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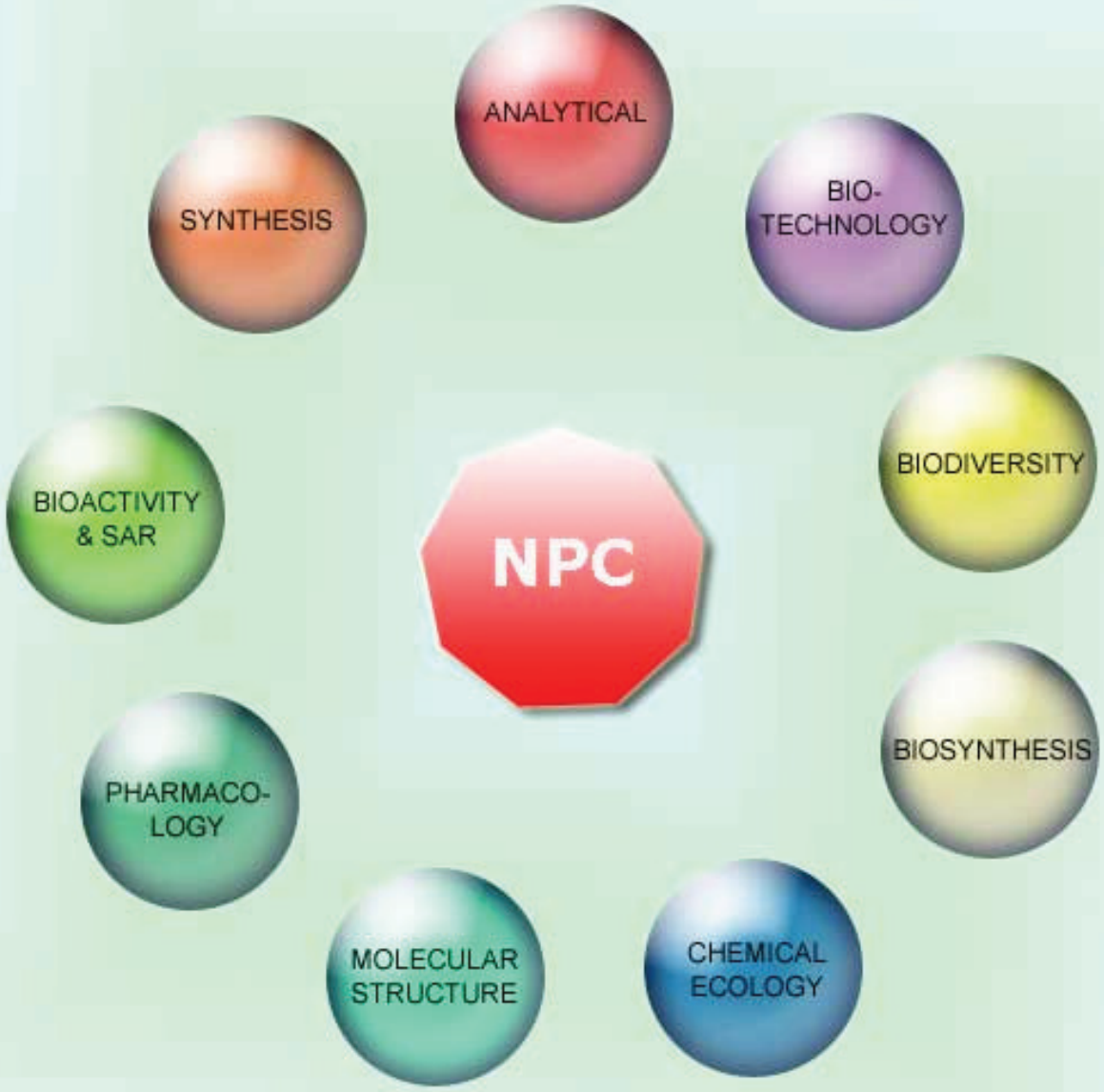

