent 5975 model), equipped with an automatic injector and a DB-5 column (J&W, 30 m × 0.25 mm × 0.25 μm, 5%-phenyl-methylpolysiloxane). Analysis conditions were as follow: injector and interface temperature were 250 and 310 °C, respectively; injection of 1 μL of sample solution at 5 mg mL^{-1} in toluene/EtOAc (1:1); split mode (10:1); carrier gas (helium) flow rate of 1 mL min^{-1}. The column oven temperature was maintained at 200 °C for 4 min, and then programmed to 290 °C at 6 °C min^{-1}, and finally changed the gradient to 305 °C at 2 °C min^{-1}. Spectrum acquisition was obtained by electron ionization (70 eV) and specified mass range of 40-600 Da. GC-flame ionization detections (GC-FID) were conducted using a Shimadzu GC-2010 gas chromatograph equipped with FID detector, automatic injector (Shimadzu AOC-20i) and RtX-5 capillary column (Restek, 30 m × 0.32 mm × 0.25 μm, 5%-phenyl-methylpolisiloxane). These analyses were performed by injecting 1.0 μL of a 1.0 mg mL^{-1} solution in EtOAc in a split mode (1:30) employing helium as the carrier gas (1 mL min^{-1}) using the same conditions described above. High-resolution atmospheric-pressure chemical-ionization mass spectra (HRAPCIMS) were acquired on an LTQ-Orbitrap XL mass spectrometer (Thermo Scientific, Marietta, USA). Samples at 0.1 mg mL^{-1} in toluene/isopropanol (1:1) were analyzed by direct infusion.

Plant material

Carnauba wax (types 1 and 4) were purchased from the local distributor J. I. Dias Ltda., Teresina-PI, Brazil.

Extraction and purification procedures

Both materials were individually grounded and subjected to maceration using hexane followed by EtOH (3 × 500 mL each solvent). Solvents were removed under reduced pressure to afford crude extracts: EH-1 (type 1 wax, hexane extract, 29 g, 3.5%), EE-1 (type 1 wax, EtOH extract, 18 g, 2.2%), EH-4 (type 4 wax, hexane extract, 8 g, 1.6%) and EE-4 (type 4 wax, EtOH extract, 16 g, 3.2%). Aliquots of the extracts EH-1 and EE-4 (15 g each) were individually subjected to CC over SiO_2 (250 g, 6 × 60 cm) eluted with increasing amounts of EtOAc in hexane. Fractionation of EH-1 afforded 8 fractions (A to H). Fraction B (600 mg) was purified over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) using hexane/CH_2Cl_2 (1:4) as eluent to provided 244 mg of a mixture composed by **3a**-**3l**. An aliquot of fraction C (320 mg) was subjected to CC over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) using hexane/CH_2Cl_2 (1:4) as eluent to afford 22 mg of a mixture composed of **2** and fatty alcohols (**6**-**9**). Fraction E (200 mg) afforded 10 mg of a mixture of sterols (**10**-**13**). Purification of fraction G (320 mg) over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) using hexane/CH_2Cl_2 (1:4) and CH_2Cl_2/acetone (3:2) as eluent gave two sub-fractions (G1 and G2). Sub-fraction G2 (90 mg) was further fractionated by flash CC over SiO_2 (2.5 × 40 cm, 20 g) eluted with hexane/EtOAc (9:1) to yield 62 mg of **1**. Fractionation of EE-4 afforded 8 fractions (I to P). CC over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) using hexane/CH_2Cl_2 (1:4) as eluent of fraction I (172 mg) produced three sub-fractions (I1 to I3). CC over SiO_2 (3.0 × 40 cm, 35 g) of sub-fraction I2 (130 mg) using increasing amounts of CH_2Cl_2 in hexane (0 to 100%) yielded 68 mg of **4**. Fraction K (325 mg) was purified by CC over SiO_2 (2.5 × 45 cm, 90 g) using increasing amounts of EtOAc in hexane (0 to 100%) to give 21 mg of **5**. Fraction M (811 mg) was partially re-suspended in hexane/CH_2Cl_2 (1:4) and the supernatant was subjected to CC over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) eluted with hexane/CH_2Cl_2 (1:4) and CH_2Cl_2/acetone (3:2) to give 3 sub-fractions (M1 to M3). Sub-fraction M2 (76 mg) was subjected to CC over SiO_2 (2.5 × 40 cm, 20 g), using increasing amounts of CH_2Cl_2 in hexane (0 to 100%) to give 19 mg of a mixture of sterols (**10**-**13**). CC over Sephadex LH-20 (2.5 × 120 cm, 1 mL min^{-1}) of fraction O (3 × 320 mg) using hexane/CH_2Cl_2 (1:4) and CH_2Cl_2/acetone (3:2) as eluent yielded 198 mg of **1**.

