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Cyanolipids from *Sapindus saponaria* L. seeds oil

[Cianolípidos en las semillas de *Sapindus saponaria* L]

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Abstract: The chemical composition of the oil extracted from the seeds of *Sapindus saponaria* L., (Sapindaceae), was investigated. Cyanolipids constituted 5% hexane extract of the seeds, whereas triacylglycerols (TAG) accounted for 90%. The oil contains type III cyanolipids (CL) 1-cyano-2-hydroxymethylprop-1-en-3-ol-diesters. Structural investigation of the oil components was accomplished by chemical, chromatographic (TLC, CC, GC-MS), and spectroscopic (IR, NMR) means. GC-MS analysis showed that fatty acids were dominant in the CL components of the oil from S. saponaria L., with cis-11-eicosenoic acid, cis-11-octadecenoic acid and eicosanoic acid as the only esterified fatty acyl chains respectively. This being the first report of this kind of natural products (CL), located in the seeds of this plant..

Keywords: Cyanolipids, *Sapindus saponaria*, Sapindaceae, Fatty acids.

Resumen: La composición química del aceite de las semillas de *Sapindus saponaria* L., (Sapindaceae), fue investigada. Cianolípidos (CL) constituyen el 5% del extracto hexanico de las semillas, mientras que los triacilgliceroles (TAG) representaron el 90%. La fracción cianolipídica estaba compuesta por el CL tipo III, el diester de 1-ciano-2-hidroximetilprop-3-en-1-ol. La investigación estructural de los componentes del aceite se logró mediante técnicas cromatografícas, (CCF, CC, GC-MS), y espectroscópicas (IR, RMN). El análisis por GC-MS mostró que los ácidos grasos tales como: ácidos cis-11-eicosenoico, cis-11-octadecanoico y eicosanoico fueron los únicos ácidos grasos esterificados ubicados en el extracto rico en CL tipo III. Siendo este el primer reporte de esta clase de productos naturales (CL) ubicados en las semilla de esta planta.

Palabras clave: Cianolípidos, *Sapindus saponaria*, Sapindaceae, Ácidos grasos..

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INTRODUCTION

The cyanolipids (CL), derived from amino acid metabolism (Møller & Seigler, 1999) are present, along with acylglycerols (AG) and triacilglicerides (TAG), in seed oils of plants belonging to the family Sapindaceae (Mikolajczak, 1977). Four types of CL structures (Figure. 1; I–IV), with fatty acid esterified (FA) to a mono or a dihydroxynitrile moiety, have been reported as occurring in this plant family (Mikolajczak *et al.*, 1970a; Mikolajczak *et al.*, 1970b); types I and IV CL are cyanogenic. Composition studies have shown that cyanolipid isolates from Sapindaceae plants posses a high content of *cis*-11-eicosenoic acid, eicosanoic acid (arachidic acid) and *cis*-11-octadecenoic acid (vaccenic acid), constituents with these acid, account for up to 50% of total cyanolips in some of species this family (Hopkins & Swingle, 1967; Spitzer, 1995; Spitzer, 1996; Lago *et al.*, 2000).

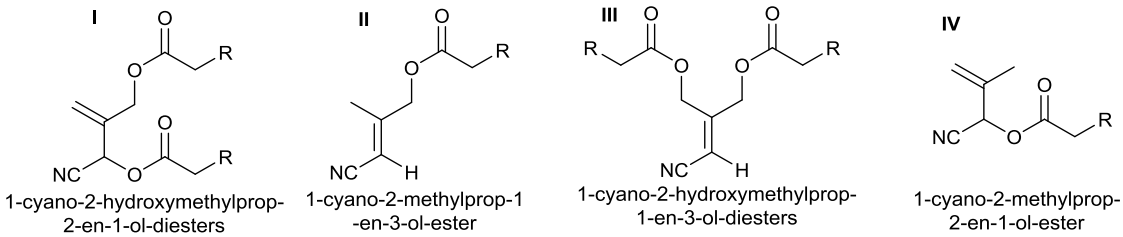


Figure 1
Chemical structures of cyanolipids I–IV

The physiological role of CL in plants is still not completely understood. These phytochemicals may serve *in vivo* as a major nitrogen source for developing seedlings (Selmar *et al.*, 1990). Nevertheless, their co-occurrence with hydroxynitrile glycosides in some species (Bjarnholt & Møller, 2008), has suggested that they represent a biosynthetic variation of hydroxynitrile glycosides with esterification to lipids possibly, serving specific functions related to storage and transport (Tava & Avato, 2014).