This Issue is Dedicated to
Professor Peter G. Waterman

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Cassane diterpenoids from *Lonchocarpus laxiflorus*

John O. Igoli[a,*], Samuel O. Onyiriuka[b], Matthias C. Letzel[c], Martin N. Nwaji[b] and Alexander I. Gray[d]

[a]*Department of Chemistry, University of Agriculture, P. M. B. 2373, Makurdi, Nigeria*

[b]*Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria*

[c]*Fakultät für Chemie, Organische Chemie I, Universität Bielefeld, 33501 Bielefeld, Germany*

[d]*Natural Products Research Group, Division of Pharmaceutical Sciences, SIPBS, University of Strathclyde, 27 Taylor Street, Glasgow G4 ONR, UK*

igolij@yahoo.com

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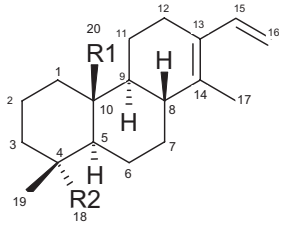
Dedicated to Professor Peter G Waterman, one of the pioneers of phytochemical research.

Phytochemical investigation of the stem bark of *Lonchocarpus laxiflorus* yielded three new cassane diterpenoids, lonchocassane A [cassa-13 (14), 15-dien-18, 20-dioic acid], lonchocassane B [cassa-13 (14), 15-dien-20-oxo-18-oic acid] and lonchocassane C [cassa-13 (14), 15-dien-20-carboxyl-18-methylcarboxylate]. The known compounds betulinic acid, betulinic acid acetate, betulin, lupeol, lupenone, trilinoleate, hexacosanyl and triacontanyl caffeates, 4-hydroxy-4-methylpentan-2-one, β-sitosterol, β-sitosterol acetate and stigmasterol were also isolated. The structures and identities of the compounds were established by spectroscopic methods.

Keywords: *Lonchocarpus laxiflorus*, Fabaceae, cassane diterpenoids, lonchocassanes, lupane triterpenoids, caffeic acid esters.

Lonchocarpus laxiflorus Guill & Perr. is one of the six *Lonchocarpus* species growing in Nigeria [1], some of which are extensively used in traditional medicine [2,3]. The Igede people of Benue State, Nigeria, use the young stems and branches of *L. laxiflorus* for dental care as chewing sticks and the bark as a component of an arrow poison [4]. The isoflavonoids lonchocarpan and laxifloran and the pterocarpinoids, philenopteran and 9-*O*-methylphilenopteran were previously isolated from the roots of the plant [2]. The crude methanol, chloroform and *n*-hexane extracts of the plant have shown a broad spectrum antimicrobial activity against several strains of bacteria and fungi. Efforts to isolate and characterize the constituents of these antimicrobial crude extracts yielded the new cassane type diterpenoids designated as lonchocassane A (**1**), lonchocassane B (**2**) and lonchocassane C (**3**), together with the known compounds betulinic acid (**4**) [5-8], betulinic acid acetate (**5**) [7,9], betulin (**6**) [9,10], lupeol (**7**) [3,9], lupenone (**8**) [11] hexacosanyl and triacontanyl caffeates (**9a**, **9b**) [12,13] trilinoleate (**10**), 4-hydroxy-4-methylpentan-2-one (**11**), β-sitosterol (**12**), β-sitosterol acetate (**13**) and stigmasterol (**14**). We now describe the structure determination of the new cassane diterpenoids.



