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Dois Novos Diterpenos do Tipo Labdano e outros Compostos de *Conchocarpus cyrtanthus* (Rutaceae)

Resumo: Dois novos diterpenos do tipo labdano denominados 16-hidroxilarixol (**1**) e 16-hidroxi-7-labden-6-ona (**2**) foram isolados de *Conchocarpus cyrtanthus*, juntamente com mais três cumarinas: seselina (**3**), xantoxiletina (**4**), luvangetina (**5**); o alcaloide dictamina (**6**); seis esteroides: β-sitosterol (**7**), estigmasterol (**8**), campesterol (**9**), 7α-hidroxi-β-sitosterol (**10**), 7α-hidroxiestigmasterol (**11**) e 7α-hidroxicampesterol (**12**); três diterpenos: manool (**13**), 16-hidroximanoiloxido (**14**) e 16-hidroxi-13-*epi*-manoiloxido (**15**) e a lignana siringaresinol (**16**). Estes compostos foram caracterizados com base na análise dos dados fornecidos por Ressonância Magnética Nuclear (RMN de ^{1}H e ^{13}C) unidimensional e bidimensional, Espectrometria de Massas de Alta Resolução (EMAR), além de comparação com dados registrados na literatura.

Palavras-chave: Rutaceae; *Conchocarpus cyrtanthus*; diterpenos; cumarinas; esteroides.

Abstract

Two new labdane-type diterpenes called 16-hydroxylarixol (**1**) and 16-hydroxy-7-labden-6-one (**2**) were isolated from *Conchocarpus cyrtanthus*, along with three coumarins, seselin (**3**), xantoxiletin (**4**), luvangetin (**5**); the alkaloid dictamin (**6**); six steroids, β-sitosterol (**7**), stigmasterol (**8**), campesterol (**9**), 7α-hydroxy-β-sitosterol (**10**), 7α-hydroxy-stigmasterol (**11**) and 7α-hydroxy-campesterol (**12**); three diterpenes, manool (**13**), 16-hydroxymanoiloxide (**14**), and 16-hydroxy-13-*epi*-manoyloxide (**15**) and the lignan siringaresinol (**16**). These compounds were characterized based on analysis of data provided by one- and two-dimensional Nuclear Magnetic Resonance (NMR of ^{1}H and ^{13}C), High-resolution Mass Spectrometry, besides comparison with data reported in the literature.

Keywords: Rutaceae; *Conchocarpus cyrtanthus*; diterpenes; coumarins; steroids.

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Two New Labdane-type Diterpenoids and others Compounds from *Conchocarpus cyrtanthus* (Rutaceae)

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1. Introduction

The Rutaceae family is represented by 155 genera and 1600 species distributed in tropical and temperate regions of the world. This family is commonly found in Tropical America, South Africa, Asia and Australia.[1] The Rutaceae family is characterized by abundance of anthranilic acid derivate alkaloids, coumarins, limonoids and flavonoids, with different types of biological activities.[2]

The *Conchocarpus* (Rutaceae) genus encloses about 47 tropical species occurring from Nicaragua to northern Bolivia and almost every Brazilian state.[3-5] Literature reports of phytochemical studies with *Conchocarpus* species have shown the presence of alkaloids, flavonoids and coumarins in addition to anti-*Trypanosome cruzy* activity.[6-9]

In the present paper, we used stems from *Conchocarpus cyrtanthus* commonly known as "Orelha de cabra" to describe the isolation and characterization of two new diterpenes 16-hydroxylarixol (**1**), 16-hydroxy-7-labden-6-one (**2**) besides twelve known compounds: three coumarins seselin (**3**), xantoxiletin (**4**) in

mixture, luvangetin (**5**), the alkaloid dictamin (**6**), six steroids ⍰-sitosterol (**7**), stigmasterol (**8**), campesterol (**9**) in mixture, 7α-hydroxy-β-sitosterol (**10**), 7α-hydroxy-stigmasterol (**11**) 7α-hydroxy-campesterol (**12**) in mixture, three diterpenes manool (**13**), 16-hydroxymanoiloxide (**14**) 16-hydroxy-13-*epi*-manoyloxide (**15**), and the lignan siringaresinol (**16**).

All these natural products isolated in this species are being described for the first time and the diterpenes 16-hydroxylarixol (**1**) and 16-hydroxy-7-labden-6-one (**2**) were first mentioned in records. The structures were established in spectral data analysis basis, mainly ^{1}H and ^{13}C (1D and 2D) NMR spectra, mass spectrometry and by comparison with data reported in the literature. The information observed in the ^{1}H-^{1}H-NOESY NMR spectrum of **15,** allowed us to propose the relative stereochemistry of this compound.

