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Synthesis of natural ether lipids and 1-O-hexadecylglycero-arylboronates via an epoxide-ring opening approach: Potential antifouling additives to marine paint coatings.

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***Abstract*—** *In this paper a new and efficient procedure for the synthesis of natural 1-O- alkyl glyceryl ethers such as chimyl (1), batyl (2) and selachyl (3) is described. Alkyl glycidyl ethers (4-6) were synthetized using solvents free reactions. A stereospecific ring-opening reaction of epoxides (4-6) with phenylboronic acid in dry dioxane, giving rise to cyclic arylboronates in high yields (90-98%). Seven new 1-O-hexadecylglycero-arylboronates (7-f) and chimyl alcohol (1) were evaluated in laboratory antifouling assays.*

Keywords*—, *Antifouling paints, Ethers lipids, Marine biofouling, Synthesis.

I. INTRODUCTION

Marine biofouling is a problem capable of generating great damages to the oil exploitation and transport sectors since platforms and vessels require constant repairs, especially on submerged surfaces. To address this issue, several coating paints and antifouling additives have been developed, since the 1950s, in order to decrease the growth of this biological community (marine bacteria, algae, mollusks). The problem is that these additives containing tin, zinc and cooper are expensive and very harmful to the environment[1-5].

In an attempt to reduce the damage caused by marine biofouling in an economically viable manner and according to prevailing environmental standards our group of research has been using the residues of production of refined soybean oil and biodiesel, such as lecithins and glycerol, as raw material to produce new biocides to be added in antifouling paints and in the treatment of ships ballast water [6-12]

The 1-O-alkyl-sn-glycerols containing palmityl (C16:0), stearyl (C18:0), and oleyl (C18:1) in alkyl chains are dubbed chimyl (**1**), batyl (**2**) and selachyl (**3)** alcohols (Fig. 1). They are isolated from marine animals such as Batoidea (rays), Chimearas (ratfish), and Selachii (sharks) [13]. We have no knowledge of biofouling process being observed on the skin of these animals.

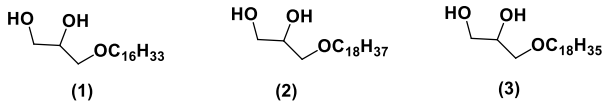

Fig. 1 -The most prevalent 1-O-alkyl-sn-glycerols found in nature, batyl (1), chimyl (2) and selachyl (3) alcohols.

II. EXPERIMENTAL

General Experimental Methods. All the chemicals were purchased commercially and used without further purification and anhydrous solvents were used in two steps. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60F-254) using UV light as a visualizing agent and an acid solution of cerium sulfate, and heat. Silica gel (particle size: 230−400 mesh) was used for flash column chromatography. Neat compounds were used for recording IR spectra. Infrared spectra were obtained using a Perkin-Elmer 1600 FTIR spectrometer and were recorded using KBr pellets for solid compounds or as liquid films in the case of oily samples. NMR spectra were recorded on either 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or 300 (^{1}H, 300 MHz; ^{13}C, 100 MHz) or 200 (^{1}H, 200 MHz; ^{13}C, 100 MHz). Mass spectrometric data were obtained using QTof-6530 ESI-MS instruments. Melting points measurements were made using a hot stage

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apparatus. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet.

Step 1

General Procedure A for the synthesis of alkylglycidyl ethers: A long-chain alcohols (1.0 mmol) were heated in the round bottomed flask to 40°C on the presence of TBAB or TBAHS (6.25 x 10^{-3} mmol) and sodium hydroxide (1.5 mmol), the reactional mixtures were stirred during 30 min. at the same temperature. Epichlorohydrin (2.0 mmol) was added and the temperature was kept between 55° and 60°C during 10.0 hours. The reaction was completed when the yield of the alkyl glycidyl ethers **4-6** (monitored by TLC) did not increase any more with the increase of reaction time. The products were extracted twice with 100 mL of *n*-hexane and was purified through flash chromatography (5% Ethyl acetate/Hexane) furnishing the desired alkylglycidyl ethers **4** (95%), **5** (98%) and **6** (92%) yields.