1: R1 = R2 = COOH
2: R1 = CHO, R2 = COOH
3: R1 = COOH, R2 = $COOCH_3$

Lonchocassane A (**1**) was obtained from the *n*-hexane, ethyl acetate (EtOAc) and methanol (MeOH) extracts by column chromatography (CC),

and the compound was purified by preparative TLC. The molecular mass of the compound was found to be 332 from EIMS and ESIMS analyses. The HREIMS revealed the molecular formula $C_{20}H_{28}O_4$ with a double bond equivalent (DBE) of seven. The UV spectrum of **1** (λ_{max} 242 nm) was indicative of a conjugated diene. Its IR spectrum showed carbonyl absorption at 1696 cm^{-1}, characteristic of a free carboxylic acid, and an olefinic absorption at 1458 cm^{-1}. The presence of an ethylene side chain was evident in the ^1H NMR spectrum from the peaks at δ 6.91 (1H, dd, *J* = 17.0 Hz and 11.0 Hz), 5.17 (1H, d, *J* = 17.0 Hz) and 5.01 (1H, d, *J* = 11.0 Hz). Only two methyl groups were observed at δ 1.62 and 1.68, while methylene and methine protons were observed between δ 1.03 and 2.96. The *J*-modulated ^{13}C NMR spectrum indicated two carboxylic acid carbons at δ 178.0 and 181.5, two olefinic C = C carbons at δ 128.9 and 137.7, and an olefinic CH and CH_2 at 136.5 and 111.5, respectively. The balance of the carbons was made up of two methyl groups, seven methylenes, three methines and two saturated quaternary carbons. The molecular formula of the compound is typical of a non aromatic diterpenoid. This is supported by the absence of an aromatic absorption in its UV and IR spectra, and also the absence of any aromatic proton and carbon signals in its NMR spectra (Table 1). The conjugated olefinic group C=C-CH=CH_2 and the two carboxylic acid groups account for a DBE of four, suggesting that the compound could be a tricyclic diterpene. Out of the most common tricyclic diterpene skeletons, only cassanes and iso-cassanes can accommodate an ethylene side chain and a conjugated double bond system involving this side chain. Using 2D NMR experiments (including ^1H-^1H COSY, NOESY, HMQC/ HC-COBIDEC and HMBC) (Table 2) the structure was deduced as the cassane diacid (**1**)

Lonchocassane B (**2**) and lonchocassane C (**3**) were obtained as a CC fraction from the *n*-hexane and EtOAc extracts, and purified by recrystallization. The same structural arguments could be adduced for compound **2** as its ^1H, ^{13}C and 2D NMR spectra were similar to those of **1**, with slight changes in the resonances for H-17 and H-19 in **2**, and the significant change in the resonance for C-20, which shifted to δ 207.5 (CHO). The 2D NMR spectrum (Table 2) showed a strong correlation, observed in its HMBC, between the 19-methyl and C-18 (COOH), indicating they were geminal and, therefore, the aldehyde must be at position C-20. The relative stereochemistry of the chiral centers in this

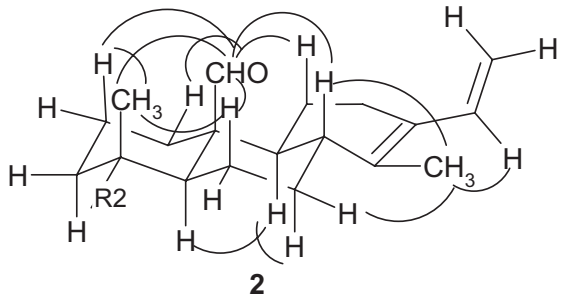


Figure 2: nOe interactions observed in the NOESY spectrum of **2**.

compound, determined from the nOe interactions observed in the NOESY spectrum, is depicted in Figure 1.

The ^1H, ^{13}C and 2D NMR spectra of lonchocassane C (**3)** were also similar to those of compounds **1** and **2**, with slight changes in the resonances for H-17 and H-19. In addition, the resonance for C-18 shifted to δ 178.6 ($COOCH_3$) and a new signal (at δ_H 3.67 and δ_C 52.1), corresponding to an OCH_3**,** was evident in the NMR spectra of **3**. This was further supported by two carbonyl absorptions at 1717 (C=O, ester) and 1687 cm^{-1} (C=O, acid) in the IR spectrum. The compound could have been considered as an artifact from the extraction process, but MeOH was not used at any stage in the extraction, isolation or purification of compound **3**. Therefore, it cannot be a methanolysis product. Moreover, only compound **1** was detected and isolated from the MeOH extract. The strong correlation between the 19-methyl and the -$COOCH_3$ observed in the HMBC spectrum (Table 2) indicated that they were geminal. Therefore, the ester group must be at position C-18.

