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Chemical compounds isolated from *Talinum triangulare* (Portulacaceae)

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ABSTRACT

This first phytochemical study of *Talinum triangulare* Leach (Portulacaceae), also known as 'cariru', which is a commonly consumed food in Northern Brazil, allowed the isolation and structural determination of four new compounds: one acrylamide, 3-N-(acryloyl, N-pentadecanoyl) propanoic acid (**5**), and three new phaeophytins named (15^1S, 17*R*, 18*R*)-Ficuschlorin D acid (3^1,3^2-didehydro-7-oxo-17^3-O-phytyl-rhodochlorin-15-acetic acid), (**13**), Talichorin A (17*R*, 18*R*)-phaeophytin b-15^1-hidroxy, 15^2,15^3-acetyl-13^1-carboxilic acid (**14**), and (15^1S, 17*R*, 18*R*)-phaeophytin b peroxylactone or (15^1S, 17*R*, 18*R*)-hydroperoxy-ficuschlorin D (**16**), together with twelve known compounds, including four phaeophytins (**11**,**12**, **15** and **17**). The structures of the compounds were established on the basis of 1D and 2D NMR, IR, HRESI-MS spectra, including GC–MS, and HPLC–UV analysis, as well as comparisons with the literature data. The CD spectra data analysis were used to define the absolute configuration of phaeophytins **12** (13^2R, 17*R*, 18*R*)-13^2-hydroxyphaeophytin a, **13** and **16**, **15** (15^1S, 17*R*, 18*R*)-3^1,3^2-didehydro-15^1-hydroxyrhodochlorin-15-acetic acid δ-lactone-15^2-methyl-**17**^{3}-phytyl ester and 17 (17*R*, 18*R*)-purpurin 18-phytyl ester.

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1. Introduction

The Portulacaceae is a relatively small family (30 genera and 400 species) of the Caryophyllales order, with a widespread distribution that is generally characterised by small herbaceous plants. Most of the family members have leaves in the range of fleshy to fully succulent and live in diverse habitats. Some of these species are considered to be invader plants, such as *Portulaca oleracea*, *Portulaca pilosa* and *Talinum triangulare* (Souza & Lorenzi, 2005).

The *T. triangulare* Leach, known as "cariru" in Brazil, is a non-conventional vegetable crop of the Portulacaceae family. It is cultivated in the margins of the Amazon River and mainly consumed as food in Northern Brazil, especially in the states of Pará and Amazonas, where the soft and highly nutritious leaves are used to substitute spinach (*Spinacea oleracea*) (Rodrigues & Furlan, 2003). It is well adapted to the hot and humid weather and the low fertile soil, which makes its cultivation an important economic activity for small growers. *T. triangulare* is also cultivated in Western Africa, Asia and South America, including other regions of Brazil, and is also used in traditional medicine as an alimentary tonic (Kohda, Yamoaka, Morinaga, Ishak, & Darise, 1992). Papers concerning the pharmacological, pharmacognostic and preliminary phytochemical studies have been published, revealing its great therapeutic value in traditional medicine (Andarwulan, Batari, Sandrasari, Bolling, & Wijaya, 2010; Liang et al., 2011; Ravindran Babu et al., 2012; Swarna & Ravindhran, 2013). However, on the other hand, some classes of metabolites indicated as present in the extract of this plant (Swarna & Ravindhran, 2013) have not been found in this phytochemical study. Therefore, this is the first study of the isolation and identification of metabolites in the extract of this plant to reveal compounds belonging to important classes of metabolites that are frequently detected in aliments, such as acrylamides, phaeophytins found in fruits and vegetables (Drogat, Barrière, Granet, Vincet, & Krausz, 2011; Ocampo & Repeta, 1999) and chlorophyll composition of commonly consumed leafy vegetables in Mediterranean countries (Žnidarčič, Ban, & Šircelj, 2011).

2. Material and methods

2.1. Materials and chemicals

All chemicals and solvents were of analytical grade and were obtained from Merck and Sigma–Aldrich Co. The melting points