Step 2

Preparation of Cyclic Boronates: In a 100 mL round-bottom flask were added 1.2 mmol of the alkyl glycidyl ethers 4-6 and 1.32 mmol of the corresponding arylboronic acids under a nitrogen atmosphere (N_2). The reaction mixture was dissolved with 10 mL of anhydrous dioxane, then 0.9 mL of boron trifluoride etherate (BF_3 -OEt_2) was added. The reaction mixture was kept under stirring for 4-6 hours at room temperature, after which time 6.1 mmol of anhydrous sodium carbonate was added under vigorous stirring. The resulting suspension was transferred to a sintered funnel and washed with dichloromethane (3 x 40 mL). The solvent was removed on a rotary evaporator and dried under reduced pressure to afford the desired cyclic boronates **7** (100%), **8** (99%) and **9** (97%).

Step 3

Transesterification Procedure: The transesterification reaction was carried out in a 100 mL round bottom flask in which 1.23 mmol of cyclic boronates **7, 8, 9** and 2,46 mmol of 1,3-propanediol were added in 5.0 mL of chloroform under nitrogen atmosphere at room temperature. After keeping the reactional mixtures for 24.0 hours under stirring the products were extracted with ethyl acetate (150 mL), the organic phase was washed with water (4 x 20 mL) and dried with anhydrous sodium sulfate.

After removal of the solvent purification of the products was carried out using flash chromatography eluting with a mixture of 25% ethyl acetate in hexane. Chimyl (**1**), batyl (**2**) and selachyl (**3**) alcohols were obtained in yields of 87, 85, and 77%, respectively.

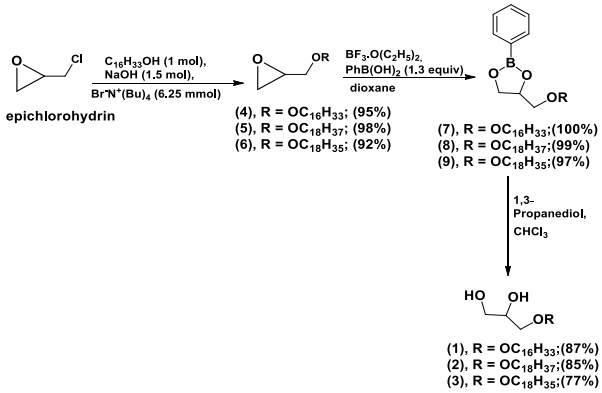
III. RESULT AND DISCUSION

A reaction medium containing the cetyl alcohol with epichlorohydrin in the presence of tetra-N-butylammonium bromide and sodium hydroxide, without solvent and under stirring, was kept between 55° and 60 °C for 10.0 hours. After the time had elapsed, and the regular work up of isolation and purification through flash chromatography had been done 1-O-hexadecyl-2, 3-epoxypropane (**4**) was obtained with a yield of 95%. The same reaction, also using epychlorohydrin as starting material was performed with stearylic and oleylic alcohols giving the corresponding 1-O- octadecyl- 2,3-epoxypropane (**5**), and 1-O-oleyl-2,3-epoxy propane (**6**) in 98% and 92% yield respectively. A similar experimental procedure was described by Yoon and coworkers [14].

The treatment of 1-O-hexadecyl-2,3-epoxypropane (**4**), 1-O- octadecyl- 2,3-epoxypropane (**5**) and 1-O-oleyl-2,3-epoxy propane (**6**) with catalytic amounts of boron trifluoride etherate and 1.3 equivalents of phenyl boronic acid dissolved in dry dioxane, provided the 1-O-hexadecylglycero-phenylboronate (**7**), 1-O-octadecylglycero-phenylboronate (**8**) and 1-O-oleylglycero-phenylboronate (**9**) in 100%, 99%, 97% yields. These products were not purified given their lack of stability under flash chromatography conditions; therefore all yields were determined by ^{1}H NMR techniques. A transesterification reaction[15] using 1,3- propanediol in $CHCl_3$ promoted the cleavage of five-membered ring boronates (**7**, **8**, **9**) furnishing after flash chromatography purification the desired natural products chimyl (**1**), batyl (**2**) and selachyl (**3**) alcohols in 87%, 85%, 77% yields. (Scheme 1)