The NOESY spectra of **1**-**3** confirmed their stereostructures by displaying the nOe interactions bewteen protons (Table 2), and revealed that all three compounds (**1**-**3**) have their 19 methyl groups at an axial position. These structures were further confirmed by comparison of their spectral data with those reported for similar compounds or moieties [14-19].

The lupane triterpenoids were isolated variously from the crude extracts. Betulinic acid (**4**) was obtained from all the crude extracts, while betulin (**5**), betulinic acid acetate (**6**), lupeol (**7**), and lupenone (**8**) were obtained from the *n*-hexane extracts only. Their physical and spectroscopic data (mp, HREIMS, EIMS, IR, ^1H and ^{13}C NMR, coupled with 2D NMR experiments) confirmed their structures when compared with literature reports [5-11, 20].

Table 1: ^{1}H and ^{13}C NMR spectral data of **1** in C_5D_5N, and **2** and **3** in $CDCl_3$ (400 and 100 MHz).

Position	Compound **1**		Compound **2**		Compound **3**	
	Chemical shift δ in ppm		Chemical shift δ in ppm		Chemical shift δ in ppm	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	36.7 (CH_2)	2.96eq, 1.05ax	31.7 (CH_2)	2.61eq, 0.85ax	35.3 (CH_2)	2.63eq, 0.97ax
2	21.0 (CH_2)	2.20ax, 1.75eq	18.7 (CH_2)	1.64eq, 1.44ax	19.6 (CH_2)	1.65eq, 1.83ax
3	38.6 (CH_2)	2.31ax, 1.86eq	37.0 (CH_2)	1.82ax, 1.64eq	37.2 (CH_2)	1.85ax, 1.57eq
4	48.8 (C)	-	47.4 (C)	-	48.1 (C)	-
5	51.5 (CH)	2.35ax	49.9 (CH)	2.15ax	50.9 (CH)	1.93ax
6	25.8 (CH_2)	2.90ax, 1.82eq	24.4 (CH_2)	1.98ax, 0.91eq	24.8 (CH_2)	2.24ax, 1.17eq
7	31.7 (CH_2)	2.27eq, 1.08ax	31.3 (CH_2)	2.40eq, 1.22ax	30.6 (CH_2)	2.22eq, 1.02ax
8	42.0 (CH)	2.83ax	42.6 (CH)	2.24ax	41.1 (CH)	2.39ax
9	52.2 (CH)	1.25ax	52.6 (CH)	1.36ax	51.6 (CH)	1.24ax
10	48.7 (C)	-	51.4 (C)	-	48.3 (C)	-
11	23.8 (CH_2)	2.21ax, 1.23eq	22.2 (CH_2)	1.98eq, 0.91ax	22.8 (CH_2)	2.04eq, 0.97ax
12	27.6 (CH_2)	2.31ax, 2.16eq	26.4 (CH_2)	2.31eq, 2.01ax	26.8 (CH_2)	2.36eq, 2.02ax
13	128.9 (C)	-	129.1 (C)	-	128.2 (C)	-
14	137.7 (C)	-	135.5 (C)	-	136.6 (C)	-
15	136.5 (CH)	6.91 (dd, *J* = 17.0, 11.0 Hz)	135.6 (CH)	6.78 (dd, *J* = 17.2, 10.8 Hz)	135.6 (CH)	6.80 (dd, *J* = 17.3, 11.0 Hz)
16	111.5 (CH_2)	5.22(d, *J* = 17.0 Hz) 5.05(d, *J* = 11.0 Hz)	111.9 (CH_2)	5.13 (d, *J* = 17.2 Hz) 5.00(d, *J* = 10.8 Hz)	111.2 (CH_2)	5.09 (d, *J* = 17.3 Hz) 4.97(d, *J* = 11.0 Hz)
17	16.3 (CH_3)	1.72	15.9 (CH_3)	1.76	15.9 (CH_3)	1.75
18	181.5 (C)	-	183.8 (C)	-	178.6 (C)	-
19	17.6 (CH_3)	1.66 ax	15.7 (CH_3)	1.08ax	16.0 (CH_3)	1.11ax
20	178.0 (C)	-	207.5 (CH)	10.17	180.8 (C)	-
-OCH_3	-	-	-	-	52.1 (CH_3)	3.67