Many species belonging to Sapindaceae family, are used commercially as food besides, are used in the folk medicine. For instance, the arils of *Nephelium lappaceum* which are a part of the seeds, are well known and eaten fresh or cooked (Almeyada *et al.*, 1979). In addition, other parts of the seeds are also eaten roasted. The arils of *Paullinia cupana* (guarana) contain caffeine and are used to prepare soft drinks and to relieve fatigue (Avato *et al.*, 2003; Hamerski *et al.*, 2013). Fruits from some *Allophylus* species are considered edible and added to traditional beverages (Reitz *et al.*, 1988; Aichholz *et al.*, 1997). Moreover, As a consequence, identification and quantification of cyanolipids in food and forage plants containing this natural product is of importance, to possibly allow their removal and avoid food poisoning.

The species *Sapindus saponaria* L., (Sapindaceae) is popularly known in Brazil as "saboneteira". This medium sized tropical tree found in South America and India, produces great quantities of small fruits where a sap is accumulated (Saha *et al.*, 2010). In the tropics these fruits are mainly used as a soap substitute. However, they are also used in the folk medicine for treating skin lesions, inflammation and ulcers (Saha *et al.*, 2010). In a recent work our group have isolated from the fruits pericarp a large quantities of a triterpene called hederagenin and produced several derivatives endowed with anti-tumor activity (Rodríguez-Hernández *et al.*, 2015; Rodríguez-Hernández *et al.*, 2016). Since there is no report on the chemistry of cyanolipids in the seeds of *S. saponaria*, in this work, we report the preliminary results of re-investigated of chemical composition of its seed oils. Chemical data and structural elucidation of the TAG and CL constituents of the seed oils from *S. saponaria* are reported and discussed in this work.

MATERIALS AND METHODS

Plant Material.

Fruits of *Sapindus saponaria* were collected in the municipality Tocantins (21°10'30"S and

43°01'04"W), Minas Gerais State, Brazil. Voucher specimens were dried and placed in the collection of the VIC Herbarium of the Plant Biology Department of Viçosa Federal University (UFV), under the register numbers VIC 35.403.

Oil extraction and purification.

The seeds broken and kernels were separated from shells. A yellow mass (30 g) was macerated in hexane with stirring for 24 hours, obtaining, after removal of the solvent, 10 g of yellow oil (33%).

Composition of the oil was first investigated by TLC eluting with hexane/Et_2O (9:1, v/v). The oil components were visualized with phosphomolybdic acid reagent (10% EtOH; Vetec, Sigma Brazil) followed by heating the plates at 110° C.

After of the study by TLC, the composition of the oil was separated by column chromatography (CC) (silica gel 60-230 mesh) eluted by gradient elution with hexane/ Et_2O. Then, the fractions obtained according to TLC analysis were grouped into 4 main fractions. Fraction 2 was composed of TAG and the fraction 3 showed CL

Transesterification of the oil components

Cyanolipids were transesterified, following the IUPAC method (Oliveros-Bastidas *et al.,* 2013) with some modifications, using the following procedure: approximately 20 mg of the fractions chosen (TAG and CL), 2 mL of hexane and 0.2 mL of methanolic 2 M solution of KOH were added to the test tube. The test tube was shaken for 5 min with Maelstrom stirrers and 2 mL of saturated sodium chloride was added, until the organic phase separated. Fatty acid methyl esters were analyzed by triplicate, after injection of a 1 μL of the organic phase into a gas chromatography coupled to a mass spectrometer.

GC–MS analysis

The organic phase was performed on a gas chromatograph-mass (GC-MS Shimadzu, model PQ5050) equipped with a Shimadzu AOC-5000 on-column auto injector and a fused silica capillary column (DB-5, 30 m × 0.25 mm ID, 0.25 μm film thickness). Operating conditions were as follows: helium as the carrier gas with a flow rate of 1.6 mL/min; column temperature 80° C for 5 min, then increasing at 24.4° C /min from 80 to 285° C; injector temperature, 290° C; volume injected, 1 μL; split ratio, 1.0. MS were recorded in electron ionization (EI) mode, with energy of 70 eV. The ion source temperature was 200° C; 5.00 min solvent cut time. The compounds were identified by comparison with the data held in the Wiley 7.0 and NIST libraries.