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were determined with a Meltemp II apparatus and were uncorrected. Infrared spectra (KBr pellets and NaCl film) were recorded on a Perkin-Elmer 1605 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-400 (400 and 100 MHz) and AC-500 (500 and 125 MHz) spectrometer using DMSO-d_6, $MeOD_4$ or $CDCl_3$ as solvents with TMS as the internal reference. Electrospray ionisation–high resolution spectra were measured on a quadrupole-time of flight instrument (micrOTOF II and UltrOTOFQ, Bruker Daltonics, Billerica, MA), while the low resolution electron impact ionisation mass spectra were acquired on a Shimadzu QP2010 instrument, through a direct probe and operating at 70 eV (GC/EM Varian Saturn 2000; GC/EM HP-5989 A). HPLC analyses were performed using a Shimadzu LC 6AD and LC 10AD photodiode detector (PDA) UV 300–600 nm column Betasil C_{18} (250 × 4.6 × 5 mm). UV and Circular dichroism spectra were realised at DC J-180 Jasco PTC423S 190-600 nm. Columns chromatography was carried out with silica gel (Vetec and Aldrich 0.05–0.20 mm) and Sephadex LH-20 (Sigma, USA); silica gel F254 G (Vetec) was used for preparative TLC; aluminium backed (Sorbent silica gel plats W/UV254 were used for analytical TLC, with visualisation under UV (254 and 366 nm), with $AlCl_3$–ETOH (1%), vanillin and Dragendorff and iodine vapour.

2.2. Plant material

The *T. triangulare* sample was collected in the summer (December–February) in Seropédica, Rio de Janeiro, Brazil. This species was identified by the botanist Pedro Germano Filho, and a voucher specimen (RBR26906) was deposited at the Herbarium RBR of Universidade Federal Rural do Rio de Janeiro Departamento de Botânica.

2.3. Extraction and isolation of the compounds

The powdered stem (2.27 g) and leaves (1.50 g) of *T. triangulare* were extracted with CH_2Cl_2, MeOH and MeOH:H_2O (8:2) at room temperature, changing the solvent every 48 h for 5 days. The solvents were removed under vacuum to give residues from the stem: **TTSD** (CH_2Cl_2, 22 g) and **TTSMW** (MeOH:H_2O, 8:2, v/v; 122 g), and from the leaves: **TTLD** (CH_2Cl_2, 36 g) and **TTLM** (MeOH, 118 g).

The residue **TTSD** was submitted to silica gel column chromatography and eluted with $C_6H_6/CH_2Cl_2/CHCl_3$/EtOAc/EtOH/MeOH, in increasing order of polarity; forty three fractions were collected. Fractions 4–10 were chromatographed by preparative TLC, eluting with mixture of $CHCl_3$/MeOH (9:1, v/v) and eleven fractions were obtained. Fraction 2 was crystallised from ketone and furnished a mixture of steroids (23 mg), which were identified as campesterol (**1**), sitosterol (**2**), stigmasterol (**3**) and scotenol (**4**). Fractions 35–37 were re-chromatographed on a silica gel column using a mixture of $C_6H_6/CHCl_3$/EtOH in increasing order of polarity as eluents. Fractions 3-8 afforded compound **5** (11 mg), which was identified as a new acrylamide, 3-(N-acryloil, N-pentadecanoil) propanoic acid.

The extract **TTSMW** was chromatographed on silica gel using mixture of $CHCl_3$/MeOH in increasing polarity as eluents; seventy three fractions were collected. Fractions 18–19 were crystallised from ketone and furnished the allantoin (**6**, 48 mg, M.P. 238 °C). Fractions 27–28 yielded malic acid (**7**, 185 mg, M.P. = 270 °C). Fraction 38 was crystallised from ketone to afford a mixture of glucopyranosyl steroids (**8** + **9**, 15 mg). A gum precipitate was obtained from fraction seven by the addition of ketone, which was identified as asparagine (**10**, 12 mg, M.P. 215 °C).

The extract from the leaves **TTLD** was submitted to a silica gel column using a mixture of $C_6H_6/CH_2Cl_2/CHCl_3$/EtOAc/EtOH/MeOH in increasing order of polarity as eluents; forty three fractions were collected. Fractions 21–29 were re-chromatographed on silica gel using a mixture of $C_6H_6/CH_2Cl_2/CHCl_3$/EtOAc/EtOH/MeOH in increasing order of polarity as eluents and yielded a number of phaeophytins. Fraction 18 yielded phaeophytin (**11**, 5 mg); fractions 23–25 furnished 13^2-hydroxyphaeophytin a (**12**, 10 mg) and fraction 34 (brown solid) yielded a mixture of **13**–**16** (15 mg). Fractions 35–42 were further separated by preparative TLC, which was eluted with a mixture of C_6H_6/EtOAc (25:75, v/v); four fractions were obtained. The less polar fraction yielded purpurin-18 (**17**, 6 mg).