(24*R**)-Methyldammar-25-en-3β,20-diol (carnaubadiol, **1**)

Amorphous solid; LREIMS *m/z* (rel. int., %) 458 ($M^{+\bullet}$, 1), 207 (10), 189 (7), 175 (3), 135 (14), 123 (100), 95 (36), 81 (27), 69 (24), 55 (26), 43 (32); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.60 (br s, H-26), 3.19 (dd, *J* 5.0, 11.5 Hz, H-3), 1.64 (br s, H-27), 1.12 (s, H-21), 1.02 (d, *J* 6.9 Hz, H-31), 0.97 (s, H-28), 0.96 (s, H-30), 0.87 (s, H-18), 0.85 (s, H-19), 0.77 (s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): see Table 1.

(24*R**)-Methyldammara-20,25-dien-3β-ol (**2**)

Amorphous solid; LREIMS *m/z* (rel. int., %) 440 ($M^{+\bullet}$, 3), 315 (4), 287 (5), 247 (17), 229 (14), 207 (79), 189 (40), 175 (18), 150 (41), 135 (72), 121 (64), 107 (69), 95 (100), 81 (88), 69 (66), 55 (72), 41 (56); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (br s, H-21a), 4.70 (br s, H-21b), 4.70 (br s, H2-26), 3.21 (dd, *J* 4.7, 11.3 Hz, H-3), 1.67 (br s, H-27), 1.03 (d, *J* 6.9 Hz, H-31), 0.99 (s, H-28), 0.98 (s, H-30), 0.87 (s, H-18), 0.86 (s, H-19), 0.78 (s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): see Table 1.

Alkyl (24*R**)-methyldammar-25-en-20-ol-3β-carboxylate (**3a**-**3l**)

Amorphous solid; IR (KBr) ν / cm^{-1} 3491, 2850, 2918, 1732, 1646, 1475, 1375, 1260, 1171; HRAPCIMS data in negative mode $[M - H]^-$: (**3a**) *m/z* 597.5263 $C_{40}H_{69}O_3$ (calcd. 597.5246), (**3b**) *m/z* 625.5588 $C_{42}H_{73}O_3$ (calcd. 625.5558), (**3c**) *m/z* 653.5923 $C_{44}H_{77}O_3$ (calcd. 653.5872), (**3d**) *m/z* 681.6223 $C_{46}H_{81}O_3$ (calcd. 681.6185), (**3e**) *m/z* 695.6348 $C_{47}H_{83}O_3$ (calcd. 695.6341), (**3f**) *m/z* 709.6536 $C_{48}H_{85}O_3$ (calcd. 709.6498), (**3g**) *m/z* 723.6673 $C_{49}H_{87}O_3$ (calcd. 723.6654), (**3h**) *m/z* 751.7012 $C_{51}H_{91}O_3$ (calcd. 751.6967), (**3i**) *m/z* 779.7323 $C_{53}H_{95}O_3$ (calcd. 779.7280), (**3j**) *m/z* 793.7438 $C_{54}H_{97}O_3$ (calcd. 793.7437), (**3k**) *m/z* 807.7638 $C_{55}H_{99}O_3$ (calcd. 807.7593), (**3l**) *m/z* 835.7899 $C_{57}H_{103}O_3$ (calcd. 835.7906); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 (br s, H-26), 4.49 (dd, *J* 5.5, 10.8 Hz, H-3), 2.30 (t, *J* 7.4 Hz, H-2'), 2.08 (t, *J* 6.9 Hz, H-24), 1.78 (m, H-16), 1.70 (m, H-17), 1.70/1.50 (m, H-2), 1.70/1.48 (m, H-12), 1.67 (m, H-1), 1.64 (br s, H-27), 1.64/1.49 (m, H-6), 1.62 (m, H-13/H-3'), 1.52 (m, H-7), 1.49/1.23 (m, H-11), 1.43/1.05 (m, H-15), 1.36 (m, H-9/H-22/H-23), 1.25 (br s, [(CH_2)m, CH_2(n'-1), CH_2(n'-2), CH_2(n'-3)], 1.12 (s, H-21), 1.02 (d, 6.9, H-31), 0.96 (s, H-30), 0.88 (m, H-5), 0.87 (s, H-18/H-19), 0.85 (s, H-28/H-29); ^{13}C NMR (125 MHz, $CDCl_3$): see Table 1.