2. Results e Discussion

The hexane and methanol extracts from stems of *C. cyrtanthus* were subjected to a classical chromatographic method to obtain three new labdane-type diterpenes 16-hydroxylarixol (**1**) and 16-hydroxy-7-labden-6-one (**2**) together with the three coumarins seselin (**3**),[10-11] xantoxiletin (**4**)[10,12] and luvangetin (**5**),[13] the alkaloid dictamin (**6**) that has been considered as a taxonomic marker of *Conchocarpus* genus,[8,9,18] the six steroids ⍰-sitosterol (**7**),[14-15] stigmasterol (**8**)[14-15], campesterol (**9**)[15] in mixture, 7α-hydroxy-β-sitosterol (**10**),[16] 7α-hydroxy-stigmasterol (**11**)[17] and 7α-hydroxy-campesterol (**12**)[16-17] in mixture, the two diterpenes manool (**13**),[19-21] 16-hydroxymanoiloxide (**14**) and 16-hydroxy-13-*epi*-manoyloxide (**15**)[22-24] and the lignan siringaresinol (**16**).[25] The structures were identified based on ^{1}H and ^{13}C-DEPTQ NMR spectral data analysis, including 2D ^{1}H-^{1}H-COSY, ^{1}H-^{1}H-NOESY, HSQC and HMBC NMR experiments which were also used to make the unambiguously ^{1}H and ^{13}C chemical shift assignments of the diterpenes **1** and **2**, the new natural products (see Figure 1).

The diterpene16-Hydroxylarixol (**1**) (Figure 1) $[\alpha]_D^{20}$= +1.5, (MeOH, *c* 2.1), was obtained as a yellow oil. Analysis of the DEPTQ-^{13}C NMR spectrum (Table 1), involving the corroboration of 1D and 2D NMR spectra, allowed us to recognize the presence of 20 signals corresponding to four quaternary carbon [3xC-sp^3: 2xC+1xC-O (⍰$_C$ 75.5), and 1xC-sp^2 (⍰$_C$ 144.1)], four methine [3xCH-sp^3: 2xCH+1xCH-O (⍰$_C$ 69.4) 1xCH-sp^2 (⍰$_C$ 140.8)], nine methylene [7xCH_2-sp^3: 6xCH_2+1xCH_2-O (⍰$_C$ 68.9) and 2xCH_2-sp^2 (⍰$_C$ 110.7 and 115.4)] and three methyl carbon atoms (Table 1), allowing us to deduce the expanded formula (C_4O)(C_4H_4O)($C_9H_{18}O$)(C_3H_9) = $C_{20}H_{31}O_3$ and the presence of three hydroxyl groups provided the molecular formula $C_{22}H_{34}O_3$ confirmed by HRESIMS (positive mode) by peak at *m/z* 345.2468 ([M+Na]$^+$, **1**, calc. 345.2406 for $C_{20}H_{34}O_3Na$, ⍰$_{m/z}$ 6.2 ppm) compatible with the molecular formula $C_{20}H_{34}O_3$ and four degrees of hydrogen deficiency, attributed to two double bonds and two rings, consistent with a diterpene structure sustaining two double bonds. This data supports the proposed structure of a diterpene with labdane skeleton.[19] The ^{1}H NMR spectrum of **1** showed three methyl signals at ⍰$_H$ 1.00 (*s*, 3H-18); 1.22 (*s*, 3H-19) and 0.98 (*s*, 3H-20), an ABX system compatible with vinyl group presented signals at ⍰$_H$ 5.83 (*dd*, *J* = 17.2; 10.7 Hz, H-14); 5.39 (*d*, *J* = 17.2 Hz, H-15a), 5.33 (*d*, *J* = 10.7 Hz, H-15b) and an AB system at ⍰$_H$ 5.04 (*br s*, H-17a) and 4.89 (*br s*, H-17b) indicating an exocyclic vinyl group in labdane-type diterpene.[19,10] The couplings observed were confirmed by ^{1}H-^{1}H-COSY spectrum.