The **TTLM** presented a pasty aspect, which was fractionated by column chromatography, giving 56 fractions. Fractions 36–37, 39 and 41–50 yielded three solids that were subjected to spectroscopic analysis and compared with the literature data. These analyses allowed the compounds to be identified as allantoin (**6**, 31 mg, M.P. 238°C), malic acid (**7**, 33 mg, M.P. = 270 °C) and a mixture of glucopyranosyl steroids (**8** + **9**, 22 mg), respectively.

3-(N-acryloil, N-pentadecanoil) propanoic acid (**5**): White oil; IR λ_{max} (NaCl cm^{-1}): 3433, 2920, 2850, 1625, 1564, 1419; HRESIMS: 390.1517 $(M+Na)^+$; 368.1709 $(M+H^+$; $C_{21}H_{38}NO_4)$, calculated 368.2800; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 8.55 (1H, brs, H—O), 6.14 (1H, dd, J = 12 and 16 Hz H-2′), 6.06 (1H, dd, J = 8 and 12 Hz, Ha-3′), 5.53 (1H, dd, J = 8 and 16 Hz, Hb-3′), 3.75 (2H, t, J = 8 Hz, H-3), 2.62 (2H, t, J = 8 Hz, H-2″), 2.14 (2H, t, J = 7 Hz, H-2″), 1.61 (2H, brs, H-3″), 1.29 (m, H-4″-14″), 0.90 (t, J = 7 Hz, H-15″), ^{13}C NMR (BBD and DPT, $CDCl_3$, 125 MHz): δ_C 181.8 (C-1), 173.8 (C-1′ and C-1″), 135.2 (CH-2′), 123.8 (CH_2-3′), 59.3 (CH_2-3), 40.0 (CH_2-2″), 37.8 (CH_2-2), 26.9- 22.1 (CH_2-3″-12″), 31.9 (CH_2-13″), 22.1 (CH_2-14″), 12.9 (CH_3-15″).

Asparagine (**10**): Solid, M.P. 215 °C; IR λ_{max}^{KBr} (cm^{-1}): 3398, 2927, 1652, 1583, 1404, 1061; ^{1}H NMR ($DMSOd_6$, 500 MHz): δ_H 7.72 (H_2N-4, s), 7.03 (H_2N-2, s), 3.40 (dd, J_1 = 10, J_2 = 5 Hz, H-2), 2.374 (dd, J_1 = 15, J_2 = 5 Hz, Ha-3), 2.33 (dd, J_1 = 15, J_2 = 10 Hz, Hb-3); ^{13}C NMR (BBD and DPT, $DMSOd_6$, 125 MHz): δ_C 177.88 (C-1), 167.91 (C-4), 58.79 (CH-2), 38.61 (CH_2-3).

3. Results and discussion

Seventeen compounds were identified in the fractions of extracts from the stem and leaves of *T. triangulare* by spectrometric data analysis and chromatographic procedures. Besides the mixture of steroids (**1**–**4**), the new acrylamide, 3-(N-acryloyl, N-pentadecanoyl) propanoic acid (**5**), allantoin (**6**), malic acid (**7**), asparagine (**10**) and a mixture of glucopyranosyl steroids (**8**–**9**) were isolated from the stem extracts. In the dichloromethane and methanolic extracts from the leaves, seven phaeophytins (**11**–**17**) were identified, including four new compounds named (15^1S, 17R, 18R)-Ficuschlorin D acid (3^1,3^2-didehydro-7-oxo-17^3-O-phytyl-rhodochlorin-15-acetic acid, **13**), (17R, 18R)-phaeophytin b-15^1-hydroxy or 15^2,15^3-acetyl-13^1-carboxilic acid (**14**) named Talichlorin A, and (15^1S, 17R, 18R)-phaeophytin b peroxylactone or (15^1S, 17R, 18R)-hydroperoxy-Ficuschlorin D (**16**), together with twelve known compounds, including four phaeophytins (**11**, **12**, **15** and **17**), as well as allantoin (**6**), malic acid (**7**) and the mixture of glucopyranosyl steroids (**8** and **9**). The IR, UV, 1D and 2D ^{1}H and ^{13}C NMR, and mass spectra analysis, including GC–MS and HPLC–MS techniques, were used to identify the compounds (Fig. 1). The absolute configurations of phaeophytins **12** (13^2R, 17R, 18R)-13^2-hydroxyphaeophytin a, **13** and **16** (as presented above), **15** (15^1S, 17R, 18R)-3^1,3^2-didehydro-15^1-hydroxyrhodochlorin-15-acetic acid δ-lactone-15^2-methyl-17^3-phytyl ester and **17** (17R, 18R)-purpurin 18-phytyl ester were defined by CD spectra data analysis and applying the quadrant rule (Crabbé, 1974) to the planar tetrapyrrole system, as described below.

