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Preparation of renewable bio-polyols from two species of *Colliguaja* for rigid polyurethane foams.

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Abstract

In this study we investigated the potential of two non-edible oil extracts from seeds of *Colliguaya Integerrima* (CIO) and *Colliguaja Salicifolia* (CSO) to use as a renewable source for polyols and eventually polyurethane foams or biodiesel. For this purpose, two novel polyols from the aforementioned oils were obtained in a one-single step reaction using a mixture of hydrogen peroxide and acetic acid. The polyol derivatives obtained from the two studied oils were characterized by spectral (FT-IR, ^{1}H NMR and ^{13}C NMR), physico-chemical (e.g. chromatographic analysis, acid value, oxidizability values, iodine value, peroxide value, saponification number, kinematic viscosity, theorical molecular weights, density, hydroxyl number and hydroxyl functionality) and thermal (TGA) analyses according to standard methods. Physico-chemical results revealed that all parameters, with the exception of the iodine value, were higher for bio-polyols (CSP and CIP polyols) compared to the starting oils. The NMR, TGA and FT-IR analyses demonstrated the formation of polyols. Finally, the OH functionality values for CIP and CSP polyols were 4.50 and 5.00, respectively. This result indicated the possible used of CIP and CSP polyols as a raw material for the preparation of polyurethane rigid foams.

Keywords: *Colliguaya Integerrima*; *Colliguaja Salicifolia*; vegetable oil; bio-polyol; renewable resources.

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1. Introduction

The high demand for products from petrochemical origin and their negative effects on the environment, parallel to the growing scarcity of these non-renewable resources, are factors that have encouraged the chemical industry to look for new sources of renewable resources as raw materials. These raw materials have contributed in a very positive way to the sustainable development of the plastics industry due to the great synthetic potential of nature and different principles of green chemistry [1, 2]. Vegetable oils are one of the most considered alternatives due to abundance, low toxicity, biodegradability, inherent fluidity and low cost [3-5]. Several vegetable oil molecules must be chemically transformed to form polyols, and these bio-polyols are used for the obtention of polyurethanes [6], polyesters [7], and epoxy [8], among others.

The synthesis of bio-polyols from fatty acids and vegetable oils has been the focus of many studies. It’s important to note that vegetable oils, with the exception of castor and lesquerella oils do not contain hydroxyl groups. For that reason, it is necessary to chemically modifiy the vegetable oils to introduce hydroxyl groups into their structures to produce polyols. According to the literature, there are five different pathways for vegetable oil-based bio-polyol production: (1) Epoxidation and oxirane ring-opening [9]; (2) Hydroformylation and hydrogenation [10, 11]; (3) Ozonolysis [12]; (4) Thiol-ene coupling [13] and (5) Transesterification/Amidation [14]. In despite of this, the first methods are the most widely used. Regularly, the researchers use this method in one or two steps. “The one step reaction consists of the in-situ epoxidation followed by hydroxylation using acetic and sulfuric acids and hydrogen peroxide. The two-step reaction deals with the triglyceride epoxidation followed by the ring-opening of oxirane, based on the use of difunctional molecules such as alcohols or amines” [15, 16]. This multi-step synthesis would unquestionably increase the cost of bio-polyol production.

It is important to mention that various vegetable oils, including palm, soybean, sunflower, rapeseed, and canola oils are used with slight modifications to produce polyols [17-22]. The great inconvenience with some of these oils are their use in food, which bring as a consequence a global imbalance to the food supply and demand in the industrial market [23].

Therefore, this study concentrates in the obtention of new bio-polyols from two non-edible oil extracts from seeds of *Colliguaya Integerrima* and *Colliguaja Salicifolia* by a one-single step reaction using a mixture of hydrogen peroxide and acetic acid. In addition, we characterized the prepared oils and polyols using various physico-chemical, spectroscopic, and thermo-analytical methods.

Colliguaja Integerrima and *Colliguaja Saliccifolia* are two varieties of the *Euphorbiaceae* family. The *Euphorbiaceae* family, with around 300 genera and over 7,000 species, is one of the

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largest and most diverse families of flowering plants [24]. Both species grow wild in South America, specifically in the phytogeographical provinces of Patagonia and Monte in Argentina and Chile [25-27]. The oil extracted from these two species are known for the diuretic activity of their aqueous extract [28]. To our knowledge, no studies have been previously reported about the production of polyols from *Colliguaja Integerrima* and *Colliguaja Saliccifolia* using a cheap and environmentally benign method.