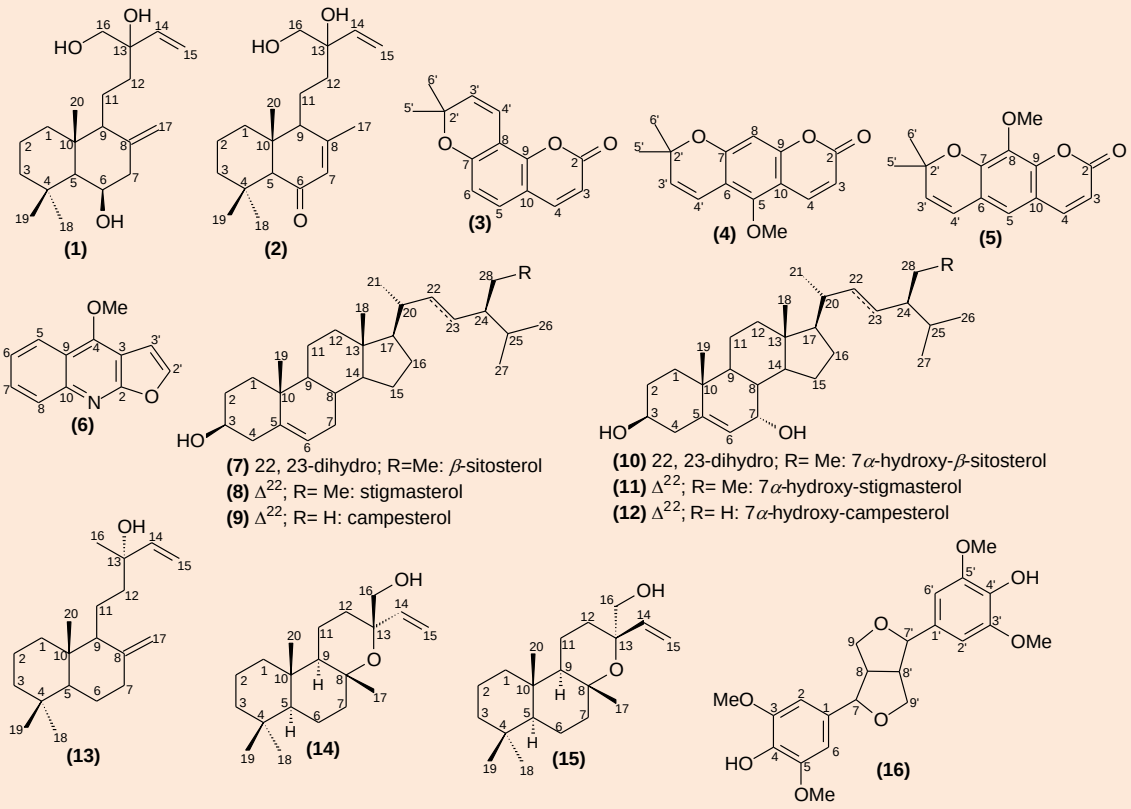

Figure 1. Chemical structures of the compounds isolated from the stems of *C. cyrtanthus*

The signals at δ_H 4.38 (*br s*, H-6) and 3.53 (*br s*, 2H-16) of the ^{1}H NMR revealed heteronuclear correlation with carbon signals at δ_C 69.4 (CH-6) and 68.9 (CH_2-16) in the HSQC spectrum confirmed the presence of two hydroxyl groups. This proposed structure for 16-hydroxylarixol (**1**) was established by 2D NMR data analysis. The chemical shifts of the hydrogen and hydrogenated carbon atoms were assigned unambiguously by ^{1}H-^{1}H-COSY analysis and HSQC spectra data (Table 1). The HMBC spectrum showed long-range heteronuclear correlations, which were also used to confirm the carbon skeleton and localization of the substituents (Table 1). The heteronuclear correlations observed in the HMBC spectrum of the hydrogens 2H-16 with carbon atoms CH_2-12, C-13 and CH-14 and H-14, 2H-15 and 2H-16 with carbon atom C-13 confirmed the presence of hydroxyl groups at 16 and 13 positions (Table 1). The DEPTQ-^{13}C NMR spectrum analysis support presence of the hydroxyl groups at (CH-6 and CH_2-12) by δ-effect present in (C-8 at δ_C 144.1 and CH-14 at δ_C 140.8) absent in the manool (**13**), *see extraction and isolation*. The comparison of the NMR of ^{13}C data with literature justify the unsaturated carbons C-8 (δ_C 144.1), CH-14 (δ_{CH} 140.8), CH_2-15 (δ_{CH2} 115.4) and CH_2-17 (δ_{CH2} 110.7) with proposed structure of a diterpene with labdane skeleton.[19] The relative stereochemistry of **1** was determined by the relevant hydrogen H-6 coupling constants located at the equatorial position on the basis of the coupling constant *J*< 2.0 Hz (H-6) eliminating axial–axial interactions. The comparison of the ^{13}C-DEPTQ-NMR data with larixol diterpene supported the proposal indicating the hydroxyl group and side chain bond at CH-9.[21] Thus, the structure of the new diterpene isolated from *C. cyrtanthus* was established as new diterpene named 16-hydroxylarixol (**1**)

16-hydroxy-7-labden-6-one (**2**) (Figure 1)$[\alpha]_D^{20}$= +11.5, (MeOH, *c* 0.8), was obtained as a yellow oil. Analysis of the DEPTQ-^{13}C NMR spectrum (Table 1), involving the

corroboration of ^{1}H NMR (1D ^{1}H NMR and 2D ^{1}H-^{1}H-COSY) and HSQC and HMBC spectra, allowed us to recognize the presence of 20 signals corresponding to five quaternary carbon [3xC-sp^{3}: 2xC+1xC-O (δ_C 75.4) and 2xC-sp^{2} (δ_C 159.0) and (δ_C 200.0)], four methine [2xCH-sp^{3} and 2xCH-sp2 (δ_{CH} 128.6) and ((δ_{CH} 140.4)], seven methylene [6xCH_2-sp^{3}: 5xCH_2+1xCH_2-O (δ_C 68.8) and 1xCH_2-sp^{2} (δ_C 115.9)] and four methyl carbon atoms (Table 1), allowing us to deduce the expanded formula $(C_5O_2)(CH)_4(CH_2)_6(CH_2O)(CH_3)_4$ = $C_{20}H_{30}O_3$ and the presence of two hydroxyl groups with the corresponding two additional hydrogen atoms to complete the molecular formula $C_{20}H_{32}O_3$ compatible with LR-EIMS by peak at *m/z* 289 attributed to radical elimination CH_2OH [M - 31]$^{+}$. The molecular formula $C_{20}H_{32}O_3$ was confirmed by HRESIMS (positive mode) by peak at *m/z* 343.2192 ([M+Na]$^{+}$, **2**, calc. 343.2249 for $NaC_{20}H_{32}O_3^{+}$, $\delta_{m/z}$ 5.7 ppm) compatible with the molecular formula $C_{20}H_{32}O_3$. The five degrees of hydrogen deficiency ($C_{20}H_{42}O_3$ – $C_{20}H_{32}O_3$ = H_{10}) were attributed to two double bonds, one carbonyl group and two rings, in accordance with a diterpene structure sustaining two double bonds, two hydroxyl groups and one group carbonyl.