(24*R**)-24-Methyldammara-20,25-dien-3-one (**4**)

Amorphous solid; HRAPCIMS data in negative mode $[M - H]^-$: *m/z* 437.3777 $C_{31}H_{49}O$ (calcd. 437.3782); LREIMS *m/z* (rel. int., %) 438 ($M^{+\bullet}$, 3), 313 (8), 285 (4), 245 (21), 205 (44), 189 (9), 175 (9), 150 (54), 135 (44), 121 (60), 107 (63), 95 (100), 81 (73), 67 (54), 55 (61), 41 (46); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (m, H-17), 0.88 (s, H-16), 0.95 (s, H-19), 4.72 (br s, H-21a), 4.70 (br s, H-21b), 4.70 (br s, H-26), 1.66 (br s, H-27), 1.09 (s, H-28), 1.05 (s, H-29), 1.01 (s, H-30), 1.04 (d, *J* 6.6 Hz, H-31); ^{13}C NMR (125 MHz, $CDCl_3$): see Table 1.

(24*R**)-Methyldammara-20,25-dien-3α-ol (**5**)

Amorphous solid; $[\alpha]_D^{25}$ +74.1 (*c* 0.1, $CHCl_3$); IR (KBr) ν / cm^{-1} 3490, 2848, 1650, 1467, 1312, 1264; HRAPCIMS data in positive mode $[M + H]^+$: *m/z* 441.4093 $C_{31}H_{53}O$ (calcd. 441.4097); LREIMS *m/z* (rel. int., %): 440 ($M^{+\bullet}$, 1), 315 (1), 287 (1), 247 (8), 229 (8), 207 (43), 189 (51), 175 (27), 150 (18), 135 (68), 121 (54), 107 (70), 95 (95), 81 (100), 69 (82), 55 (85), 41 (70); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 (br s, H-21a), 4.62 (br s, H-21b/H-26), 3.39 (t, *J* 3.3Hz, H-3), 1.66 (br s, H-27), 1.02 (d, *J* 7.0 Hz, H-31), 0.98 (s, H-30), 0.95 (s, H-28), 0.88 (s, H-18), 0.87 (s, H-19), 0.84 (s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): see Table 1.

Transesterification of compounds **3a**-**3l**

To a mixture of **3a**-**3l** (12 mg) were added 0.1 mL of concentrated H_2SO_4 and 5 mL of anhydrous MeOH. The system was heated with stirring at 70 °C during 4 h. After addition of 10 mL of saturated NaCl and extraction with EtOAc (3 × 10 mL), the organic phase was dried over $MgSO_4$, filtered and analyzed by GC-FID.[15] Identification of methyl esters of fatty acids was performed by comparison of retention times to each compound with those of authentic samples.

Results and Discussion

Crude hexane and EtOH extracts from carnauba wax (types 1 and 4) were subjected to chromatographic procedures to yield triterpenes **1**-**5**, being **3a**-**3l** obtained in a mixture (Figure 1). In addition, alcohols [eicosanol (**6**), docosanol (**7**), tetracosanol (**8**), and hexacosanol (**9**)] and sterols [cholesterol (**10**), campesterol (**11**), stigmasterol (**12**), and sitosterol (**13**)] were identified in mixtures. Structures of the obtained substances were defined by analysis of their respective IR, mass spectra (LREIMS and HRAPCIMS), GC-LREIMS, ^{1}H and ^{13}C NMR spectra, including 2D experiments.