The steroids mixture was identified by ^{1}H and ^{13}C NMR spectra analysis, and each component in this mixture was defined by

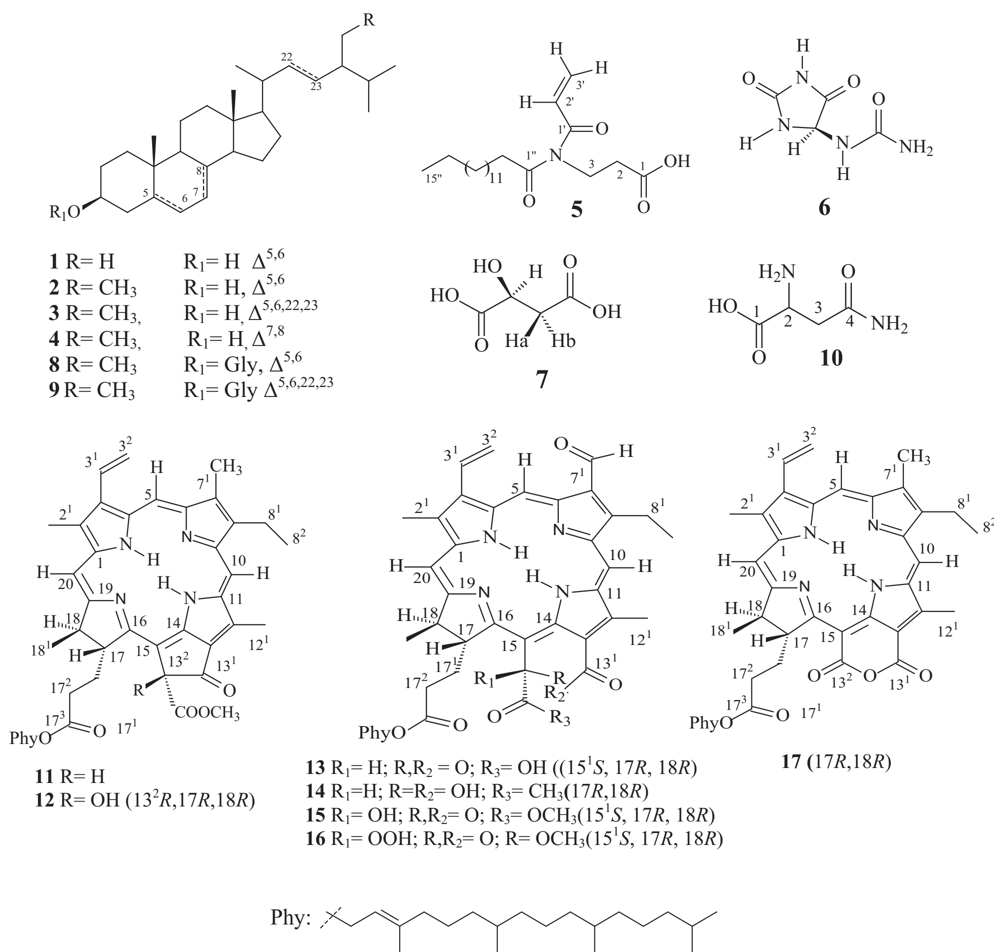

Fig. 1. Compounds isolated of extract from stem and leaves at *T. triangulare*.

mass-spectra analysis, corresponding to each peak detected by GC–MS, followed by comparison with the literature equipment library (Nist 08). Campesterol (**1**, Ret. Time 19.517), sitosterol (**2**, Ret. Time 20.067), stigmasterol (**3**, Ret. Time 20.311), and scotenol (**4**, Ret. Time 21.416) were identified (Fig. 1).