2. Experimental Procedures

2.1. Chemicals and reagents

Diethyl ether ($C_4H_{10}O$), *n*-hexane, glacial acetic acid (AcOH), hydrogen peroxide (H_2O_2), toluene (C_7H_9), sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_4), sodium thiosulfate pentahydrate and potassium hydroxide (KOH) were supplied by Arquimed (Santiago, Chile). Iodine monochloride solution (Wijs reagent), Starch solution, tetrahydrofuran (THF) and Phenolphthalein reagent were purchased from Sigma-Aldrich (St. Louis, MO, USA). All used reagents were of analytical grade with exception of *n*-hexane and tetrahydrofuran (HPLC purity grade). For GC-MS analysis, Supelco® 37 component fatty acid methyl esther (FAME) mix in dichlorometane (varied concentrations) was purchased from Sigma-Aldrich.

2.2. Colliguaya integerrima and Colliguaya salicifolia sedds.

The seeds of *Colliguaya Salicifolia* and *Colliguaya Integerrima* were collected in Cayurranquil, a geographic area in the Cauquenes Province (725468, 6017270) and the Pehuenche International Pathway, Los Cóndores, at the foothills of Talca (348271, 6026739) Chile, respectively.

2.3. Vegetable oil extraction

Oil extraction was performed according to the AOAC method Am2-93 [29]. About 250 g of *Colliguaya integerrima* seeds were extracted using *n*-hexane (150 mL) as an extraction solvent in a Soxhlet apparatus. After 8 hours, the *n*-hexane was removed by distillation under reduced pressure at 40 ºC. The *Colliguaya integerrima* orange oil (CIO) obtained was stored at 4 ºC under inert atmosphere until further investigation. The extraction was performed in triplicate for each harvested sample obtaining a 26% yield. The same procedure was used for the *Colliguaya salicifolia*, but in this case the oil (CSO) obtained had a yellow coloration with 23% of yield.

2.4. Synthesis of Colliguaja Integerrima and Colliguaja Salicifolia polyol

The synthesis of the polyols was carried out following the methodology described by Monteavaro et al. [30], with slight modifications (See Scheme 1). As Scheme 1 shows, the idealized structure of polyols has a saturated hydrocarbon structure with one OH and one acetate group per double bond. A solution of 5g (5,6 mmol) of *Colliguaja Integerrima* oil and 9.30 mL (0.162 mol) of glacial acetic acid in 20 mL of toluene with some drops of sulfuric acid were placed into a 3-necked

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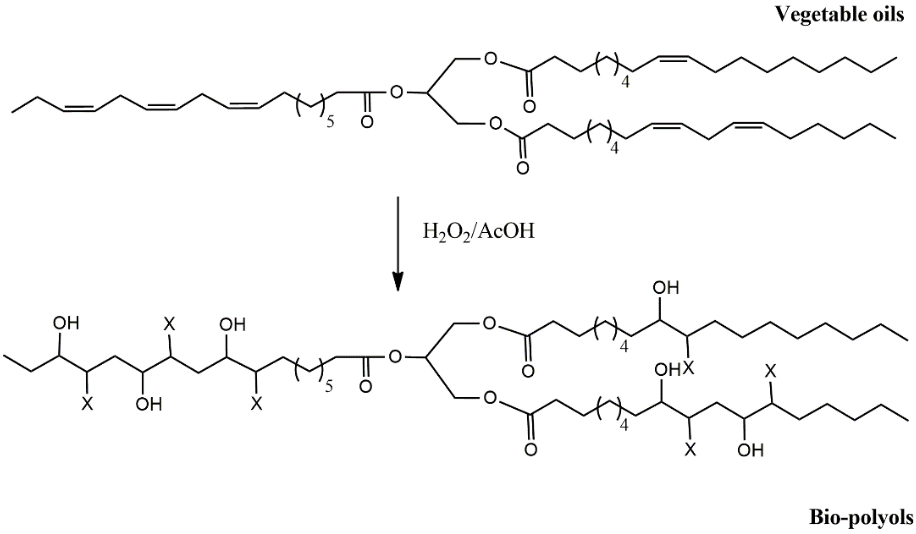
flask equipped with a mechanical stirrer, reflux condenser and isobaric funnel. The mixture was mechanically stirred at room temperature until complete homogenization. After that a solution of 30% H_2O_2 (5.30 mL) was slowly added controlling the temperature When the H_2O_2 addition was completed, the mixture was heated to 60°C for 12 hours. Then the reaction mixture was cooled to room temperature and a 10% wt/vol sodium bisulfide solution was added and the mixture was stirred for 20 min to eliminate excess peroxide. After that, 50 ml of ethyl ether was added to the mixture, and the organic phase was washed several times with 10% wt/vol sodium carbonate solution to neutral pH. Finally, the organic phase was dried over sodium sulfate and concentrated under vacuum to eliminate the ethyl ether to obtain the *Colliguaja Integerrima* polyol (CIP). The same procedure was used for the synthesis of *Colliguaya salicifolia* polyol (CSP).



where X = AcO

Scheme 1. Synthesis of vegetable oil-based polyols without unsaturation.