FTIR

Infrared spectra were recorded on a Varian 660-IR, equipped with GladiATR scanning from 4000 to 500 cm^{-1}.

NMR

The ^{1}H, ^{13}C NMR and two-dimensional (COSY) spectra were recorded on a Varian Mercury 300 instrument at 300 MHz and 75 MHz, respectively, using $CDCl_3$ as a solvent and TMS as internal reference.

RESULTS AND DISCUSSION

General

Lipid extracts obtained from the seeds of *S. saponaria* were first investigated by TLC. Inspection of the extract by TLC elution in hexane/Et_2O (9:1, v/v) showed the presence of three components at R_f = 0.75 (TAG), 0.57 (CL), 0.51 and 0.25 (Others). The TLC data readily suggested the presence of types of CL in the oil seed from this plant.

Purification of the oil components was accomplished by CC with hexane/Et_2O as eluent in gradient, the principal fractions showed TAG, and CL, (type III). In total, the main isolated constituents amounted to 90% (TAG), 5% CL (type III) and 5% others. The purified fractions were characterized by chromatographic and spectroscopic analysis.

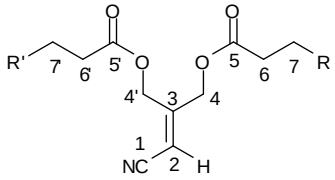
CL identification

The IR spectra of the CL**s** are distinct for each structural type I–IV (Mikolajczak *et al.,* 1970a; Mikolajczak *et al.,* 1970b). As expected, the fraction identified by us as the CL constituents showed the common absorption maxima found in acyl lipids spectra, that is, bands at 3004 (C–H olefins), 2922–2852 (aliphatic C–H stretching), 1746 (C=O stretching), 1462 (aliphatic C–H bending), and 1156 (C–O stretching) cm^{-1} in addition, this first attempt to identify the type of CL contained in our extracts was supported by the presence of a narrow absorption band at 2224 cm^{-1} attributed to a nitrile group after double bond (Barbosa, 2011). This is normally found in the spectra of acyl lipids and is reported as diagnostic for type II and III CL (Figure 1) (Mikolajczak *et al.,* 1970b).

More structural information on the nature of

the CL came from their ^{1}H and ^{13}C spectral data (Table 1) and, COSY correlations also facilitated the assignments of the relative signals. Signals at δ = 114.78, belonging to nitrile carbon, and the singlet at δ = 5.57, corresponding to hydrogen adjacent to the nitrile group. This was further supported by the signal at δ = 98.72, assignable to a vinylic carbon bearing the cyanide function. On the other hand, the downfield shift was observed two signals assigned to the hydrogen-4' *cis* at δ = 4.70, and *trans*, H-4 at δ = 4.88, of methylenes adjacent to the oxygen atoms of the dihydroxybutenyl cyanide moiety (Mikolajczak *et al.*, 1970b; Avato *et al.*, 2005).

TABLE 1
^{1}H and ^{13}C NMR data of Cyanolipid (CL) Type III from seed oil of *S. saponaria*



^{1}H	δ (*J*, Hz)	^{13}C	δ (*J*, Hz)
C<u>H</u>$_2$OCO	4.70 H-4' and 4.88 H-4, s	<u>C</u>H-CN; C-2	98.72
=C<u>H</u>-CN	5.57, s	=<u>C</u>; C-3	155.03
C<u>H</u>$_2$-C=O(O)	2.36 H-6' H-6, t (7.4)	<u>C</u>N; C-1	114.78
C<u>H</u>$_2$-CH$_2$-C=O(O)	1.63, m	C-4; C-4'	61.71; 62.77
C<u>H</u>$_3$ ω1	0.87, t (6.8)	C-5; C-5'	173.04; 172.66
n-C<u>H</u>$_2$	1.25, m	C-6 ; C-6'	33.91; 34.06
-CH=CH-C<u>H</u>$_2$-(*cis*)	2.00, m	C-7 ;C-7'	24.88; 24.92
Olefinic (*cis*)	5.33, m	CH$_3$ ω1	14.24
		CH$_2$ ω2	22.81 (ω7, Sat, ω9)
		<u>C</u>H$_2$ ω3	32.03; 32.05 (ω7/Sat, ω9)
		n-<u>CH$_2$</u>	29.89-29.20
		-<u>C</u>H$_2$-C=C-<u>C</u>H$_2$	27.34; 27.27
			129.77 (C-11 EI)
		CH=<u>C</u>H[a]	129.95 (C-11 VA)
			130.05 (C-12 VA)
			130.18 (C-12 EI)