Compound **5** was isolated as a white amorphous solid. The ^{1}H NMR (1D and 2D) spectra exhibited signals with an ABC system with δ_H 6.14 (dd, $J_1 = 12$ and 16 Hz, H-2′), 6.06 (dd, $J_1 = 8$ and $J_2 = 12$ Hz, Ha-3′), 5.53 (dd, $J_1 = 8$ and $J_2 = 16$ Hz, Hb-3′) and a A_2B_2 system with δ_H 3.75 (t, $J = 8$ Hz, H-3), 2.62 (t, $J = 8$ Hz, H-2). The ^{13}C (BBD and DEPT) and HMQC spectrum analysis allowed the identification of the corresponding connected carbons with $\delta_{C:}$ 135.2(CH-2′), 123.8 (CH_2-3′), 59.3 (CH_2-3), 40.0 (CH_2-2) for both systems. The additional analysis of the ^{13}C and HMBC NMR spectra allowed the identification of carbonyl groups [δ_C 181.8 (C-1) 173.8 (C-1′)] and enabled the completion of the systems of an acrylamide and the 3-amino-propanoic acid. Other signals at δ_H 2.14 (t, $J = 8$ Hz, H-2″), 1.61(brs, H-3″), 1.29 (m), 0.90 (t, $J = 8$ Hz, H-15″), permitted the identification of a long chain of acyl units that was confirmed by 2D NMR spectra analysis. These data and the m/z value at 390.1517 $[M+Na]^+$, 368.1709 $(M+H^+)$, detected by HR-ESI-MS, were used to propose the molecular formula as $C_{21}H_{38}NO_4$ (calc. 368.2800) and to define the structure of **5** as 3-(N-acryloyl, N-pentadecanoyl) propanoic acid.

The analysis of IR, NMR, and mass spectra of compounds **6–10**, including ^{1}H, ^{1}Hx^{1}H-COSY, HMQC, HMBC and ^{13}C (DEPTQ) experiments, besides comparison with the data of allantoin, malic acid, 3-O-βD-glucopyranosyl-sitosterol, 3-O-βD-glucopyranosyl-stigmasterol and asparagine, respectively, allowed these known compounds to be identified (Fig. 1).

The compounds **11**, **12** and **17** were isolated as dark-green solids, which the ^{1}H and ^{13}C NMR, including 2D, besides UV and mass spectra, were compatible with phaeophytins structures. The compounds **12** and **17** showed similar data to **11**, such as the UV/VIS with principal maxima at 405 and 750 nm (Fig. 2b). The ^{1}H NMR,

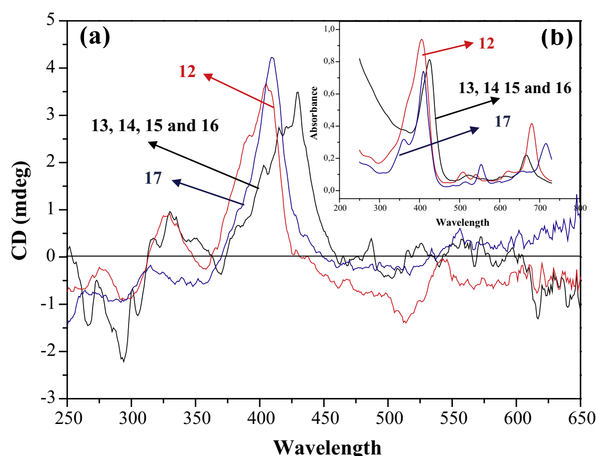

Fig. 2. Circular dichroism (a) and UV (b) spectra of compounds 12 (0.156 mg/mL), 13, 14, 15 and 16 (0.151 mg/mL) and 17 (0.991 mg/mL) in MeOH.

and HMQC spectra showed signals of three sharp singlets of methyl groups at δ_H 3.23, 3.42, 3.91 (s, 3H, H-7^1,2^1 and 12^1) connected with δ_{CH3} 11.2, 12.1, 12.1, respectively; three proton singlets in the aromatic system at δ_H 9.38, 9.52 and 8.58 (H-5, H-10 and H-20), connected to carbons with δ_{CH} 97.5, 104.4, and 93.5, respectively, of the tetrapyrrole moiety of the pheophytins. This was confirmed by additional analysis of the ^{1}H and ^{13}C NMR, including ^{1}Hx^{1}H-COSY, and HMBC experiments and comparison of all data with those of the literature (Matsuo, Ono, & Nozari, 1996). Besides the phytyl propionate, it was possible to identify the signals of the methyl group (H-18^1, δ_{CH3} 22.7), CH (H-17, and 18, δ_H/δ_{CH} 4.24/51.2, and 4.49/50.1, respectively), characteristic of the pheophytin structure registered in the literature (Lin et al., 2011).

The proposed structure of **11**, as pheophytin a, was defined by the additional signal in the NMR spectra of a methoxy group δ_H/δ_{CH3} 3.70/53.1(H_3CO-13^4); δ_H/δ_{CH} 6.21/64.7(CH-13^2) and δ_C 189.6 (C-13^1), 172.9 (C-13^3), which were identical to the data registered in the literature (Matsuo et al., 1996) and by the *m/z* 871.5737([M$^+$+1]) detected in the HRESI mass spectrum, which was compatible with the molecular formula $C_{55}H_{74}N_4O_5$. On the other hand, the absence of nOe between H-13^2 and H-17^1, and observed nOe of H-18/H-17 and H-13^4/H-17^1 allowed the final structure of **11** to be defined as *Rel.(*13^2*S*,17*R*,18*R*)-phaeophytin a, isolated from the leaves of *Ficus microcarpa* (Lin et al., 2011), and from the liverwort *Plagiochila ovalifolia* (Matsuo et al., 1996).