2.5. Characterization methods used for oils and polyols.

The *Colliguaja Integerrima* and *Colliguaja Salicifolia* oils and polyols were characterized determining the fatty acid composition, the oxidizability value (Cox), acid value (AV), iodine value (IV), saponification number (SN), kinematic viscosity, peroxide value (PV), density, hydroxyl number, thermogravimetric analysis (TGA), Fourier-transform infrared (FT-IR), ^{1}H and ^{13}C NMR spectroscopy. It is important to note, that the fatty acid composition, peroxide value and the oxidizability value were performed only for the studied oils, the rest of the characterization techniques were done for the *Colliguaja Integerrima* and *Colliguaja Salicifolia* oils and polyols.

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The fatty acid profile was determined only for the *Colliguaja Integerrima* and *Colliguaja Salicifolia* oils as fatty acid methyl esters by gas chromatography-mass spectrometry. The methyl esters were prepared using the method described by Morrison and Smith [31]. The separation of the fatty acid esters was performed using QP 5000 Shimadzu (Kioto, Japan) gas chromatographer with mass spectrometer and autosampler was used, as well as the 1.2 Classs-5000. A fused-silica column coated with the DB-5 stationary phase was utilized (30 m X 0.2 mm inner diameter, dry film thickness of 0.25 µm, J & W Scientific). The initial oven temperature was 60 ºC, which was kept for 5 minutes; a 2 ºC min^{-1} temperature increase was programed until it reached 220 ºC; this temperature was kept for 30 minutes. The injector temperature was 220 ºC. Helium was used as a carrier gas with a 1.0 mL min^{-1} flow. The injection volume was 1 µL (1% solution in CH_2Cl_2) with a 1:10 slipt ratio. Column pressure was 100 kPa. Mass detector conditions were the following: source temperature, 240 ºC; electron impact mode (EI), 70 eV; scan rate of 1 scan s^{-1}, and acquisition range, 29-450 u. Components were identified by comparing retention times related to a linear standard made with Supelco® 37 Component FAME Mix in dichlorometane (varied concentrations) of an alkane series (C9-C24) and their mass spectra to those from the Wiley 330000 database and the ones reviewed from the literature. In addition, with the percentage of unsaturated fatty acids we calculated the oxidizability values (Cox) of *Colliguaja Integerrima* and *Colliguaja Salicifolia* oils, applying the formula proposed by Fatemi et al. [32]:

$$Cox = \frac{[1(16{:}1\%+18{:}1\%+20.1\%)+10.3(18{:}2\%+20{:}2\%)+21.6(18{:}3\%)]}{100} \quad (1)$$

The acid value, iodine value, peroxide value and saponification number of the obtained samples (*Colliguaja Integerrima* and *Colliguaja Salicifolia* oils and polyols) were determined according to the AOCS Official Method Cd 3d-63, AOAC Official Method 920.158 (Hanus method), AOAC Official Method 965.33 and the AOAC Official Method 920.160, respectively [33, 34].

The structure of samples (*Colliguaja Integerrima* and *Colliguaja Salicifolia* oils and polyols) were analyzed by ^{1}H, ^{13}C NMR and FT-IR spectroscopy combined with hydroxyl number measurement. ^{1}H and ^{13}C NMR spectra were conducted with a Varian Inova 300 (Varian, Inc., Palo Alto, CA, USA), 300 MHz, using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. FT-IR spectra were recorded by using Agilent Cary 360 FTIR in the range of 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans on ATR (Agilent Technologies, Palo Alto, CA, USA). 2 mL of the *Colliguaja Integerrima* and *Colliguaja Salicifolia* oil and polyol samples were put directly on the equipment plate without any previous treatment. The hydroxyl number of the *Colliguaja Integerrima* and *Colliguaja Salicifolia* polyols was determined according to ASTM 4274-05 [35]. The viscosity of the *Colliguaja Integerrima* and *Colliguaja Salicifolia* oil and polyol samples were measured by

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Brookfield viscometer (LVDV-II, Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts) at 25 ± 0.5 °C. The density of the *Colliguaja Integerrima* and *Colliguaja Salicifolia* oil and polyol samples were measured by means of a pycnometer at 25 ± 0.5 °C. Finally, thermal stability of the oils and polyols were performed in a termogravimetric analyzer NETZSCH TG 209F1 Iris (NETZSCH Company, Germany) with 10 ºC min^{-1} constant heating rate. The heating was from 30 ºC to 500 ºC in inert atmosphere with a flow rate of 60 mL min^{-1}.