Compared to other procedures described in the present literature [13, 16, 17, 18, 19, 20, 21, 22] the synthesis of chimyl (**1**), batyl (**2**) and selachyl (**3**) alcohols described herein is an efficient synthetic approach, which presents a straightforward chemical transformation of an epoxide function to cyclic phenylboronate intermediates.

*Scheme 1- Synthetic route for the preparation of compounds **1-3**.*



In order to confirm this result solutions of chimyl (**1**), batyl (**2**) and selachyl (**3**) alcohols with phenyl boronic acid in

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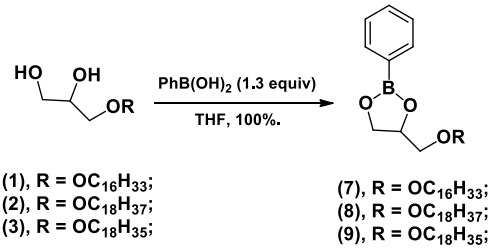
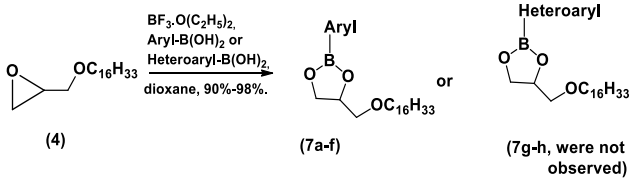
dry THF were stirred for 24.0 hours, and after the removal of the solvent only the corresponding 1-O-hexadecylglycero-phenylboronate (**7**), 1-O-octadecylglycero-phenylboronate (**8**) and 1-O-oleylglycero-phenylboronate (**9**) were obtained in quantitative yields. (Scheme 2)

Scheme 2 - Reaction of boronation of 1,2-diols with phenylboronic acid in dry THF, in good overall yields.



On scheme 3 we demonstrate other examples of this same type of chemical transformation to obtain the new 1-O-hexadecylglycero-arylboronates (**7a-7f**) in good overall yields (Scheme 3). Unfortunately, this type of conversion does not work with the heteroaryl boronic acids such as 2-furyl boronic acid and 3-piridinyl boronic acid to form the corresponding 1-O-hexadecylglycero-heteroarylboronates (**7g-7h)**.

*Scheme 3- Chemical transformation of epoxide **4** to obtain the new 1-O-hexadecylglycero-arylboronates.*



The unsuccessful attempt to yield the 1-O-hexadecylglycero-furylboronate (**7g**) is probably related to the opening of the furan ring system by BF_3-monohydrated (H_2O^+-$^-BF_3$) which is an efficient and strong acid catalyst formed during the reactional process [23]. In addition to that, the reaction also did not work well to obtain (**7h**) due the reactivity of $BF_3.O(C_2H_5)_2$ which interacts preferably with the nitrogen atom of the pyridinyl ring instead of promoting the desired pathway of chemical transformation (Table 1).

*Table 1- The effects of the boronic acid type on the conversion rate of epoxide **4** to the boronic ester.*