Phaeophytin **12** was identified as (13^2*S*,17*R*,18*R*)-13^2-hidroxypheophytin a by the same analysis and the signals at δ_C 89.0 ppm (C-13^2), 191.9 (δ C-13^1, justifying the beta effect of the hydroxyl group at 13^2) and 173.6/172.8 (δ C-13^3/δ C-17^3), detected in the ^{13}C (DEPTQ) and HMBC NMR spectra, as well as the *m/z* 887.5675 ([M$^+$+1]), which was compatible with the molecular formula $C_{55}H_{75}N_4O_6$. The absolute configuration of **12** was defined by the positive Cotton effect detected in the CD spectrum (Fig. 2) at λ_{max} 409 nm (ψ_{obs} + 6.3 mdeg), which was consistent with the planar projection of tetrapyrrole ring in the horizontal plane of quadrant rules, used for aromatic systems (Crabbé, 1974); in this case the methyl (C-18^1) or methylene (C-17^1) was located in the vertical plane of quadrant for each asymmetric centre, and the positive contribution of methylene or the methyl group, respectively, was observed. This phaeophytin has been isolated from the n-hexane extract of leaves and stems of *Amaranthus tricolor* (Jerz, Arrey, Wray, DU, & Winterhalter, 2007), but the absolute stereochemistry has not been defined.

Compound **17** was identified by the same analysis and comparison of the proton and carbon-13 chemical shift of phaephorbide isolated from *Gossypium mustelinum* (Malvacea) and with the data for the phaeophytins described above, as well as the HRESI mass spectrum analysis, which showed the value of the quasi molecular ion at *m/z* 843.5418 [M$^+$+H]. This was compatible with the molecular formula $C_{53}H_{71}N_4O_5$ (calc. 843.5424) and by the *m/z* 565.2950 ([M−phytyl+H]$^+$), detected in the MS2. The NOESY spectrum analysis allowed the *trans* relation between H-18^1/H-17^1 to be defined. The CD spectrum of **17** (see Section 2) was identical to **12** with EC+ at 412 nm (ψ_{obs} + 6.0 mdeg). Therefore, these analyses allowed the structure of **17** to be defined with the absolute configuration as 17*R*,18*R*-purpurin18 phytyl ester, registered in the literature, which was isolated from the marine organism, *Ruditapes philippinarum*, (Ocampo & Repeta, 1999), cyanobacterium, *Spirulina maxima* (Drogat, Barrière, Granet, Vincet, & Krausz, 2011), and identified as a product of chlorophyll extracted from spinach leaves.