3. Results and Discussion

3.1. Physico-chemical characteristics of vegetable oils

The chemical composition and characteristics of the precursor of polyols (*Colliguaja Integerrima* and *Colliguaja Salicifolia* oils) used in this study are shown in Table 1. In addition, we determined the acid value, cox value, iodine value, peroxide value, saponification number, kinematic viscosity, theorical molecular weights and density of these oils.

As can we see, the saturated fatty acids (SFA) of the oils differ very little, because the percentage of palmitic acid, which is the main SFA, is similar in the two studied oils. On the other hand, the percentages of unsaturated fatty acids (UFA), were 87.36 and 88.23% for CIO and CSO, respectively. Specifically, the dominant constituents (over 80%) of both studied oils are C18 fatty acids in despite of there also being about 7 % of C20 fatty acids. The percentage value of linoleic acid (C 18:2) was observed in 31.11% and 20.40% for CIO and CSO, respectively. The main differences between CIO and CSO oils are derived from the percentage of linolenic acid (C 18:3), observed in 26.39 and 46.60, respectively. Figure 1 shows the chemical structures of linoleic and linolenic acids found in CIO and CSO oils. It is important to note, that this difference in the distribution of the double bonds in the fatty acid chains are fundamental for knowing the possibilities of increasing OH groups in the polyols synthetized using these oils and directly proportional to their potential as a future polyurethane foam.

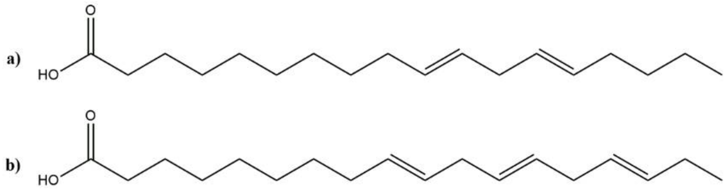

Figure 1. Chemical structures of linoleic (a) and linolenic (b) acids found in CIO and CSO oils.

Taking into account the above mentioned and using the measured composition (lipid profile), we measured the degree of unsaturation by the iodine value (IV), which is directly related to the Cox

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value for CIO and CSO oils. The results for CIO and CSO oils indicated values of IV (143.8 and 179.3 g I_2/100 g, respectively) and Cox (9.35 and 12.46, respectively), providing it a particular resistance to oxidation. The saponification value (SN), which is a parameter related with the molecular mass of the fatty acids found in the oil, was also studied. The SN values for CIO and CSO oils were 196 and 194 mg KOH/g oil, respectively, which are in the average SN range of 175-250 mg/g reported for common vegetable oils [36]. It should be noted that these values don't show significant differences, which means that the fatty acid composition of the studied oils are similar in molecular weight. It is known that acid value (AV) measures the number of carboxylic acid groups present in fat or oil; this value must not be too high, because it is a result of the hydrolysis of triglycerides. The highest acid value was found for CSO (0.25 mg KOH/g oil), however, the AV for both studied oils was less than 1.0 mg KOH/g oil (See Table 1), indicating that oils did not undergo hydrolytic processes. Additionally, the peroxide value (PV) of CIO and CSO were similar and less than 20 meq/kg, respectively, indicating that these oils were unoxidized and of high initial quality.

Table 1 also gives the approximate average molecular weights (M_w) for CIO and CSO. The M_w of oils were calculated averaging the individual molecular weights of each constituent triglyceride, according to Stavarache et al. [37]. The results showed values of 873.7 and 872.9 g/mol for CIO and CSO, respectively. It is important to highlight that the calculated theoretical molecular weight is based on the assumption that no dimers and trimers were formed.

Finally, we also measured the kinematic viscosity and density for CIO and CSO oils. Generally, the kinematic viscosity is related to a measure of the internal friction or resistance of an oil to flow. According to Krisnangkura et al. [38], viscosity may be considered the interaction forces of molecules. The viscosity values shown in Table 1 were 58.6 and 48.8 mm^2/s for CIO and CSO oils, respectively. The difference in these values is due to the degree of unsaturation presented in both studied oils and are in concordance with the results reported by Rodrigues Jr et al. [39]. In this research, Rodrigues Jr reported that one double bond increased the viscosity, whereas, two or three double bonds caused a decrease in the viscosity of the systems. On the other hand, density is an important physical characteristic of any substance and is the weight of a unit volume of fluid [40]. In this case, the values reported in Table 1 are 0.884 and 0.896 g/cm^3 for CIO and CSO oils, respectively. It is important to know that all reported values shown in Table 1 (physical characteristics) of CIO and CSO oils had a drastic change in their numerical values when the oils became their respective polyols.