Three methyl groups linked to sp^{3} carbon atoms were identified by singlet signals in the ^{1}H-NMR spectrum at δ_H 1.15 (*s*, 3H-18), 1.18 (*s*, 3H-19) and 0.86 (*s*, 3H-20), the signals at δ_H 5.84 (*dd*, *J* = 17.3 and 10.8 Hz, H-14), 5.42 (*dd*, *J* = 17.4 and 1.2 Hz, H-15a) and 5.36 (*dd*, *J* = 10.8 and 1.2 Hz, H-15b) were attributed to an ABX system compatible with a vinyl group. The signal of olefinic hydrogen at δ_H 5.77 (*m*), correlated in the HSQC spectrum with carbon signal at δ_C 128.6 (CH-7). The presence of one methyl group signal at δ_H 1.95 (1.4 Hz, 3H-17) in the ^{1}H NMR spectrum linked at C-8 is supported by heteronuclear long-range correlations with CH-7 (δ_C 128.6, $^{3}J_{CH}$), C-8 (δ_C 159.7, $^{2}J_{CH}$) and CH-9 [δ_C 56.8, $^{3}J_{HC}$, that also revealed interaction with 3H-20 (δ_H 0.86, $^{3}J_{HC}$)] observed in the HMBC spectrum (Table 1). The presence of the carbonyl group was corroborated by the heteronuclear long-range correlation showed in H-5 (δ_H 2.05) HMBC spectrum with carbonyl carbon at C-6 (δ_C 200.0, $^{2}J_{HC}$) and resonance effect that is a further larger chemical shift in δ-carbon and a shield in carbonyl carbon. Additional heteronuclear long-range correlations observed in the HMBC spectrum were summarized in Table 1.

The DEPTQ-^{13}C NMR spectrum showed additional carbons of methyl and methylenes sp^{2}, a signal at δ_C 68.8 (CH_2-16) characteristic of oxygenated sp^{3} carbon correlated with hydrogen signals at δ_H 3.53 (*br s*, *J* = 10.9 Hz, H-16a) and 3.57 (*br s*, *J* = 10.9 Hz, H-16b) in HSQC spectrum, confirming the presence of hydroxyl group. The chemical shifts of the hydrogen and hydrogenated carbon atoms were unambiguously assigned by ^{1}H-^{1}H-COSY and HSQC spectra data analysis (Table 1). Thus, comparison with literature[19] and all spectral data allowed us to characterize the compound **2** as new labdane-type diterpene named 16-hydroxy-7-labden-6-one (**2**).

The chemical shifts of the other hydrogens and hydrogenated carbon atoms were unambiguously assigned by ^{1}H-^{1}H-COSY and HSQC spectrum analysis (Table 1). The other long-range heteronuclear correlations observed in the HMBC spectrum, which were also used to confirm the carbon skeleton and the localization of the substituents, are summarized in Table 1.

Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of **1** and **2** in $CDCl_3$*