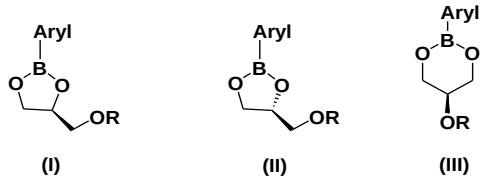
Boronic acids	Product	Yield (%)
4-methoxyphenyl-	1-O-hexadecylglycero-4-methoxyphenylboronate (**7a**)	90%
3,4-methylenedioxy-	1-O-hexadecylglycero-3,4-methylenedioxyphenylboronate (**7b**)	93%
3,5-dimethoxypheny l-	1-O-hexadecylglycero-3,5-dimethoxyphenylboronate (**7c**)	91%
3,4-dimethoxypheny l-	1-O-hexadecylglycero-3,4-dimethoxyphenylboronate (**7d**)	98%
2,3-dimethoxypheny l-	1-O-hexadecylglycero-2,3-dimethoxphenylboronate (**7e**)	93%
4-fluorophenyl-	1-O-hexadecylglycero-4-fluorophenylphenylboronate (**7f**)	94%
2-furyl-	1-O-hexadecylglycero-2-furyl-boronate (**7g**)	XX
3-pyridyl-	1-O-hexadecylglycero-3-pyridyl-boronate (**7h**)	XX

* All yields and diastereoselectivity were determined by ^{1}H NMR (300 MHz).

Regioselective and stereoselective epoxy-ring opening reactions are widely employed as important tools on the synthesis of natural products with biological activities [24, 25, 26].

We observed herein that in all epoxy-ring opening using the O-alkyl-glycidyl esters (**4, 5, 6**) as starting materials in the presence of aryl boronic acids using dioxane as solvent, and catalyzed by $BF_3.O(C_2H_5)_2$, only products (**7-7f, 8, 9**) with the configuration syn **(I)** were formed. We did not observe anti (**II**) or six-membered ring products (**III**) which could be formed via epioxonium ions as described by Miyashita and coworkers [27] via a ring-opening mechanism of the epoxy sulfides by a similar reaction through the formation of the episulfonium ions (Figure 2).

Fig. 2- Chemical structure of the possible aryl boronic esters produced in this step.



R= $C_{16}H_{33}$or $C_{18}H_{37}$ or $C_{18}H_{35}$

Theoretical studies were carried out for compounds (**I**) and (**II**) using Density Functional Theory (DFT), with a GAUSSIAN 09 program with the B3LYP hybrid density functional combined with the 6-31G (d, p) basis set [28]. The calculation of frequencies used to find the minimum geometries does not have imaginary values. Analysis of the geometry optimization showed that compound (**I**) is 50 Kcal/mol more stable than compound (**II**), indicating the greater stability compound (**I**) with respect to compound (**II**), as observed experimentally in the synthesis of these compounds.

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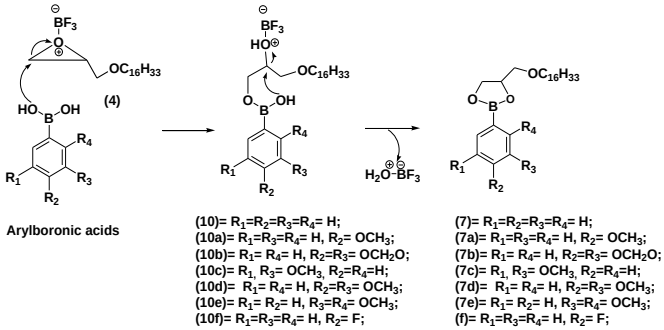
The 1-O-hexadecylglycero-arylboronates (**7-7f**) were obtained in a single step from (**4**). A mechanistic proposal to explain this result is demonstrated on scheme 4. Due to the nucleophilic characteristic of the intermediates (**10-10f**) to promote an internal attack through the hydroxyl groups of the phenyl boronic species on the carbon attached to the leaving group the corresponding 1-O-hexadecylglycero-aryl**b**oronates (**7-7f**) will be promptly generated (Scheme 4).

*Scheme 4- Mechanistic proposal for the formation of 1-O-hexadecylglycero-arylboronates **(7-7f)**.*



Compounds (**1 and 7-f**) were selected and evaluated against biofilm-forming bacterias and the best results are demonstrated on Figure 1. The chimyl (**1**) and 1-O-hexadecylglycero-arylboronates (**7a**, **e**) showed potential activity to be used as additives in antifouling paint coatings on ships and platforms. Specifically, chimyl (**1**) demonstrated better antibacterial activity compared to $CuSO_4$ [29, 30] (Table 2).