Table 1.

Chemical composition and characteristics of *Colliguaja Integerrima* (CIO) and *Colliguaja Salicifolia* (CSO) oils.

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Parameters	**Oils**	
	CIO	**CSO**
Fatty acid (%)		
Myristic, $C_{14:0}$	0.06	0.04
Palmitic, $C_{16:0}$	10.54	8.46
Palmitoleic, $C_{16:1}$	0.05	0.08
Margaric, $C_{17:0}$	0.00	0.00
Stearic, $C_{18:0}$	2.03	2.06
Oleic, $C_{18:1}$	23.50	15.08
Linoleic, $C_{18:2}$	31.11	20.40
Gamma- linolenic's, $C_{18:3}$	0.48	0.00
Alpha-linolenic's, $C_{18:3}$	26.39	46.60
Gondoic, $C_{20:1}$	5.35	6.34
Eicosadienoic $C_{20:2}$	0.48	0.73
Cox value	9.35	12.24
AV [mg KOH/g oil]	0.17	0.25
IV [g I_2/100 g oil]	143.8	179.3
PV [meq O_2/kg oil]	19	18
SN [mg KOH/g oil]	196	194
Kinematic Viscosity [mm^2/s]	58.6	48.8
Density [g/cm^3]	0.884	0.896
Molar Mass [g/mol]	873.7	872.9

3.2. Synthesis and characterization of Colliguaja Integerrima and Colliguaja Salicifolia polyols prepared by a one-step synthesis

The main goal of our research was to prepare polyols from CIO and CSO oils, respectively. *Colliguaja Integerrima* and *Colliguaja Salicifolia* polyols (CIP and CSP, respectively) were prepared by a one-step synthesis using the acetic acid/H_2O_2 system. The results reveal a wide difference of physicochemical characteristics among both obtained polyols and its starting oils. The measures of OH functionality was given an idea of the characteristics of the polyol obtained. For example, if the reaction was complete we obtained a polyol with high OH functionality. On the contrary, if the reaction was partial we obtained a polyol with remaining epoxy groups. These two results will be depending on the reaction conditions. As previously mentioned, we obtained CIP and CSP polyols

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with OH numbers of 225.0 and 240.8 mg KOH/g (See Table 2), respectively. According to these values, it is evident that both hydroxylation reactions to obtain the CIP and CSP polyols were complete, which are coherent with the NMR and FT-IR results.

3.2.1. ^{1}H and ^{13}C NMR Analysis

The functional group present in the CIP and CSP polyols with their respective starting oils were confirmed by ^{1}H NMR and FT-IR analysis and the results are shown in Figure 2 and 3, respectively. Due to the large quantity of obtained results, we reported in Figure S1 (See supporting information) the ^{13}C NMR spectra of the studied samples (CIP CSP CIO and CSO). It is known that polyols are a complex blend of products. For that reason, the NMR spectra analysis was performed by zone because each zone gives indications about the average structure of polyols.

Figure 2a and c shows the ^{1}H NMR spectra of CIP and CSP polyols, respectively. The main difference between polyols and their corresponding oils (Figure 2b and d) in the ^{1}H NMR spectra were the appearance of new peaks in the zone between 3.27 - 3.83 ppm, which are assigned to the presence of methylene protons attached to the hydroxyl group (-CH-OH). In addition, the signal corresponding to the olefinic hydrogen (-CH=CH-) that appeared in the zone between 5.32 - 5.44 ppm disappeared, suggesting that polyol structures were practically without unsaturation. Finally, the absence of signals in the zone between 2.8 and 3.2 ppm, relative to the epoxide groups (-CH(O)CH-), confirmed the occurrence of the hydroxylation reaction to obtain the CIP and CSP polyols.

On the other hand, the ^{13}C NMR spectra of CIP and CSP polyols with their respective starting oils offers similar information. These spectra were characterized by the almost disappearance of the ethenic double bond signs of both starting oils and the appearance of a new sign in 75.32 ppm, which corresponds to -CH-OH groups formed during the epoxy opened ring. In agreement with the results obtained by the ^{1}H NMR spectra, the signals centered in 54.38 ppm, relative to the epoxide groups nonappearance, proved the formation of polyols. Finally, the signal found at 173-175 ppm, relative to the carbonyl ester, showed a peak present in both oils and polyols.