[a]Identified unsaturated chains: EI, *cis*-11-eicosenoic; VA, vaccenic acid. Sat, saturated; cyanolipid III (1-cyano-2-hydroxymethylprop-1-en-3-ol-diesters)

Further evidence came from the two-dimensional spectrum (COSY) where a stronger cross peak was observed between the signal of H-4' and the vinyl hydrogen, compared with the weaker correlation peak between H-4 and again the vinyl hydrogen (Figure 2). The identification of this fraction of CL as **1-cyano-2-hydroxymethylprop-1-en-3-ol-diesters** was confirmed by the presence of two extra carbon signals at δ = 62.77 and δ = 61.71, which were assigned to the methylenes (C-4' and C-4) neighbors of dihydroxybutenyl nitrile group, respectively (Avato *et al.*, 2005) (Table 1).

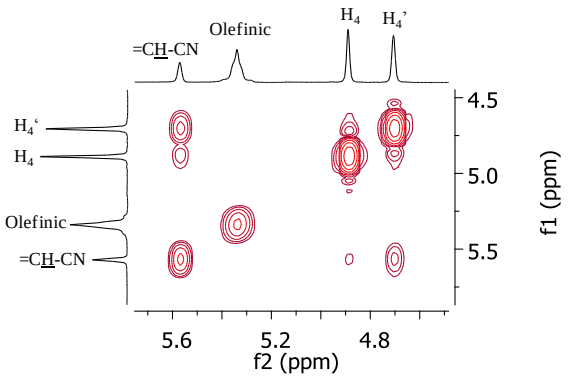


Figure 2
Expansion of two-dimensional spectrum (COSY) of cyanolipid (CL) from seed oil of *S. saponaria*

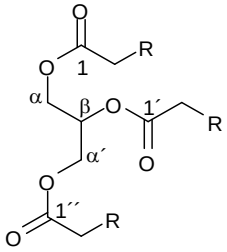
TAG *determination*

The IR spectra of TAG compounds showed typical absorption bands at 3004 (C-H olefins), 2924, and 2852 (aliphatic C–H stretching), 1746 (C=O stretching), 1462 (aliphatic C–H bending), 1162 (stretching C–O), and 722 cm^{-1} (Barbosa, 2011). TAG isolated from the seed oil of *S. saponaria* was also subjected to ^{1}H and ^{13}C NMR analysis (Table 2).

NMR spectra clearly indicated that the isolated lipids were TAG. Signals relative to glycerol α- and β-carbons were present NMR spectra. For example, in the 1H NMR spectra at δ = 4.11 and δ = 4.27 the signals corresponding to a double doublet, were observed for the methylenes hydrogen α and α'. In addition, at δ = 5.23, the methine hydrogen β. On the other hand, en the 13C NMR spectra at δ = 62.09, was observed both the α and α'-carbon atoms while, at δ = 68.95 the β-carbon atom is observed. The presence of the three signals at δ = 173.09, C-1, at δ = 173.12, C1'' and δ = 172.70 C-1' confirmed the ester carbonyl, corroborated that the isolated lipids were TAG (Avato et al., 2003; Gunstone, 1990). As in the CL, the hydrogen and carbon resonances allowed the determination of the fatty acid chains esterifies to the glycerol moiety (Gunstone, 1990; Gunstone, 1991). Another important evidence came from two-dimensional spectrum (COSY), where, the vicinal couplings were observed between the hydrogen of the methylene-α and CH2-α' with hydrogen CH-β of glycerol unit, confirming the presence of triacylglycerides (TAG) (Figure 3).