Compounds **1**, **2** and **4** were identified as (24*R**)-methyldammar-25-ene-3β,20-diol (carnaubadiol), (24*R**)-methyldammara-20,25-dien-3β-ol and (24*R**)-24-methyldammara-20,25-dien-3-one, respectively, by comparison of recorded spectral data with those previously reported in the literature.[7,16,17]

IR spectrum of mixture composed by **3a**-**3l** exhibited absorption bands at 1732 cm^{-1}, characteristic of C=O stretch of esters, and at 1260 and 1171 cm^{-1}, attributed to C–O stretching. ^{1}H NMR spectrum of **3a**-**3l** was different from that reported to **1**[7] as it displayed one signal at δ_H 4.49 (dd, *J* 5.5 and 10.8 Hz) assigned to H-3. The observed unshielded effect suggested the presence of an ester bond instead of a hydroxyl group at C-3.[17] ^{13}C NMR data (Table 1) confirmed the presence of triterpenoid derivatives with a similar skeleton to **1**, except to the signal observed at δ_C 80.8 which was attributed to a less shielded oximethine carbon (C-3) caused by esterification.[18] In the HMBC (heteronuclear multiple bond correlation) spectrum were observed correlations of the signals at δ_H 4.49 (H-3) and at δ_H 2.30 (α-carbonyl hydrogens) with the signal at δ_C 173.9 (C-1', carbonyl ester group), contributing to confirm the saturated hydrocarbon chains ester derivatives of **1** at position C-3. Finally, HRAPCIMS of **3a**-**3l**, in negative mode, displayed peaks in the spectrum that corresponded to deprotonated molecular ions $[M - H]^-$ at *m/z* 597.5263,

Table 1. ^{13}C NMR spectral data for **1**, **2**, **3a**-**3l**, **4** and **5** (δ, 125 MHz, $CDCl_3$)

Position	1	2	3a-3l[a]	4	5
1	39.1 (CH_2)	39.3 (CH_2)	38.9 (CH_2)	40.3 (CH_2)	33.7 (CH_2)
2	27.6 (CH_2)	27.7 (CH_2)	24.0 (CH_2)	34.1 (CH_2)	25.0 (CH_2)
3	78.9 (CH)	79.2 (CH)	80.8 (CH)	218.1 (C)	76.3 (CH)
4	39.0 (C)	39.2 (C)	38.2 (C)	47.4 (C)	37.6 (C)
5	55.9 (CH)	56.1 (CH)	56.2 (CH)	55.3 (CH)	49.6 (CH)
6	18.3 (CH_2)	18.5 (CH_2)	18.4 (CH_2)	19.6 (CH_2)	18.3 (CH_2)
7	35.2 (CH_2)	35.7 (CH_2)	35.4 (CH_2)	34.7 (CH_2)	35.3 (CH_2)
8	40.4 (C)	40.7 (C)	40.7 (C)	39.9 (C)	40.7 (C)
9	50.7 (CH)	51.2 (CH)	50.8 (CH)	50.3 (CH)	50.8 (CH)
10	37.1 (C)	37.5 (C)	37.3 (C)	36.9 (C)	37.4 (C)
11	21.5 (CH_2)	21.6 (CH_2)	21.8 (CH_2)	21.9 (CH_2)	21.2 (CH_2)
12	24.7 (CH_2)	29.4 (CH_2)	24.9 (CH_2)	29.1 (CH_2)	29.3 (CH_2)
13	42.3 (CH)	45.7 (CH)	42.5 (CH)	45.5 (CH)	45.4 (CH)
14	50.3 (C)	49.7 (C)	50.6 (C)	49.4 (C)	49.6 (C)
15	31.2 (CH_2)	31.6 (CH_2)	31.5 (CH_2)	31.3 (CH_2)	31.3 (CH_2)
16	27.4 (CH_2)	25.2 (CH_2)	27.8 (CH_2)	25.0 (CH_2)	25.4 (CH_2)
17	49.5 (CH)	47.8 (CH)	49.8 (CH)	47.5 (CH)	47.6 (CH)
18	16.5 (CH_3)	16.2 (CH_3)	16.8 (CH_3)	16.0 (CH_3)	16.0 (CH_3)
19	16.2 (CH_3)	16.4 (CH_3)	16.5 (CH_3)	15.8 (CH_3)	16.1 (CH_3)
20	75.2 (C)	153.4 (C)	75.5 (C)	153.1 (C)	153.4 (C)
21	25.5 (CH_3)	107.3 (CH_2)	25.8 (CH_3)	107.2 (CH_2)	107.1 (CH_2)
22	39.1 (CH_2)	32.7 (CH_2)	39.3 (CH_2)	32.4 (CH_2)	32.5 (CH_2)
23	29.0 (CH_2)	33.9 (CH_2)	29.1 (CH_2)	33.7 (CH_2)	33.8 (CH_2)
24	41.7 (CH)	41.2 (CH)	42.0 (CH)	40.9 (CH)	41.0 (CH)
25	149.9 (C)	150.2 (C)	150.1 (C)	149.9 (C)	150.0 (C)
26	109.5 (CH_2)	109.7 (CH_2)	109.8 (CH_2)	109.5 (CH_2)	109.5 (CH_2)
27	18.8 (CH_3)	19.1 (CH_3)	19.1 (CH_3)	18.9 (CH_3)	18.9 (CH_3)
28	28.0 (CH_3)	28.3 (CH_3)	28.2 (CH_3)	26.7 (CH_3)	22.1 (CH_3)
29	15.4 (CH_3)	15.6 (CH_3)	16.7 (CH_3)	21.0 (CH_3)	28.3 (CH_3)
30	15.3 (CH_3)	15.8 (CH_3)	15.7 (CH_3)	15.3 (CH_3)	15.6 (CH_3)
31	19.9 (CH_3)	20.0 (CH_3)	20.2 (CH_3)	19.8 (CH_3)	19.8 (CH_3)
1'	–	–	173.9 (C)	–	–
2'	–	–	35.1 (CH_2)	–	–
3'	–	–	25.4 (CH_2)	–	–