		1			**2**		
		HSQC		HMBC	HSQC		HMBC
Atom	Type	δ_C	δ_H	$J_{H\rightarrow C}$	δ_C	δ_H	$J_{H\rightarrow C}$
1	CH_2	42.0	1.79-1.78 (*m*), 1.05-1.04 (*m*)	20	39.2	1.90-1.89 (*m*), 1.56-1.55 (*m*)	20
2	CH_2	19.5	1.77-1.72 (*m*), 1.50-1.48 (*m*)		20.6	1.56-1.55 (*m*)	
3	CH_2	43.5	1.40-1.39 (*m*), 1.20-1.19 (*m*)	18; 19	43.2	1.41-1.40 (*m*), 1.13-1.12 (*m*)	5; 18; 19
4	C	35.8	-	18; 19	32.0	-	
5	CH	57.5	1.10-1.06 (*m*)	18; 19; 20	63.6	2.05 (*s*)	6; 10; 18; 19; 20
6	CH	69.4	4.38 (*br s*)		200.0	-	
7	CH_2	47.7	2.37-2.33 (*m*)	17	128.6	5.80-5.77 (*m*)	17
8	C	144.1	-		159.0	-	
9	CH	58.0	1.77-1.72 (*m*)	17; 20	56.8	2.04-2.03 (*m*)	17; 20
10	C	41.0	-		43.0	-	
11	CH_2	17.1	1.66-1.65 (*m*), 1.47-1.45 (*m*)		18.2	1.62-1.60 (*m*), 1.50-1.49 (*m*)	
12	CH_2	35.8	1.85-1.84 (*m*), 1.31-1.30 (*m*)	16	38.8	1.90-1.89 (*m*), 1.21-1.20 (*m*)	
13	C	75.5	-		75.4	-	
14	CH	140.8	5.83 (*dd*, 17.2, 10.7)	13, 16	140.4	5.84 (*dd*, 17.3, 10.8)	15
15	CH_2	115.4	5.39 (*d*, 17.2), 5.33 (*d*, 10.7)	13, 14	115.9	5.42 (*dd*, 17.4, 1.2) 5.36 (*dd*, 10.8, 1.2)	
16	CH_2	68.9	3.53 (*br s*)	13	68.8	3.57 (*d*, 10.9) 3.53 (*d*, 10.9)	
17	CH_2	110.7	5.04 (*br s*), 4.89 (*br s*)		-	-	-
17	CH_3	-	-		22.1	1.95 (*t*, 1.4)	8
18	CH_3	33.7	1.00 (*s*)	19	33.5	1.15 (*s*)	5; 19
19	CH_3	23.6	1.22 (*s*)	18	21.5	1.18 (*s*)	18
20	CH_3	17.0	0.98 (*s*)	10	14.7	0.86 (*s*)	5

* Number of hydrogens bound to carbon atoms deduced by comparative analysis of BBD- and DEPTQ NMR spectra. Chemical shifts and coupling constants (*J* in Hz, within parentheses) obtained from 1D ^{1}H-NMR spectrum. Superimposed ^{1}H signals are described without multiplicity and chemical shifts deduced by HSQC, HMBC and ^{1}H-^{1}H-COSY spectra.

3. Experimental Section

3.1. General Experimental Procedures

ESI-MS (high resolution) mass spectra were obtained by using an ESI-IT-OF-MS SHIMADZU mass spectrometer, using the positive ion mode of analysis. Chromatographic purifications were carried out by using silica gel 60 (0.063–0.200 mm) (Merck). The solvents Synth were used for chromatography separation.

The NMR analysis were made in the Instituto de Ciências Exatas-UFRRJ by a Brüker Utrashield 500 Plus spectrometer operating at 500 (^{1}H) and 125 (^{13}C) MHz, ^{1}H and ^{13}C-NMR spectra were measured. $CDCl_3$ was used as solvent with TMS as internal reference. Chemical shifts are given in the □ scale (ppm) and coupling constants (*J*) in Hz. One dimensional (1D) ^{1}H and ^{13}C-NMR spectra were acquired under standard

conditions by using a direct detection 5 mm $^{1}H/^{13}C$ dual probe. Standard pulse sequences were used for two dimensional spectra by using a multinuclear inverse detection 5 mm probe with field gradient.

3.2. Plant Material

Stems of *Conchocarpus cyrtanthus* were collected at the Atlantic Rainforest at Cia Vale do Rio Doce (CVRD), in May 2011, Linhares City, Espírito Santo State, Brazil and was identified by Domingos A. Folly. A voucher specimen is deposited at the Vale Cia herbarium, under the code CVRD 6498.

3.3. Extraction and Isolation

The dried and powdered stems (2.5 kg) of *C. cyrtanthus* were extracted by maceration using hexane and MeOH at room temperature, to produce 4.7 g of crude hexane extract EH and 84.5 g of crude MeOH extract EM after solvent evaporation. The hexane extract EH was chromatographed on silica gel column with a gradient of hexane/AcOEt providing eleven fractions. Fraction EH-7 (842.1 mg) was rechromatographed on a silica gel column with a gradient of hexane/AcOEt providing eleven fractions. Fraction EH-7.5 (92.0 mg) was rechromatographed on a silica gel column with a gradient of hexane/AcOEt yielding compounds **3** + **4** (4.9 mg) in mixture. Fraction EH-7.8 (23.0 mg) provided compounds **7** + **8** + **9** in mixture. Fraction EH-10 (192.8 mg) was rechromatographed on a silica gel column with a gradient of hexane/ethyl acetate providing fifteen fractions. Fraction EH-10.9 (14.9 mg) was submitted to preparative TLC and eluted with hexane/CH_2Cl_2/AcOEt (1:2:7, v/v/v), providing the compound **1** (3.0 mg). Fraction EH-11 (246.1 mg) was rechromatographed on a silica gel column with a gradient of hexane/AcOEt providing seven fractions. Fraction EH-11.3 (30.4 mg) was submitted to preparative TLC and eluted with hexane/CH_2Cl_2/AcOEt (1:2:7, v/v/v), resulting in the compound **2** (2.3 mg) and the compounds **10** + **11** +**12** (4.5 mg) in mixture. The MeOH extract EM was chromatographed on silica gel column with a gradient of CH_2Cl_2/MeOH providing ten fractions. Fraction EM-2 (754.1 mg) was rechromatographed on a silica gel column with a gradient of CH_2Cl_2/MeOH providing compound **13** (14.9 mg). Fraction EM-3 (567.9 mg) was rechromatographed on a silica gel column with a gradient of hexane/ethyl acetate providing eighty fractions. Fraction EM-3.2 (48.0 mg) was submitted to preparative TLC eluted with hexane/AcOEt (7:3, v/v), resulting in the compounds **15** (2.1 mg) and **14** (2.4 mg), respectively. Fraction EM-3.6 (224.0 mg) was rechromatographed on a silica gel column with a gradient of hexane/acetone (8:2, v/v) providing nine fractions. Fraction EM-3.6.6 (64.5 mg) was rechromatographed on a silica gel column with hexane/CH_2Cl_2/AcOEt (5:4:1, v/v/v) resulting in the compounds **5** (6.0 mg) and **6** (7.1 mg), respectively. Fraction EM-4 (1.1 g) was rechromatographed on a silica gel column with a gradient of hexane/acetone providing the compound **6** (81.3 mg). Fraction EM-5 (3.2 g) was rechromatographed on a silica gel column with a gradient of hexane/acetone providing ten fractions. Fraction EM-5.9 (554.6 mg) was rechromatographed on a silica gel column with a gradient of CH_2Cl_2/MeOH providing ten fractions. Fraction 5.9.3 (66.2 mg) was submitted to preparative TLC eluted with CH_2Cl_2/AcOEt (9:1, v/v), resulting in the compound **16** (14.1 mg).