The carbon resonance of terminal methyl, ω1, along with methylene signals ω2 and ω3, were useful in determining the chains of TAG constituents. For example, ω9 (oleic acid and *cis*-11-eicosenoic acids), ω7 (vaccenic acid and paullinic acid) and ω3 (linoleic acid) (Table 2). In the NMR spectrum of TAG, ω2 and ω3 signals relative to 18:2 chains have a higher intensity than CL, suggesting a larger presence of these FA in the oil mixture. Nevertheless, in agreement with what is found for cyanolipid compounds, the signals ω2 to ω3 relative to saturated and unsaturated chains resonate as paired peaks, which can be assigned to ω7 (lower chemical shifts) and ω9 (higher chemical shifts) belonging to fatty acyl chains (Avato *et al.,* 2003).

Table 2
^{1}H and ^{13}C NMR data of triacylglycerides (TAG) from Seed Oil of *S. saponaria.*



^{1}H	δ (*J*, Hz)	^{13}C	δ (*J*, Hz)
C<u>H</u>$_2$-2	2.27 m	<u>C</u>H$_3$, ω1	14.10 (18:2), 14.14 (ω7,Sat, ω9)
C<u>H</u>$_2$-3	1.57 m	<u>C</u>H$_2$, ω2	22.63 (18:2), 22.74 (ω7,Sat, ω9)
-CH=CH-C<u>H</u>$_2$-*cis*	1.97 m	=CH-<u>C</u>H$_2$-CH=	24.89
=CH-C<u>H</u>$_2$-CH=	2.73 m	CH$_2$, C-3	24.91, 25.67
Olefinic *(cis)*	5.33 m	-CH=CH-<u>C</u>H$_2$-*cis*	27.21, 27.26
n-C<u>H</u>$_2$	1.25 m	n-CH$_2$	29.09-29.82
C<u>H</u>$_3$ ω1	0.84 m	<u>C</u>H$_2$ ω3	31.58 (18:2), 31.97 (ω7,Sat, ω9)
Glicerol α C<u>H</u>$_2$	4.10 dd (5.8, 11.7)	Glicerol α and α' <u>C</u>H$_2$	62.09
Glicerol α' C<u>H</u>$_2$	4.27 dd (11.9, 4.1)	Glicerol β <u>C</u>H	68.95
Glicerol β C<u>H</u>	5.23 m		127.93 (C-12 LA)
			128.11 (C-10 LA)
			129.66 (C-11 EI, VA)
			129.68 (C-12, C-13 PA)
		CH=CH [a]	129.79 (C-9 OL)
			129.90 (C-9 LA)
			129.98 (C-12 EI, VA; C-10 OL)
			130.14 (C-13 LA)
		C-1	173.12
		C-1''	173.09
		C-1'	172.70
		C-2, C-2'	34.03, 34.19

[a]Identified unsaturated chains: LA, linoleic acid ; OL, oleic acid; EI, *cis*-11 eicosenoic acid; PA, paullinic acid; VA, vaccenic. Acid. Sat, saturated.

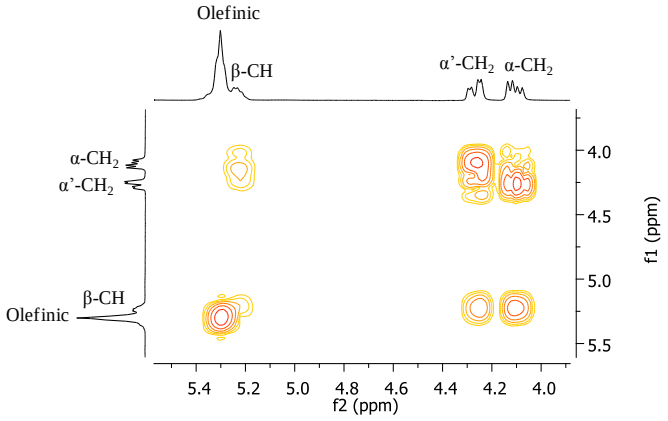


Figure 3
Expansion of two-dimensional spectrum (COSY) for triacylglycerides (TAG) from seed oil of *S. saponaria*