ax = axial; eq = equatorial

Table 2: Significant 2D NMR correlations for compounds **1**-**3**.

	Multiple bond correlations (^{1}H-^{13}C correlations in HMBC)		
	1	**2**	**3**
H-1	-	C-20	-
H-5	C-4, C-6, C-10, C-20	C-4, C-6, C-10, C-20	C-4, C-6, C-10, C-20
H-9	C-10, C-11, C-20	C-10, C-20	C-10, C-20
H-15	C-12, C-13, C-14	C-12, C-13, C-14	C-12, C-13, C-14
H-16	C-13, C-15	C-13, C-15	C-13, C-15
H-17	C-8, C-13, C-14	C-8, C-13, C-14	C-8, C-13, C-14
H-19	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18
H-20	-	C-1, C-9, C-10	-
H-21	-	-	C-18

NOESY correlations (^{1}H-^{1}H nOe interactions)					
1		**2**		**3**	
1.66 (H-19ax)	2.20 (H-2ax), 2.90 (H-6ax)	10.17 (H-20ax) (CHO)	1.08 (H-19ax), 2.15 (H-6ax), 2.24 (H-8ax), 2.61 (H-1eq), 1.44 (H-2ax), 0.91 (H-11ax)	1.11 (H-19ax)	1.83 (H-2ax), 1.57 (H-3eq), 2.24 (H-6ax)
1.72 (H-17)	2.27 (H-7eq), 2.83 (H-8ax), 6.91 (H-15)	1.76 (H-17)	2.24 (H-8ax), 2.40 (H-7eq), 6.78 (H-15)	2.39 (H-8ax)	0.97 (H-11ax)
5.05 (H-16)	5.22 (H-16), 6.91 (H-15)	1.08 (H-19ax)	1.44 (H-2ax), 2.15 (H-6ax)	1.75 (H-17)	2.22 (H-7eq), 2.39 (H-8ax), 6.80 (H-15)
5.22 (H-16)	2.16 (H-12eq), 2.31 (H-12ax), 5.05 (H-16)	2.15 (H-5ax)	1.36 (H-9ax), 1.22 (H-7ax)	1.24 (H-9ax)	1.93 (H-5ax)
1.08 (H-7ax)	1.25 (H-9ax), 2.35 (H-5ax)	5.00 (H-16)	6.78 (H-15)	4.97(H-16)	6.80 (H-15)

An *n*-pentane-dichloromethane extract of the plant material gave compound **6** and the caffeic acid esters **9a** and **9b** as a mixture. Exact mass measurement (HREIMS) of the molecular ion of compound **9a** gave the molecular formula $C_{35}H_{60}O_4$. The compound gave a carbonyl absorption at 1686 cm^{-1} indicative of an ester. The presence of an aromatic ring was indicated in its ^{13}C and ^{1}H NMR spectra, while the long alkyl chain was also inferred from its EIMS and ^{1}H NMR spectrum. The difference of 56 mass units resulting from four additional CH_2-units indicated that **9a** and **9b** were analogues. The isolation of the esters **9a** and **9b** as a mixture has been previously reported [12]. The spectroscopic data obtained for the compounds were in agreement with those reported [12,13]. The triglyceride, trilinoleate (**10**), was obtained as a yellowish oil from the *n*-hexane extract and the 4-hydroxypentan-2-one (**11**) was also obtained as an oil from the MeOH extract, while the steroids β-sitosterol (**12**), β-sitosterol acetate (**13**) and stigmasterol (**14**) were obtained from all the crude extracts as crystalline white solids. Their ^{1}H and ^{13}C NMR spectra confirmed their structures when compared with authentic samples and literature/database (Aldrich NMR Lib. 1992, NIST 2006 and SDBS, 2006) reports.