Seselin (**3**): ^{13}C δ (ppm): 161.0 (C-2); 112.5 (CH-3); 79.7 (C-2'); 130.2 (CH-3'); 115.0 (CH-4'); 144.0 (CH-4); 127.8 (CH-5); 113.5 (CH-6); 144.2 (C-7); 144.1 (C-8); 108.8 (C-9); 113.1 (C-10); 28.1 (CH_3-5'/6). ^{1}H δ (ppm): (6.25 *d* 9.4; H-3); (5.75 *d* 10.0; H-3'); (6.91 *d* 10.0; H-4'); (7.62 *d* 9.5; H-4); (7.24 *d* 8.4; H-5); (6.74 *d* 8.5; H-6); (1.48 *s*; 3H-5'/3H-6').

Xantoxiletin (**4**): ^{13}C δ (ppm) ($CDCl_3$): 161.0 (C-2); 110.4 (CH-3); 139.0 (CH-4); 156.5 (C-5); 102.6 (C-6); 79.7 (C-2'); 127.6 (CH-3'); 115.0

(CH-4'); 28.2 (CH_3-5'/CH3-6'); 157.5 (C-7); 95.4 (CH-8); 103.9 (C-9); 153.3 (C-10); 56.0 (OCH_3-5). ^{1}H δ (ppm): (6.15 *d* 9.7; H-3); (7.98 *d* 9.6; H-4); (5.60 *d* 10.0; H-3'); (6.82 *d* 10.0; H-4'); (1.48 *s*; 3H-5'/3H-6'); (6.26 *s*; H-8); (3.90 *s*; 3HCO-5).

Luvangetin (**5**): ^{13}C δ (ppm) ($CDCl_3$): 160.0 (C-2); 113.3 (CH-3); 143.6 (CH-4); 119.1 (CH-5); 114.4 (C-6); 77.8 (C-2'); 131.3 (CH-3'); 121.1 (CH-4'); 28.2 (CH_3-5'/CH_3-6'); 149.1 (C-7); 135.8 (C-8); 147.9 (C-9); 113.0 (C-10); 61.5 (OCH_3-8). ^{1}H δ (ppm) ($CDCl_3$): (6.26 *d* 9.5; H-3); (7.59 *d* 9.5; H-4); (6.86 *s*; H-5); (5.73 *d* 9.8; H-3'); (6.36 *d* 9.9; H-4'); (1.54 *s*; 3H-5'/3H-6'); (4.00 *s*; 3HCO-8).

Dictamin (**6**): ^{13}C δ (ppm) ($CDCl_3$): 163.8 (C-2); 103.5 (C-3); 143.6 (CH-2'); 104.8 (CH-3'); 156.3 (C-4); 122.2 (CH-5); 123.9 (CH-6); 130.2 (CH-7); 128.1 (CH-8); 118.7 (C-9); 145.6 (C-10); 59.7 (OCH_3-4). ^{1}H δ (ppm) ($CDCl_3$): (7.65 *d* 2.7; H-2'); (7.10 *d* 2.6; H-3'); (8.29 *d* 8.3; H-5); (7.46 *t* 7.7; H-6); (7.70 *t* 7.7; H-7); (8.03 *d* 8.5; H-8); (4.48 *s*; 3HCO-4).