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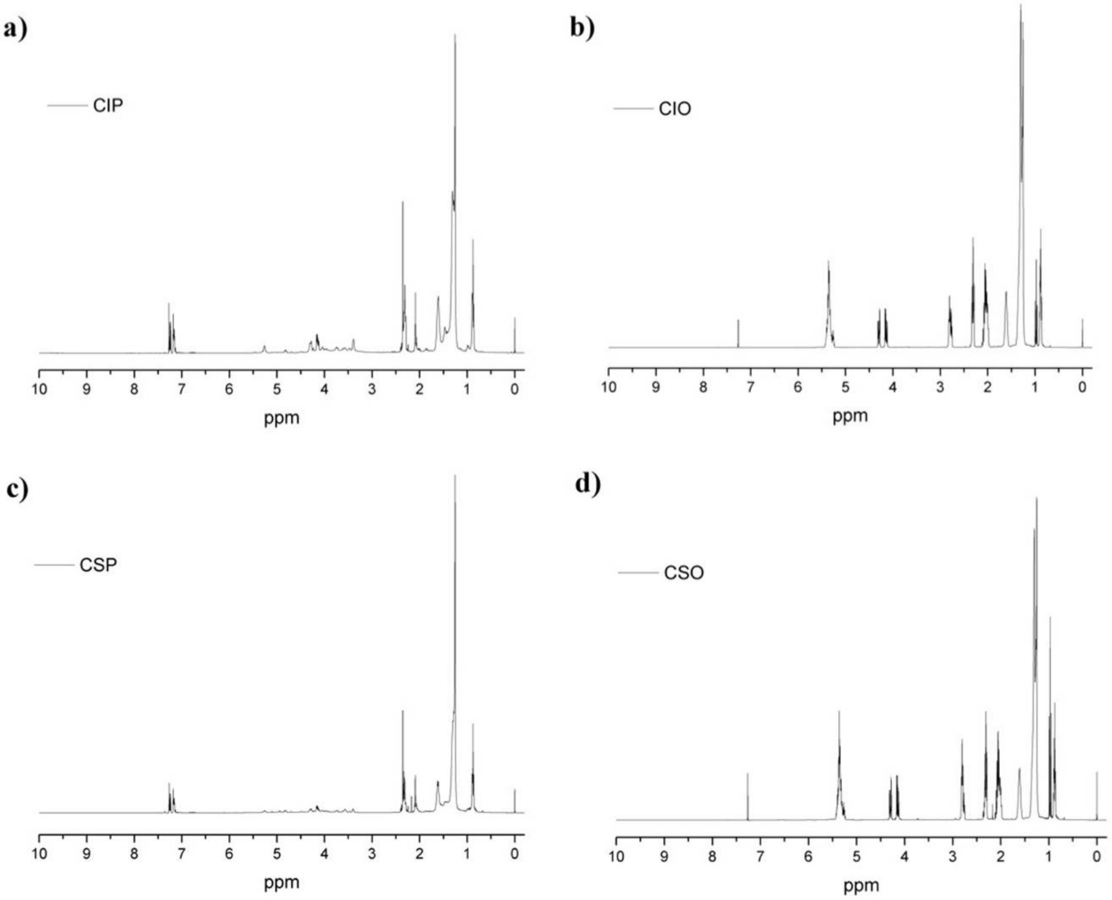

Figure 2. ^{1}H NMR spectra of CIP (a), CSP (c) polyols whit their respective CIO (b) and CSO (d) oils.

3.2.2. FT-IR Analysis

In order to complement the NMR analysis, the successful conversion of CIO and CSO oils into polyols was confirmed qualitatively by FTIR spectroscopy. These spectra are compared in Figure 3a-d, respectively. Figure 3a and c shows the FT-IR spectra of CIP and CSP polyols, respectively. Both polyols FT-IR spectra exhibited a broad peak centered approximately at 3400 cm^{-1}, which were assigned to the presence of hydroxyl (-OH) stretching vibration. Another difference between CIP and CSP polyols with their respective oils was the most intensive band (C=O, carbonyl stretching), attributed to the presence of the ester linkage. It slightly shifted from 1748.0 to 1738.8 cm^{-1} for CIO oils and CIP polyol, respectively. The same behavior was found for CSO oils and the CSP polyol, in this case the band slightly shifted from 1743.7 to 1734.3 cm^{-1}, respectively. Another important asymmetrical stretching band present in both FTIR spectra polyols corresponded to C-O-C groups at 1158 cm^{-1}. It is important to mention that the absence of the bands at around 870 and 920 cm^{-1},

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assigned to the epoxy groups in both spectra polyols, corroborate that the hydroxylation reaction of the oils was complete. Finally, the bands at 2919.6 and 2846.1 cm^{-1} and 2924.3 and 2850 cm^{-1} assigned to asymmetrical and symmetrical stretching CH groups, for CIP and CSP polyols, respectively, were also detected. This evidence from FTIR analysis confirmed the formation of polyols and the results obtained by ^{1}H and ^{13}C NMR.