Table 2- Representative results of antifouling activity tests performed in laboratory. Degree of inhibition of bacteria growth (++++ = higher; +++ = promising; ++ = acceptable, + = minimum); $CuSO_4$ 0,4miliM (main active component of standard commercial antifouling paints).

IV. BACTERIAS PRESENT ON BIOFOULING PROCESS			
Compounds (100 mg L^{-1})	*P. fluorescens*	*Pseudoaltero mo-nas elyakovii*	*Vibrio estuarians*
(1)	+++++	+++	+++++
(7a)	+++	++	+++
(7e)	+++	++	+++
(7)	+	+	++
(7b)	+	+	+
(7c)	+	+	+
(7d)	+	+	+
(7f)	+	+	+
$CuSO_4$	+++	+++	+++

Chimyl alcohol (**1**): (0.9g) 87%; pale yellow solid (mp. 62-64°C); **IR** (KBr, ν_{max}/cm^{-1}) : 3368 (OH), 2954 – 2850 (CH), 1471 (CH), 1.124 (C-O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.73 (m, 3H), 3.50 (m, 4H), 3.87 (m, 2H), 1.58 (m, 4H), 1.26 (s, 24H), 0.89 (t, J= 6.0, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 72.02, 71.41, 70.02, 63.82, 31.46, 25.62, 13.65.

Batyl alcohol (**2**) : (0.9g) 85%; white solid (mp. 70-72°C); **IR** (KBr, ν_{max}/cm^{-1}) : 3363 (OH), 2954 – 2850 (CH), 1471 (CH), 1.123 (C-O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.87 (m, 2H), 3.73 (m, 3H), 3.65 (m, 4H), 1.58 (d, J= 6Hz, 4H), 1.26 (s, 26H); 0.89 (t, J= 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 72.04, 71.41, 69.99, 63.83, 31.47, 25.62, 13.65.

Selachyl alcohol (**3**): (0.8g) 77%; colorless oil; **IR** (KBr, ν_{max}/cm^{-1}) : 3383 (OH), 3004 – 2854 (CH), 1732 – 1654 (C=C), 1464 (CH), 1120 (C-O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.36 (m, 2H), 3.86 (m, 2H), 3.67 (m, 3H), 3.48 (m, 4H), 2.03(d, J= 6Hz, 4H), 1.59 (m, 6H), 1.28 (d, J= 6Hz, 18H), 0.89 (t= 6.0, J= 6Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.52, 72.06, 71.40, 69.97, 63.84, 31.45, 28.86, 26.76, 25.62, 22.23, 13.66.

1-O- hexadecyl-2,3-epoxypropane **(4):** was obtained with a yield of 95% (1,2 g) as a white solid (mp. 24-26ºC); **IR** (KBr, ν_{max}/cm^{-1}) : 3048- 2851 (CH), 1467 (CH) , 1253 (C-O), 1114 (C-O), 906 (C-C), 852 (C-C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.72 (dd, J = 11.6 e 3.1 Hz, 2H), 3.51 – 3.35 (m, 2H), 3.18 – 3.13 (m, 1H), 2.79 (t, J = 9 Hz, 1H), 2.61 (dd, J = 4.9 e 2.9 Hz, 1H), 1.60 – 1.56 (m, 2H), 1.25 (s, 26H); 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 72.1, 71.8, 51.3, 44.7, 32.3, 30.8, 29.9, 29.7, 29.5, 23.1, 14.5.

1-O- Octadecyl-2,3-epoxypropane **(5):** 1,1 g (98%), white solid (mp. 42-45°C), **IR** (KBr, ν_{max}/cm^{-1}) : 3052 (CH), 3000- 2850 (CH), 1473-1378 (CH), 1251 (C-O), 1125 (C-O), 906 (CH), 852 (CH), 729 (CH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.72 (dd, J = 11.6 e 3.1 Hz, 2H), 3.53 – 3.37 (m, 2H), 3.18 – 3.15 (m, 1H), 2.80 (t, J = 5 Hz, 1H), 2.61 (dd, J = 5 and 5 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.26 (s, 30H); 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 71.5, 71.2, 50.6, 44.1, 31.6, 30.8, 29.4, 29.1, 25.8, 22.4, 13.8.