[a]δ_C 29.4-29.9 (CH_2)m, 28.2 [C-(n'-3)], 32.2 [C-(n'-2)], 22.9 [C-(n'-1)], 14.4 (C-n'); multiplicities were obtained by analysis of ^{13}C DEPT 135°/90° spectra.

625.5588, 653.5923, 681.6223, 695.6348, 709.6536, 723.6673, 751.7012, 779.7323, 793.7438, 807.7638, and 835.7899, consistent with molecular masses of triterpene esters derived from **1** and saturated fatty acids with hydrocarbon chain ranging from C_9 to C_{26} (**3a**-**3l**), that have not previously been described in the literature. Finally, proposed structures were confirmed by transesterification of triterpenoids **3a**-**3l** using $MeOH/H_2SO_4$ followed by analysis using GC-FID (see Experimental section) allowing the identification of methyl esters of saturated fatty acids (C_9, C_{11}, C_{13}, C_{15}-C_{18}, C_{20}, C_{22}-C_{24}, and C_{26}) by comparison of retention times with those obtained to authentic standards.

^{13}C, DEPT 135° and DEPT 90° NMR spectra of compound **5** showed 31 signals attributed to seven methyl, twelve methylene, six methine and six quaternary carbons. The molecular formula $C_{31}H_{52}O$ was confirmed by interpretation of ^{13}C NMR and HRAPCIMS (*m/z* 441.4093 $[M + H]^+$) data, indicating six degrees of unsaturation. The