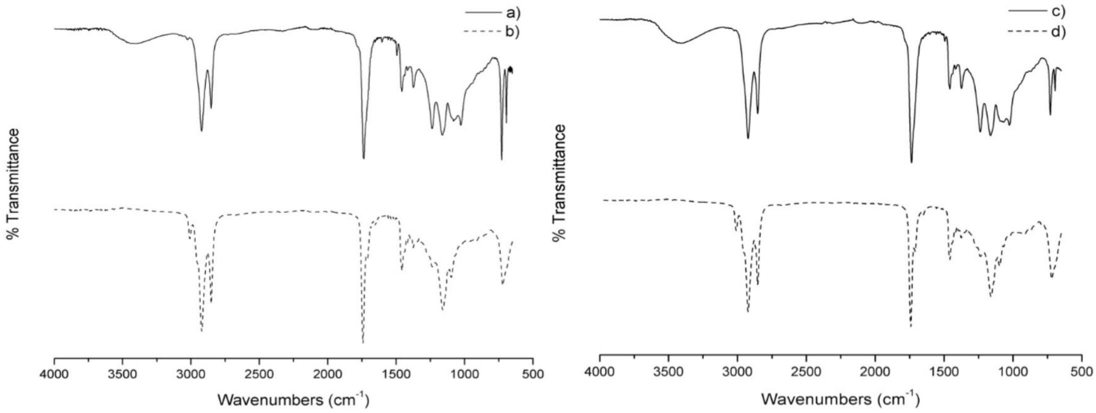

Figure 3. FT-IR spectra of CIP (a), CSP (c) polyols whit their respective CIO (b) and CSO (d) oils.

3.2.3. TGA Analysis

In order to investigate the influence of the structure and composition on thermal stability of the oils and polyols, thermogravimetric analysis was performed in the interval from 30 to 600 ºC. The TGA (TG) curves and their calculated derivatives (DTG) are shown in Figures 4 and S2 (See supporting information), respectively. Following the same analysis used for NMR and FTIR discussion, we compare the thermograms obtained for polyols and their respective oils. As seen in Figure 3a and c, the weight loss curves for the thermal degradation of both polyols closely resembles the TG and DTG curves of their starting oils. Specifically, CIP and CSP polyols exhibited slightly minor thermal stability compared to its oil. In addition, the initial weight loss observed under 100ºC in the TG curve in both polyols could be attributed to the loss of the residual water molecules. In the oils at 100ºC this weight loss was not observed. The total weight loss for both polyols was about 95%, meanwhile oils degrade completely [41]. We suggest that these results could be due to the presence of hydroxyl groups in the polyol.

The TG curve of CIP polyol indicates another degradation stage (Figure 4a), which is reflected as a single peak in the DTG curve (Figure S2a) at 400.24ºC. On the other hand, a quite different decomposition was observed for the CSP polyol; its major decomposition occurred in three steps starting at 196 ºC, 390ºC and 428ºC, respectively.

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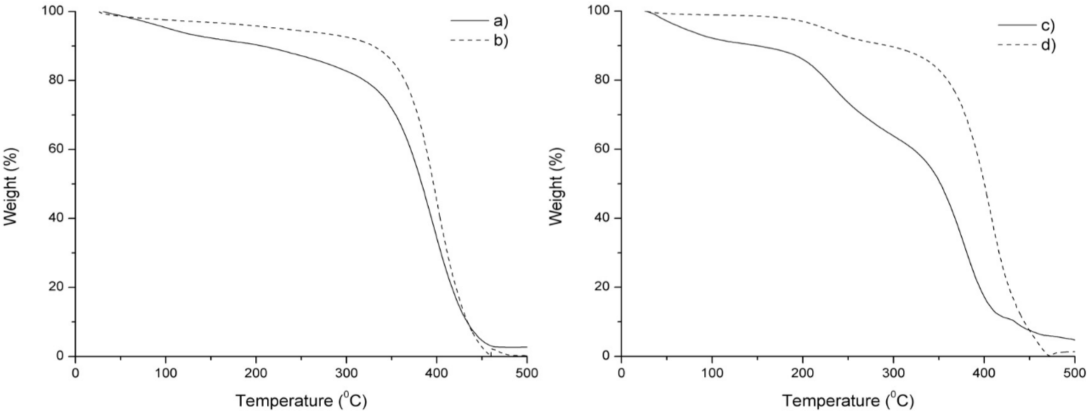

Figure 4. TGA curve of CIP (a), CSP (c) polyols with their respective CIO (b) and CSO (d) oils.