7α-hydroxy-β-sitosterol (**10**): ^{13}C δ (ppm) ($CDCl_3$): 37.0 (CH_2-1); 31.4 (CH_2-2); 71.4 (CH-3); 42.0 (CH_2-4); 146.3 (C-5); 123.9 (CH-6); 65.3 (CH-7); 36.1 (CH_2-8); 42.3 (CH-9); 36.9 (C-10); 20.7 (CH_2-11); 39.1 (CH_2-12); 41.7 (C-13); 49.5 (CH-14); 24.4 (CH_2-15); 28.9 (CH_2-16); 55.7 (CH-17); 12.0 (CH_3-18); 18.3 (CH_3-19); 40.9 (CH-20); 21.0 (CH_3-21); 33.9 (CH_2-22); 25.9 (CH_2-23); 45.9 (CH-24); 29.2 (CH-25); 21.0 (CH_3-26); 19.8 (CH_3-27); 23.1 (CH_2-28); 12.3 (CH_3-29). ^{1}H δ (ppm) ($CDCl_3$): (1.80; 1.25; 2H-1); (1.70; 1.55; 2H-2); (3.62 *m*; H-3); (2.36 *dd* 15.0; 5.0; 1H-4); (2.30 *t* 15.0; 1H-4); (5.64 *br s*; H-6); (3.87 *br s*; H-7); (1.47; H-8); (1.25; H-9); (1.55; 2H-11); (2.05; 1.35; 2H-12); (1.39; H-14); (1.32; 2H-15); (1.80; 2H-16); (1.21; H-17); (0.71 *s*; 3H-18); (1.00 *s*; 3H-19); (1.04 *d* 10.0; H-21); (1.65; 0.89; 2H-22); (1.18; 2H-23); (1.80; H-25); (0.87; 3H-29).

7α-hydroxy-stigmasterol (**11**): ^{13}C δ (ppm) ($CDCl_3$): 37.0 (CH_2-1); 31.4 (CH_2-2); 71.4 (CH-3); 42.0 (CH_2-4); 146.3 (C-5); 123.9 (CH-6); 66.1 (CH-7); 37.5 (CH-8); 42.3 (CH-9); 36.9 (C-10); 20.7 (CH_2-11); 39.2 (CH_2-12); 41.7 (C-13); 49.4 (CH-14); 24.3 (CH_2-15); 28.3 (CH_2-16); 55.7 (CH-17); 11.7 (CH_3-18); 18.3 (CH_3-19); 40.5 (CH-20); 19.0 (CH_3-21); 138.2 (CH_2-22); 129.2 (CH_2-23); 51.2 (CH-24); 31.9 (CH-25); 18.8 (CH_3-26); 19.8 (CH_3-27); 25.4 (CH_2-28); 11.8 (CH_3-29). ^{1}H δ (ppm) ($CDCl_3$): (1.80; 1.25; 2H-1); (1.70; 1.55; 2H-2); (3.62 *m*; H-3); (2.36 *dd* 15.0; 5.0; 1H-4); (2.30 *t* 15.0; 1H-4); (5.64 *br s*; H-6); (3.87 *br s*; H-7); (1.49; H-8); (1.25; H-9); (1.55; 2H-11); (2.05; 1.35; 2H-12); (1.48; H-14); (1.73; 2H-15); (1.93; 2H-16); (1.12; H-17); (0.69 *s*; 3H-18); (1.00 *s*; 3H-19); (2.07; H-20); (0.94 *d* 10.0; H-21); (5.17 *dd* 15.0; 5.0; H-22); (5.07 *dd* 15.0; 10.0; 2H-23); (1.56; 3H-24); (1.88; H-25); (1.44; H-28); (0.87; 3H-29).

7α-hydroxy-campesterol (**12**): ^{13}C δ (ppm) ($CDCl_3$): 37.0 (CH_2-1); 31.4 (CH_2-2); 71.4 (CH-3); 42.0 (CH_2-4); 146.3 (C-5); 123.9 (CH-6); 65.3 (CH-7); 36.1 (CH_2-8); 42.3 (CH-9); 36.9 (C-10); 20.7 (CH_2-11); 39.1 (CH_2-12); 41.7 (C-13); 49.5 (CH-14); 24.4 (CH_2-15); 28.9 (CH_2-16); 55.7 (CH-17); 12.0 (CH_3-18); 18.3 (CH_3-19); 40.9 (CH-20); 21.0 (CH_3-21); 33.9 (CH_2-22); 25.9 (CH_2-23); 45.9 (CH-24); 29.2 (CH-25); 21.0 (CH_3-26); 19.8 (CH_3-27); 12.3 (CH_3-28). ^{1}H δ (ppm) ($CDCl_3$): (1.80; 1.25; 2H-1); (1.70; 1.55; 2H-2); (3.62 *m*; H-3); (2.36 *dd* 15.0; 5.0; 1H-4); (2.30 *t* 15.0; 1H-4); (5.64 *br s*; H-6); (3.87 *br s*; H-7); (1.47; H-8); (1.25; H-9); (1.55; 2H-11); (2.05; 1.35; 2H-12); (1.39; H-14); (1.32; 2H-15); (1.80; 2H-16); (1.21; H-17); (0.71 *s*; 3H-18); (1.00 *s*; 3H-19); (1.04 *d* 10.0; H-21); (1.65; 0.89; 2H-22); (1.18; 2H-23); (1.80; H-25); (0.87; 3H-28).