1-O- oleyl-2,3- epoxy propane **(6)**: 1,1 g (92%), colorless oil, **IR** (KBr, ν_{max}/cm^{-1}) : 3052 (CH), 3002-2854 (CH), 1732 – 1655 (C=C), 1465 (CH), 1253 (C-O), 1125 (C-O); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5,36 (m, 2H); 3,72 (dd, J = 11.5 and 3.2 Hz, 2H); 3.52 – 3,36 (m, 2H), 3.19 – 3.14 (m, 1H), 2.80 (t, J = 9 Hz, 1H), 2.62 (dd, J = 4.9 and 2.9 Hz, 1H), 2.02 – 1.98 (m, 4H), 1.63 – 1.54 (m, 2H), 1.30 (d, J= 6, 22H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.5, 129.5 , 72.1, 71.9, 51.3, 44.7, 32.3, 30.1, 29.7, 29.6, 27.6, 26.5, 23.1, 14.5.

1-O-hexadecylglycero-phenylboronate **(7)**: 1.3g (100%); colorless oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2852 – 2920 (CH), 1354 (B-O), 1121 – 1219 (C-O), 700 – 756 (CH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J= 6, 2H), 7.54- 7.39 (m, 3H), 4.74- 4.71 (m, 2H), 4.44 (t, J=9, 1H), 4.19 (t, J=

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6, 2H), 3.66- 3.49 (m, 2H), 1.58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.4, 131.0, 75.7, 72.2, 71.6, 68.1, 31.5, 29.2, 29.1, 28.9, 25.6, 22.2, 13.6.

1-O-hexadecylglycero-4-methoxyphenylboronate (**7a**): 1.3g (90%); dark brown oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2850 – 2917 (CH), 1379 (B-O), 1123 (C-O); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.76 (d, J= 4, 2H), 6.94 (d, J= 8Hz, 2H), 4.78- 4.67 (m, 2H), 4.41 (t, J=8Hz, 1H), 4.16 (t, J= 6 Hz, 2H), 3.61- 3.49 (m, 2H), 1.58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 136.7, 110.8, 76.1, 72.8, 72.1, 68.5, 32.0, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-hexadecylglycero-3,4-methylenedioxyphenylboronate (**7b**): 1.4g (93%); brown oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2851 – 2920 (C-H), 1339 (B-O), 1121 (C-O), 1029 (B-C), 679 – 760 (C-H); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.37 (d, J= 8, 1H), 6.87 (d, J= 8Hz, 1H), 5.98 (s, 2H), 4.73- 4.63 (m, 2H), 4.40 (t, J=8Hz, 1H), 4.16 (t, J= 6 Hz, 3H), 3.62- 3.48 (m, 2H), 1.58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 147.3, 130.0, 114.1, 100.8, 76.2, 72.7, 72.1, 68.6, 32.0, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-hexadecylglycero-3,5-dimethoxyphenylboronate (**7c**): 1.4g (91%); brown oil; **IR** (KBr, ν_{max}/cm^{-1}): 2850 – 2917 (CH), 1348 (B-O), 1120 (C-O), 674 – 798 (CH); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6,98 (s, 2H), 4.76 – 4.689(m, 2H), 4.43 (t, J= 8 Hz, 1H), 4.19 (t, J= 6 Hz, 2H), 3.82 (s, 6H), 3.64-3.48 (m, 2H), 1,58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 111.8, 104.7, 76.3, 72.7, 76.3, 68.6, 32.0, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-hexadecylglycero-3,4-dimethoxyphenylboronate (**7d**): 1.5g (98%); pale yellow oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2850 – 2918 (CH), 1380 (B-O), 1122 (C-O), 1038 (B-C), 671 – 734 (CH); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.47 (d, J= 6 Hz, 1H), 7.32 (s, 1H), 6.93 (d, J=8 Hz, 1H), 4.78 – 4.68(m, 2H), 4.42 (t, J= 8 Hz, 1H), 4.17 (t, J= 6 Hz, 2H), 3.93 (s, 6H), 3.64-3.48 (m, 2H), 1,58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.9, 148.4, 128.8, 116.8, 110.8, 76.2, 72.8, 72.1, 68.5, 55.9, 55.7, 32.0, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-hexadecylglycero-2,3-dimethoxphenylboronate (**7e**): 1.3g (93%); dark brown oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2852 – 2921 (CH), 1347 (B-O), 1263 – 1059 (C-O), 721 – 792 (CH); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.09 (d, J= 8 Hz, 2H), 6.93 (m, 1H), 4.78 – 4.68(m, 2H), 4.43 (t, J= 8 Hz, 1H), 4.20 (t, J= 6 Hz, 2H), 3.82 (s, 6H), 3.61-3.48 (m, 2H), 1,58 (m, 2H), 1.27 (s, 26H), 0.90 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 152.6, 128.1, 124.1, 120.9, 111.8, 75.9, 72.7, 72.0, 68.5, 56.0, 55.9, 32.0, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-hexadecylglycero-4-fluorophenylphenylboronate (**7f**): 1.3g (94%); brown oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2850 – 2920 (CH), 1353 (B-O), 1122 (C-O), 1074 (C-O), 1198 (C-F); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.70 (t, J= 6 Hz, 2H), 4.76- 4.69 (m, 2H), 4.29 (t, J= 8Hz, 1H), 4.05 (t, J= 6 Hz, 2H), 3.61- 3.49 (m, 2H), 1.45 (m, 2H), 1.27 (s, 26H), 0.76 (t, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.3, 137.1, 115.2, 114.8, 76.2, 72.7, 72.1, 68.6, 32.0, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1.