The brown solid containing a mixture of compounds **13–16** was submitted to the same analysis as the phaeophytins described above, as well as the comparison with ^{13}C NMR data with those of the literature (Lin et al., 2011) and of **11** and **12**, and mass spectra. These analysis allowed the additional signals of δ_C 207.1, 111.3–111.5, δ_{CH} 187.8–187.9, 78.7, 72.1, and δ_{CH3} at 52.9, 53.3, 27.8 to be observed, besides some differences in δ_C or δ_{CH} values, and the absence of δ_{CH} 99.9 (CH-5), which justified the aldehyde (δ_{CH-7} 187.8) of pheophytin b derivatives. Table 1 presents the chemical shifts compatible with the proposed structures. The HRMS analyses led to four peaks to be identified, corresponding to the quasi molecular ions ([M$^+$+H]), at *m/z* 887.5654 of **13** ($C_{54}H_{71}N_4O_7$, calc. 887.5323), *m/z* 903.5578 of **14** ($C_{55}H_{75}N_4O_7$, calc. 903.5636), *m/z* 917.5417 of **15** ($C_{54}H_{73}N_4O_8$, calc. 917.5428), and m/z 933.5352 ($C_{55}H_{73}N_4O_9$, calc. 933.5377). The analyses of the ^{13}C NMR, HMQC and HMBC spectra allowed signals to be identified that were used to define each structure of **13–16** (Fig. 1). The additional values of δ_C 170.3, 162.9 and δ_{CH} 78.8/7.5(^{1}J$_{HC}$) were used to confirm the functional groups used in the structure **13** (Table 1), defined as Ficuschlorin D acid (3^1,3^2-didehydro-7-oxo-17^3-O-phytyl-rhodochlorin-15-acetic acid). The δ_C 207.0, 163.1, δ_{CH} 72.8/5.3, and δ_{CH3} 27.9/1.99 (^{2}J$_{HC}$ 207.0) was compatible with the structure **14**, named Talichlorin A (phaeophytin b-15^1-hidroxy or 15^2,15^3-acetyl, 13^1-carboxilic acid). The δ_C 170.3, 163.1, δ_C 111.1 and δ_{OCH3} 53.3/3.57 (^{3}J$_{HC}$ 170.3) were used to propose structure **15** 3^1,3^2-didehydro-15^1-hydroxyrhodochlorin-15-acetic acid δ-lactone-15^2-methyl-17^3-phytyl ester compared with the literature (Gandul-Rojas, Gallardo-Guerrero, & Minguez-Mosquera, 1999). The structure of **16** was defined with the δ_C 170.1, 163.1, δ_C 111.3 and δ_{OCH3} 53.1/3.57 (^{3}J$_{HC}$ 170.3) of the groups used to complete the molecular formula that corresponded to the phaeophytin b peroxylactone or hydroperoxy-Ficuschlorin D. The values of λ_{max}: 430 nm and the EC+ at 429 nm (ψ_{obs} + 3.0 mdeg), detected in the UV and CD spectra, respectively, are in accordance with the effect of 7-formyl, which enhanced the delocalisation of π-electrons, as cited by Lin et al. (2011). The relative stereochemistry of C-18^1/C-17^1/C-15^1 of **13**, **15** and **16**, and C-18^1/C-17^1 of **14**, were proposed by the NOESY spectra analyses, and by carbon-13 chemical shift values. The positive signal of Cotton effect was used to attribute the same configuration proposed to **12** (13^2*R*, 17*R*, 18*R*), and **17** (17*R*, 18*R*) (Fig. 2).

Table 1
^{13}C and ^{1}H-NMR (500 MHz in $CDCl_3$, δ in ppm, *J* in Hz) data for compounds **13–16**.

C	δ_C* [δ_H (mult., *J* in Hz)] **13**-/-**14**-/-**15**-/-**16**	C	δ_C* [δ_H (mult., *J* in Hz)] **13**-/-**14**-/-**15**-/-**16**
1	142.1–144.7	12^1	12.4–12.5
2	132.0–132.3/132.9	13	113.8–113.9
2^1	12.1–11.9 [3.6 (s)]	13^1-CO	162.9–163.1
3	136.8–136.9 [8.0 (dd,18, 12]	14	135.8–137.8
3^1	128.6–128.7 [6.20 (dd,18, 1.5); 6.30 (dd, 12, 1.5)]	15	111.3/111.4
3^2	123.9(t, br)	15^1	78.8/72.8/98.7/99.0 [7.5 (s)]
4	136.7–136.9	15^2-CO	170.1/207.0/170.3/169.9
5	103.2–103.3 [10.3 (s)]	15^3-CH_3 15^3-OCH_3	27.9 [2.1 (s)] 52.9–53.3 [3.5 (s); 3.4 (s)]
6	151.2–151.4	16	162.9–163.0
7	132.8–132.9	17	50.6(d, br) [4.4 (brd, 8)]
7^1	187.7–187.9 [11.1 (s)]	17^1	29.8(t, br) [1.9–2.0 (m)]
8	146.3–146.5	17^2	31.9(t, br) [1.9 (m)]
8^1	19.1–19.2 [3.78 (m)]	17^3	170.7(s, br)
8^2	19.5–19.7 [1.82 (t, 8)]	18	44.14 [1.7 (s)]
9	159.5–159.7	18^1	22.8 [1.6 (d, 8)]
10	106.2; 106.7; 107.3	19	174.8
11	140.5; 143.5	20	93.68 [8.64 (s)]
12	131.7–132.1 [3.9 (s)]	*Intervals mean several peaks together.	

Phytyl δ_C/C-atoms: 62.0 (17^4), 117,8 (17^5), 143.5 (17^6), 39.5 (17^7), 25.0 (17^8), 36.9 (17^9), 32.1 (17^{10}), 37.6 (17^{11}), 21,6 (17^{12}), 37.6 (17^{13}), 32.1(17^{14}), 37.6 (17^{15}), 24.4 (17^{16}), 39.5 (17^{17}), 27.9 (17^{18}), 22.7 (17^{19}), 22.9 (17^{20}), 14.3 (17^{21}), 19.9 (17^{22}), 19.7 (17^{23}).