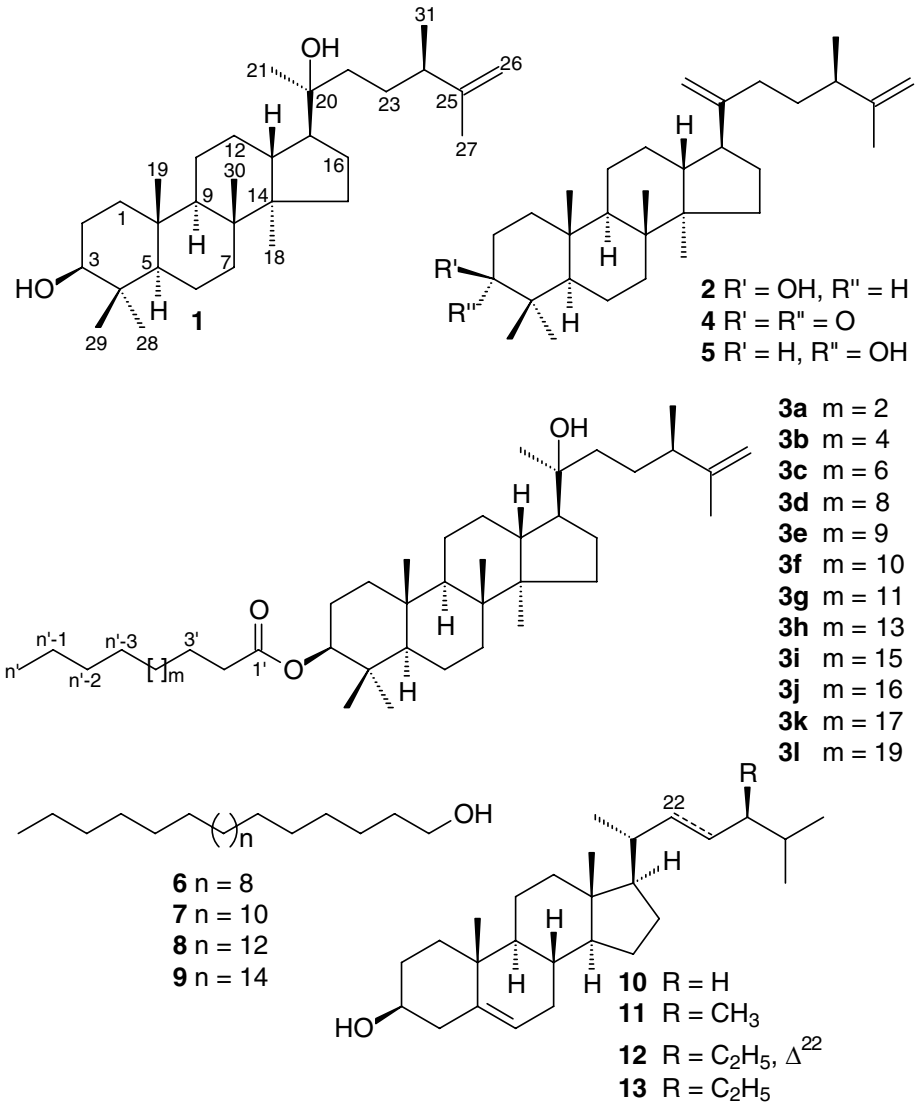

Figure 1. Structures of compounds obtained from carnauba (*C. prunifera*) wax.

broad singlets at δ_H 4.64 and 4.62 observed in the ^{1}H NMR spectrum were assigned to the olefinic hydrogens of two gem-dissubstituted double bonds (H_2-21 and H_2-26), while signals at δ_C 153.4/107.1 and 150.0/109.5, in the ^{13}C NMR spectrum, were attributed to C-20/C-21 and C-25/C-26, respectively. Although the general profile of the ^{1}H NMR spectrum of compound **5** was similar to that reported to triterpenoid **2**, the signal attributed to H-3 was observed as a triplet at δ_H 3.39 (*J* 3.3 Hz), suggesting a 3α-OH stereochemistry.[16,19] This proposal was confirmed by presence of the signal attributed to one oximethine carbon at δ_C 76.3 (C-3) that was correlated to the signal at δ_H 3.39 (H-3) in the HSQC (heteronuclear single quantum correlation) spectrum.[20,21] Comparison of obtained ^{13}C NMR data with those reported to 3α-hydroxy-25,26,27-trinordammar-22,23-en-24,20α-olide,[22] especially to carbons C-1 to C-10, C-19, C-28 and C-29, confirmed the proposal stereochemistry to C-3. Finally, comparison of the ^{13}C NMR data of **5** to the structurally similar compounds[7,17] allowed the structure characterization of the previously undescribed triterpenoid (24*R**)-methyldammara-20,25-dien-3α-ol. Therefore, the results reported in this work indeed corroborate the tendency of *C. prunifera* to behave differently of the other species belonging to *Copernicia* since produce 24-methyldammarane triterpenoids which are rarely found in this genus. However, related dammarane-type esters had previously been reported in species of the Betulaceae, Burseraceae, Celastraceae, Oleaceae and Rhizophoraceae.[23-28]

Conclusions

In this work, sixteen dammarane-type triterpenoids were identified, including thirteen new derivatives, four fatty alcohols and four sterols from carnauba (*C. prunifera*)

wax (types 1 and 4). Based in the obtained results, this work contribute with chemosystematics of *C. prunifera*, whose wax material is extremely versatile with several technological and medical applications.

Supplementary Information

Supplementary 1D and 2D NMR, MS and IR spectroscopic data of compounds **1**-**5** are available free of charge at http://jbcs.sbq.org.br.

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