Experimental

General: Melting points (uncorr.) were taken on a Buchi B-540 melting point apparatus. The ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AMX 400 and/or DRX 500 spectrometers with $CDCl_3$ or C_5D_5N as solvent and TMS as internal standard. ESIMS were run using a Bruker Esquire 3000, while exact masses were measured using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, now Micromass, Manchester, UK). IR and UV/VIS spectra were obtained using Perkin-Elmer 841 and Perkin – Elmer UV/VIS – spectrometer Lambda 40, respectively. Column chromatographic separations were performed in glass columns using silica gel MN-60 (Macherey-Nagel GmbH & Co. KG) and spots on tlc were visualized using vanillin-H_2SO_4 reagent. Optical rotations were determined using a Perkin Elmer Polarimeter 341. Column chromatography (CC) was performed on silica gel.

Plant material: The stem bark of *Lonchocarpus laxiflorus* Guill & Perr. was collected in July 2002 and 2006 from mature trees growing in Igwoke in the Uwokwu locality of Benue State, Nigeria. The plant was identified by the Forestry and Wildlife Department of the University of Agriculture, Makurdi, where a voucher specimen was deposited. It was also authenticated at the Royal Botanical Garden Edinburgh, Herbarium reference: Family 194 and Genus 249

Extraction and isolation: The dried ground bark (1 kg) was Soxhlet-extracted, successively, using *n*-hexane, EtAOc and MeOH ((2.5 L each). The solvents were removed to obtain 5.92 g, 3.06 g and 138.0 g of the crude extracts, respectively. CC of the *n*-hexane and EtOAc extracts, eluting with *n*-hexane, EtOAc in *n*-hexane and finally MeOH in EtOAc yielded **10** (142.0 mg), **8** (44.3 mg), **7** (12.8 mg), **6** (13.3 mg), **5** (10.3 mg), **12** (10.5 mg), **13** (3.9 mg), **14** (11.6 mg) **3** (96.0 mg), **2** (74.0 mg), **4** (127.5 mg) and **1** (56.0 mg).

A second batch of the plant material (0.25 kg) was extracted with *n*-pentane-dichloromethane (1:1) and thereafter with MeOH to obtain 1.73 g of the *n*-pentane-dichloromethane extract and 25.85 g of the methanol extract. The *n*-pentane-dichloromethane extract, on addition of *n*-pentane, gave a solid (0.371 g). This was subjected to CC and eluted with *n*-pentane, ethyl formate in *n*-pentane and then ethyl formate to obtain **5** (12.0 mg), **9a** and **9b** (41.0 mg). The MeOH extract (25.85 g) was re-dissolved in MeOH (300 mL) and extracted continuously with *n*-pentane to give an oily paste (0.561 g), which was subjected to CC and eluted with *n*-pentane-dichloromethane (1:1), dichloromethane, and MeOH in dichloromethane to obtain **11** (120 mg), **4** (23.0 mg) and **1** (23.8 mg).

Although the plant belongs to the family Fabaceae, species of which frequently yields flavonoids of a wide range of structural types [21,22], surprisingly no flavonoid could be found in this plant. Cassane diterpenoids have been shown to possess antibacterial, antifungal and antioxidant activities [19,23].