Manool (**13**): ^{13}C δ (ppm) ($CDCl_3$): 38.4 (CH_2-1); 19.1 (CH_2-2); 42.2 (CH_2-3); 33.6 (C-4); 55.6 (CH-5); 24.5 (CH_2-6); 39.1 (CH_2-7); 148.8 (C-8); 57.2 (CH-9); 37.3 (CH-10); 17.7 (CH_2-11); 41.1 (CH_2-12); 73.7 (C-13); 145.2 (CH-14); 111.6 (CH_2-15); 28.1 (CH_3-16); 106.4 (CH_2-17); 33.7 (CH_3-18); 21.7 (CH_3-19); 14.5 (CH_3-20). ^{1}H δ (ppm) ($CDCl_3$): (1.52 *m*; H-5); (1.55 *m*; H-9); (5.93 *dd*; 17.1; 10.6; H-14); (5.23 *d*; 17.1; H-15); (5.08 *d*; 10.6; H-15); (1.29 *s*; 3H-16); (4.82 *br s*; H-17); (4.49 *br s*; H-17); (0.89 *s*; 3H-18); (0.82 *s*; 3H-19); (0.69 *s*; 3H-20).

16-hydroxymanoiloxide (**14**): ^{13}C δ (ppm) ($CDCl_3$): 38.9 (CH_2-1); 18.5 (CH_2-2); 41.9 (CH_2-3); 38.4 (C-4); 56.5 (CH-5); 20.1 (CH_2-6); 43.7 (CH_2-7); 75.5 (C-8); 52.9 (CH-9); 37.2 (C-10);

14.5 (CH_2-11); 27.2 (CH_2-12); 76.3 (C-13); 143.9 (CH-14); 114.0 (CH_2-15); 68.5 (CH_2-16); 25.8 (CH_3-17); 33.6 (CH_3-18); 21.7 (CH_3-19); 15.1 (CH_3-20). ^{1}H δ (ppm) ($CDCl_3$): (1.55; 0.90; 2H-1); (1.59; 1.43; 2H-2); (1.42; 1H-3); (1.16 *dt* 13.7; 4.0; 1H-3); (0.95 *dd* 8.7; 2.0; H-5); (1.70; 1.30; 2H-6); (1.89 *dt* 12.4; 3.2; 1H-7); (1.59; 1H-7); (1.58; H-9); (1.60; 1.44; 2H-11); (2.10; 1.68; 2H-12); (5.82 *dd* 17.4; 10.9; 2H-14); (5.27 *dd* 17.4; 1.4; 1H-15); (5.13 *dd* 10.9; 1.4; 1H-15); (3.34 *d* 11.0; 1H-16); (3.30 *d* 11.0 1H-16); (1.30 *s*; 3H-17); (0.89 *s*; 3H-18); (0.82 *s*; 3H-19); (0.82 *s*; 3H-20).

16-hydroxy-13-epi-manoyloxide (**15**): ^{13}C δ (ppm) ($CDCl_3$): 39.3 (CH_2-1); 18.6 (CH_2-2); 42.1 (CH_2-3); 31.9 (C-4); 56.4 (CH-5); 19.8 (CH-6); 42.8 (CH_2-7); 76.1 (C-8); 58.4 (CH-9); 37.5 (C-10); 15.2 (CH_2-11); 28.3 (CH_2-12); 75.9 (C-13); 144.0 (CH-14); 113.5 (CH_2-15); 69.6 (CH_2-16); 24.0 (CH_3-17); 33.3 (CH_3-18); 21.3 (CH_3-19); 15.9 (CH_3-20). ^{1}H δ (ppm) ($CDCl_3$): (1.65; 0.85; 2H-1); (1.60; 1.45; 2H-2); (1.42; 1.16 2H-3); (0.96 *dd* 12.2; 2.3; H-5); (1.60; 1.25; 1H-6); (1.80, 1.42; 2H-7); (1.16; H-9); (1.55; 1.48; 2H-11); (2.05; 1.75; 2H-12); (5.93 *dd* 18.2; 10.9; 2H-14); (5.13 *d* 18.2; 1H-15); (5.12 *d* 10.9; 1H-15); (3.39 *d* 10.7; 1H-16); (2.99 *d* 10.7 1H-16); (1.27 *s*; 3H-17); (0.88 *s*; 3H-18); (0.81 *s*; 3H-19); (0.75 *s*; 3H-20).

4. Conclusions

The phytochemical study on *C. Cyrtanthus* led to isolation and structural determination of two new diterpenoids **1-2** along with fourteen known compounds. Furocoumarins are common in *Conchocarpus* genus, however, the pyranocoumarins **3-5** and the steroids **10-12** were isolated in the *Conchocarpus* genus for the first time. The alkaloid dictamin **6** has been considered a chemotaxonomic marker of *Conchocarpus* genus.

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