* Values taken from the spectra DEPTQ, HSQC, HMBC; br of carbon: means more them one signal together.

4. Conclusion

Seventeen compounds were identified in the stem and leaves of *T. triangulare*, including four new compounds: one acrylamide and three pheophytins. The quiroptical data of pheophytins are presented for the first time. These detailed analyses do not confirm the presence of some classes of metabolites as proposed by Swarna and Ravindhran (2013) in an extract of *T. triangulare*. On the other hand, this study showed that the stem and leaves of *T. triangulare* are rich in nitrogenated compounds that are certainly responsible for the biological properties of this plant. The CD spectra analysis can be used to identify these kinds of phaeophytins in fractions from the plants extracts.

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References

Andarwulan, N., Batari, R., Sandrasari, D. A., Bolling, B., & Wijaya, H. (2010). Flavonoid content and antioxidant activity of vegetables from Indonesia. *Food Chemistry, 121*, 1231–1235.

Crabbé, P. (1974). *Actividad optic, dispersion rotatoria optica y dicroismo circular en química orgânica*. Universidad Nacional Autónoma de México, D.F., México y Unirvisité Scientifique et Médicale Grenoble, France (41–45).

Drogat, N., Barrière, M., Granet, R., Vincet, S., & Krausz, P. (2011). High yield preparation of purpurin-18 from *Spirulina maxima*. *Dyes and pigments, 88*, 125–127.

Gandul-Rojas, B. B., Gallardo-Guerrero, L., & Minguez-Mosquera, M. I. (1999). Identification of oxidized chlorophylls and metallochlorophyllic complexes of copper in table olives (cv. Gordal) with green staining alteration. *Journal of Food Protection, 62*(10), 1172–1177.

Jerz, G., Arrey, T. N., Wray, V., DU, Q., & Winterhalter, P. (2007). Structural characterization of 13^2-hydroxy-(13^2-S)-phaeophytin-a from leaves and stems of *Amaranthus tricolor* isolated by high-speed counter-current chromatography. *Innovative Food Science & Emerging Technologies, 8*, 413–418.

Kohda, H., Yamoaka, Y., Morinaga, S., Ishak, M., & Darise, M. (1992). Saponins from *Talinum triangulare*. *Chemical & Pharmaceutical Bulletin, 40*(9), 2557–2558.

Liang, D., Zhou, Q., Gong, W., Wang, Y., Nie, Z., He, H., et al. (2011). Studies on the antioxidant and hepatoprotective activities of polysaccharides from *Talinum triangulare*. *Journal of Ethnopharmacology, 136*, 316–321.

Lin, H., Chiu, H., Lan, Y., Tzeng, C., Lee, T., Lee, C., et al. (2011). Ficuschlorins A–D, lactone chlorins from the leaves of *Ficus microcarpa*. *Chemistry & Biodiversity, 8*, 1701–1707.

Matsuo, A., Ono, K., & Nozari, H. (1996). Phaeophytins from a cell suspension culture of the liverwort *Plagiochila ovalifolia*. *Phytochemistry, 47*(2), 427–430.

Ocampo, R., & Repeta, D. J. (1999). Structural determination of purpurin-18 (as methyl ester) from sedimentary organic matter. *Organic Geochemistry, 30*, 189–193.

Ravindran Babu, P., Rama Rao, D., Prasada Rao, M., Krishna Kanth, J. V., Srinivasulu, M., & Hereesh, V. (2012). Hypoglycaemic activity of methanolic extract of *Talinum triangulare* leaves in normal and streptozotocin induced diabetic rats. *Journal of Applied Pharmaceutical Science, 02*(05), 197–201.

Rodrigues, M. I. A., & Furlan, A. (2003). Livro de resumos do 54° Congresso Nacional de Botânica 3ª Reunião Amazônica de Botânica Local do Evento: Universidade da Amazônia – UNAM, R0165–1.

Souza, V. C., & Lorenzi, H. (2005). Plantas Medicinais no Brazil. Botânica Sistemática, Instituto Plantarum de Estudos da Flora Ltda, Nova Odessa, Brazil.

Swarna, J., & Ravindhran, R. (2013). Pharmacognostical and phytochemical evaluation of *Talinum triangulare* (Jacq.) Willd. *International Journal of Pharmacy and Pharmaceutical Sciences, 5*(2), 249–256.

Žnidarčič, D., Ban, D., & Šircelj, H. (2011). Carotenoid and chlorophyll composition of commonly consumed leafy vegetables in Mediterranean countries. *Food Chemistry, 129*(3), 1164–1168.