GC–MS analysis

TAG and CL isolated from the seed oil of *S. saponaria* were also subjected to a transesterification before GC–MS analyses. FA esterified to the nitrile moiety of the CL were analyzed as their methyl ester derivatives by GC–MS. The identification of the constituents of AG and CL oil fraction, were by comparison with the data held in the Wiley 7.0 and NIST libraries, the chromatograms are showing in the Figure 4. The AG was represented by monounsaturated isomers such as: *cis*-11-octadecenoic acid (*cis*-vaccenic acid) (**1**), *cis*-9-octadecenoic acid (*cis*-oleic acid) (**2**), linoleic acid (**3**), paulinic acid (**4**), *cis*-11-eicosenoic acid (**5**) and saturated eicosanoic acid (arachidic acid) (**6**). In contrast, the constituents of CL were represented by monounsaturated isomers such as: *cis*-11-octadecenoic acid (*cis*-vaccenic acid) (**1**), *cis*-11-eicosenoic acids (**5**) and saturated eicosanoic acid (arachidic acid) (**6**) (Figure 4**)**. Data were in agreement with NMR findings.

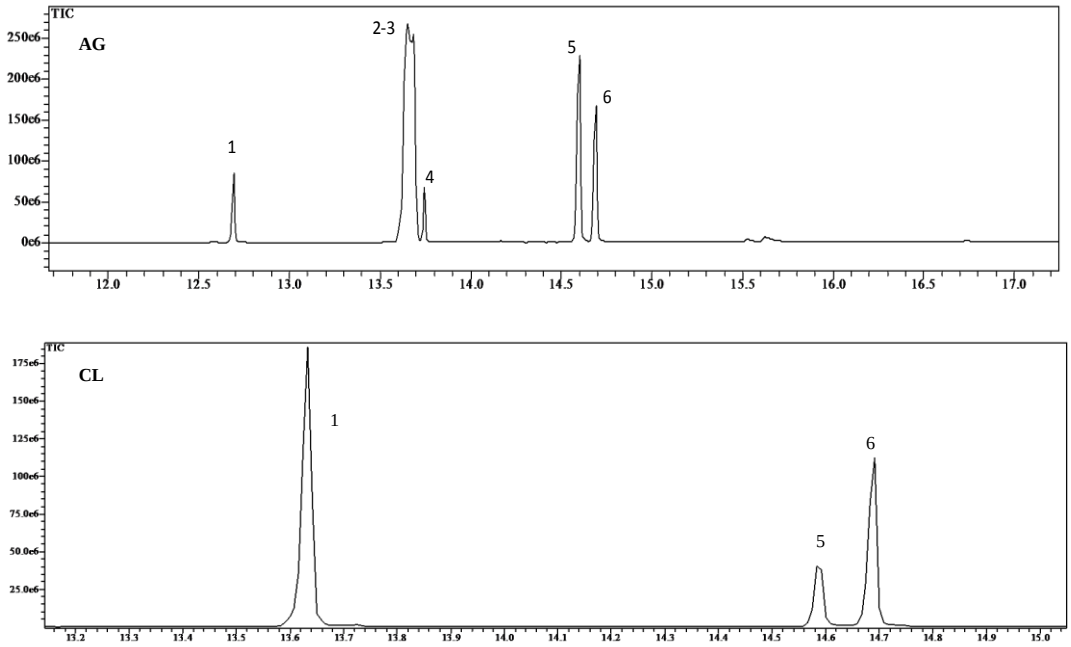


Figure 4
Gas chromatograms of transesterification products of AG and CL

On the other hand, previous detailed investigations on the total FA composition of seed oils from other members of the Sapindaceae (Mikolajczak, 1977) showed that they were very peculiar due to that *cis*-vaccenic acid and arachidic acid were the principal components; these have been proposed as chemotaxonomic markers for this plant family. In fact, *cis*-vaccenic acid normally occurs in seed oils in low amounts, and arachidic acid, are closely related to cyanolipids (Ucciani *et al.*, 1994). Both acids are present in the seeds of *S. saponaria* confirming the chemotaxonomic information related to this family plant.

CONCLUSION

To our knowledge, this is the first detailed compositional study of the FA occurring in the oil lipid fractions (TAG and CL), from seeds of *S. saponaria*. In the oil was isolated and identified the cyanolipid (type III), as **1-cyano-2-hydroxymethylprop-1-en-3-ol-diesters**.

In addition, were identified the FA bonded to CL. This is the first report of cyanolipids in the seeds of *S. saponaria*, this result is a contribution to the chemotaxonomy of this family, characterized by biosynthesize these natural products in their seeds.

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