Lonchocassane A (**1**)
[**Cassa-13 (14), 15-diene-18, 20-dioic Acid**]

White needles obtained from MeOH-chloroform.
MP: 174-176^{o}C.
$[\alpha]_D^{20}$: -30^o (*c* 0.10, MeOH).
R_f : 0.46 (EtOAc/*n*-hexane (4:6).
IR ν_{max}^{KBr}: 2948 (C-H), 1696 (C=O acid), 1629 (C=C), 1458 (C=C), 1272, 1224 (C-O), 895 (C-H cyclohexane) cm^{-1}.
UV λ_{max}^{MeOH} (log ε): 242 (8.7) nm.
^{1}H NMR (400 MHz, C_5D_5N): Table 1.
^{13}C NMR (100 MHz, C_5D_5N): Table 1.
EIMS *m/z* (rel. int.): 332 [M$^+$] (40), 286 [M-HCOOH]$^+$ (100), 241 [M-2HCOOH]$^+$(39), 190 (21), 147 (42), 133 (46), 91 (63), 55 (58).
ESIMS (neg.) *m/z* (rel. int.): 331.19 [M-H]$^-$ (100).
ESIMS (pos.) *m/z* (rel. int.) 355.15 [M+Na]$^+$ (50).
HREIMS: *m/z* 332.1993 [M]$^+$, $C_{20}H_{28}O_4$ requires 332.1988.

Lonchocassane B (**2**)
[**Cassa-13 (14), 15-diene-20-oxo-18-oic acid**]

White needles obtained from MeOH-chloroform.
MP: 168-170^{o}C
$[\alpha]_D^{20}$: -44^o (*c* 0.10, MeOH).
R_f : 0.68 (EtOAc/*n*-hexane (4:6).
IR ν_{max}^{KBr}: 2931 (C-H), 2863 (C-H aldehyde), 1693 (C=O), 1629 (C=C), 1459 (C=C), 1286, 1201 (C-O), 895 (C-H cyclohexane) cm^{-1}.
UV λ_{max}^{MeOH} (log ε): 244 (12.5) nm.
^{1}H NMR (400 MHz, C_5D_5 N): Table 1.
^{13}C NMR (100 MHz, C_5D_5 N): Table 1.
EIMS *m/z* (rel. int.): 316 [M]$^+$(11), 298 [M-H_2O]$^+$(15), 148 (35), 147 (45), 135 (50), 134 (100), 119 (29), 55 (18).

ESIMS (neg.) *m/z* (rel. int.): 351.10 $[M+Cl]^-$ (100).
ESIMS (pos.) *m/z* (rel. int.) 317.10 $[M+H]^+$ (100).
HREIMS *m/z* 317.2111 $[M+H]^+$, $C_{20}H_{29}O_3$ requires 317.2117

Lonchocassane C (**3**)
[**Cassa-13 (14), 15-diene-20-carboxyl-18-methyl-carboxylate**]

White crystals obtained from MeOH-chloroform.
MP: 133-135°C.
$[\alpha]_D^{20}$: -47° (*c* 0.10, MeOH).
R_f: 0.74 (EtOAc/*n*-hexane (4:6).
IR ν_{max}^{KBr}: 2967 (C-H), 1717 (C=O ester), 1687(C=O acid), 1627 (C=C), 1461 (C=C), 1247, 1158 (C-O), 901 (C-H cyclohexane) cm^{-1}.
UV λ_{max}^{MeOH} (log ε): 242 (10.9) nm.
^1H NMR (400 MHz, C_5D_5N): Table 1.
^{13}C NMR (100 MHz, C_5D_5N): Table 1.
EIMS *m/z* (rel. int.): 346 $[M]^+$(20), 300 $[M-HCOOH]^+$ (100), 286 $[M-HCOOCH_3]^+$ (13), 240 $[M-HCOOH- HCOOCH_3]^+$ (21), 171 (14), 134 (20), 91 (26), 79 (20).
ESIMS (neg.) *m/z* (rel. int.): 345.82 $[M-H]^-$ (25).
HREIMS *m/z* 346.2145 $[M]^+$, $C_{21}H_{30}O_4$ requires 346.2144.

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