1-O-octadecylglycero-phenylboronate **(8)**: 1.3g (99%); yellow oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2850 – 2917 (CH), 1369 (B-O), 696 – 758 (CH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J= 4 Hz, 2H), 7.56- 7.40 (m, 3H), 4.76- 4.73 (m, 2H), 4.45 (t, J=8 Hz, 1H), 4.20 (t, J= 4 Hz, 2H), 3.68- 3.51 (m, 2H), 1.60 (m, 2H), 1.29 (s, 30H), 0.92 (t, J = 4Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.9, 132.7, 127.9, 76.1, 72.7, 72.0, 68.5, 31.9, 29.7, 29.6, 29.3, 26.0, 13.6.

1-O-oleylglycero-phenylboronate **(9)**: 1.3g (97%); yellow oil; **IR** (KBr, ν_{max}/cm^{-1}) : 2881 (CH), 1600 (C=C), 1362 (B-O), 690 – 756 (CH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J= 4, 2H), 7.56- 7.40 (m, 3H), 5,38 (m, 2H), 4,76- 4.73 (m, 2H), 3,72 (dd, J = 11.6 and 3.1 Hz, 2H), 3,65- 3.50 (m, 2H), 3,19 – 3,14 (m, 1H), 2,05 – 2.03 (m, 4H), 1,59 (m, 2H), 1,30 (s, 16H), 0.91 (t, J = 6.6 Hz, 3H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.8, 131.4, 130.2, 127.9, 76.1, 72.0, 68.5, 32.3, 31.9, 29.7, 29.5, 29.3, 27.2, 26.0, 14.5.

V. CONCLUSION

In this research we prepared the natural 1-O-alkyl-sn-glycerols (**1, 2 and 3**) using as starting material epichlorohydrin a cheap chemical product synthetized from glycerin a residue of the biodiesel industry. Our synthetic route displayed better yields compared to other procedures described in the present literature to the same compounds. The alcohol chimyl (**1**) demonstrated a biocide activity higher than copper sulfate against three marine biofilm-forming bacteria. This natural compound is eligible to be used as a potential additive in antifouling paints for coating metal surfaces on oil platforms and merchant shipping and military shipping vessels.

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