3.2.3.4. Physico-chemical characteristics of vegetable polyols

Moreover, we determined the acid value (AV), iodine vale (IV), saponification number (SN), kinematic viscosity (υ), theorical molecular weights (M_w), density (ρ), and OH numbers of the polyols and the results are also included in Table 2.

The AV and SN for the polyol samples were higher when compared to the starting oils. It is important to mention that the CIP and CSP polyol samples did not contain free acids other than fatty acids; then, the acid value may be directly converted to percent free fatty acids. Hence, the slight increase in the AV and SN could be associated with the possible deterioration of the studied oils at the moment of producing polyols, such as rancidity. Dileesh et al. reported that the cause for rancidity is the hydrolytic or oxidative cleavage of triglycerides causing the formation of free fatty acids in oils or fats [42]. The same behavior occurred with the values of kinematic viscosity and density, both values are major as expected. In the case of the viscosity, the values for CIP and CSP polyols were 3638.48 and 5748.86 mm^2/s, respectively. The big difference in these values were due to the hydrogen bonding, which was directly proportional to the major amount of OH groups present in the CSP polyol (see OH functionality in Table 2). The obtained results showed a similarity tendency with the results reported by Knothe and Steidly [43]. In this study the authors mentioned that free fatty acids or compounds with hydroxy groups possessed significantly higher viscosity than the starting material without hydroxy groups. Additional proof that the hydrolysis reaction of CIO and CSO had occurred was reflected in the iodine values of their respective polyols. While examining the iodine values for the CIP and CSP polyols and their respective oils, the values decreased dramatically, which was evident since the unsaturation (C=C bonds) in the CIO and CSO oils were replaced by hydroxyl groups.

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Furthermore, we determined the OH functionality, which is an important indicator of the crosslinking that can be obtained in future polyurethane foams. To calculate this parameter, we used the OH number obtained by a procedure described in section 2.5, and the formula proposed by Zlatanić et al. [44].

The OH numbers of the CIP and CSP polyols were 225.0 and 240.8 mg KOH/g, respectively. The theoretical molecular weight (M_w) shown in Table 2 for CIP and CSP polyols (1122,4 and 1166.1 g/mol, respectively) were calculated from the composition of polyols based on assumption that no oligomers were formed and considering that one OH group was formed per double bond. The OH functionality results showed values of 4.50 and 5.00 for CIP and CSP polyols, respectively. It's important to note that these differences between the OH values were due to the fatty composition of the starting oils. According to these values, we can expect the preparation of rigid foams [45]. Rigid polyurethane foams are widely used in engineering applications such as thermal insulation, building materials, chemical pipelines, space filling, among others [46].

Table 2.

Chemical composition and characteristics of *Colliguaja Integerrima* (CIP) and *Colliguaja Salicifolia* (CSP) polyols.

Parameters	**Polyols**	
	CIP	**CSP**
AV [mg KOH/g]	4.50	12.95
IV [g I_2/100 g]	0.2	0.5
SN [mg KOH/g]	227	235
Kinematic Viscosity [mm^2/s]	3638.48	5748.86
Density [g/cm^3]	1.012	0.921
Molar Mass [g/mol]	1122.4	1166.1
OH numbers [mg KOH/g]	225.0	240.8
OH functionality	4.50	5.00

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4. Conclusion

Two novel polyols were successfully synthesized from two non-edible vegetable oils, *Colliguaja Integerrima* and *Colliguaja Salicifolia*, by in situ epoxidation and hydroxylation of oils in a one single step. The physico-chemical and spectroscopic analysis presented above successfully characterized the reaction of polyols formation. Specifically, the FTIR, TGA and NMR spectroscopic results confirmed complete disappearance of the signature of the double bonds present in the vegetable oils and the incorporation of hydroxyl groups to form their respective polyols. In addition, the iodine value, acid value, hydroxyl number, hydroxyl functionality, density and viscosity of the synthesized polyols were also successfully determined. All these values were higher for CIP and CSP polyols when compared to starting oils, with the exception of the iodine value which decreased near to 0. Finally, the data collected in this study have established an essential starting point for the obtention of new materials. Specifically, we plan for a future study to examine the obtention of a new class of rigid polyurethane foams that could be used in engineering applications.

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