Polymerization Studies of Creosote Bush (*Larrea tridentata*) Phenolic Resin with Formaldehyde

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Synopsis

About 25% of the surface area of Mexico is covered by the shrub *Larrea tridentata,* also known as creosote bush. Therefore, an intense study of the shrub as a source of industrial raw materials was started. Presently, we have studied the polymerization of the phenolic resin of *Larrea* with formaldehyde. This polymerization has been carried out in bulk and in aqueous suspension with acid catalysts such as oxalic and hydrochloric acids. The molar ratio of *Larrea* resin/formaldehyde was 1/1, 1/3, and 1/4 at different reaction times. *Larrea* resin and the formaldehyde condensation products were characterized by gel permeation chromatography (GPC), proton nuclear magnetic resonance (NMR), and vapor pressure osmometry (VPO).

INTRODUCTION

Larrea tridentata, also known as creosote bush, is an important component of the Chihuahua, Sonora, and Mojave deserts in North America. *Larrea divaricata,* which is considered conspecific with *Larrea tridentata,* is the dominant shrub in the Monte or central semidesert of Argentina.[1]

Larrea tridentata extracts are known to contain more than 100 chemical compounds that include waxes, volatile compounds, saponins, and phenolic compounds. The phenolic compounds comprise about 90% of the total extract, with lignans and flavonoids listed as the main phenolic components without specifying their relative content ratio.[2] All listed lignans are substituted pyrocatechols such as nordihydroguaiaretic acid (NDGA) and others. A review of the chemical literature has shown that no work has been done on the polymerization of the resin of *Larrea* with formaldehyde although considerable literature has been published regarding phenol–formaldehyde resins in general.[3,4] In this paper we discuss the studies of the polymerization of *Larrea* resin with formaldehyde and the characterization of the products.

EXPERIMENTAL

Materials

Leaves and green twigs from *Larrea* were harvested on the road to Zacatecas at about 20 miles from Saltillo, Coahuila, Mexico. The intact material was extracted with reagent-grade chloroform at its boiling point for about 6 min. The solvent was evaporated under vacuum by means of a rotary evaporator. The resin obtained was kept over night at 70°C under vacuum to free it from any traces of solvent until constant weight was obtained. The softening point of the extracted resin is 60°C. The wax (less than 10% of the resin weight) was isolated and identified by its NMR spectrum.[5]

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Formaldehyde aqueous solution (38% by weight), concentrated hydrochloric acid (37% by weight), and oxalic acid (all reagent grade) were obtained from the Fisher Scientific Co. and were used without further preparation. The NDGA (Fig. 1) was obtained from Burdick and Jackson Laboratories, Inc., Muskegon, Michigan.

Polymerizations

Bulk Polymerization. In a thick-walled tube were placed 5 g (0.014 mole) *Larrea* resin, formaldehyde solution (1.05, 4.2 ml to obtain, respectively, a *Larrea* resin/formaldehyde ratio of 1/1 or 1/4), and 0.05 g (0.00055 mole) oxalic acid. The sealed tube was introduced in a temperature-controlled oil bath at 100 ± 1°C for 8, 24, and 48 hr. Two replicates were run for each experiment. At the end of the specified time, the sealed tubes were opened and the contents were extracted with hot (100°C) reagent-grade dimethylformamide (DMF). Percent of insoluble material and molecular weight of the soluble portion were determined on each sample. Gel permeation chromatography (GPC) was performed on the soluble portion of extracts obtained with boiling GPC-grade tetrahydrofuran.

Suspension Polymerization. In a 250-ml three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and external heating mantle were placed 10.0 g (0.028 mole) *Larrea* resin, 6.3 ml (0.086 mole) of an aqueous formaldehyde solution (38%), 20 ml water, 1 ml methanol, and 0.27 ml 38%

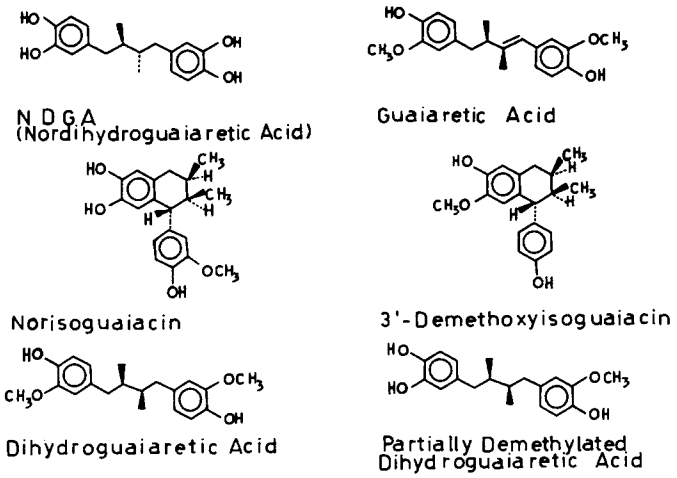

Fig. 1. Lignans from *Larrea tridentata*.

TABLE I
Nuclear Magnetic Resonance Spectrum of NDGA (TMS as Internal Reference)

Position, ppm	Multiplicity	Number of hydrogens	Area ratio[a]	Hydrogen type
0.75	doublet, J = 7 cps	6	1.00	2 aliphatic methyls
1.2–2.8	complex	6	1.00	—CH_2— and —$\underset{|}{C}H$—
6.0–7.0	complex	6	1.00	aromatic
7.4	broad singlet	4	0.66	phenolic O—H

[a] Normalizing the two aliphatic methyls to 1.00.

concentrated hydrochloric acid. The reaction mixture was refluxed, with constant stirring, for 2.3 hr. During this time the resin (insoluble in the reaction medium) becomes more viscous. At the end of the specified time, the reaction mixture is cooled down to room temperature and the polymerized resin is washed thoroughly with water and then dissolved in 40 ml isopropyl alcohol. The solution is poured slowly and with constant stirring into 2 liters ice water acidulated to pH 3 with hydrochloric acid. The light-tan precipitate is filtered, washed with water until all the acid is removed, and then dried under vacuum in the presence of phosphorous pentoxide to remove any traces of water. Softening point is 100°C.

Equipment and Test Methods

The gel permeation chromatography (GPC) measurements were performed on a Waters Model 200 under the following conditions: column combination, 60, 60, 100, 200, 500, 1000 Å; solvent, tetrahydrofuran with 250 ppm BHT (2,6-di-*t*-butyl-4-methylphenol), flow rate, 1 ml/min; temperature, 40°C; input solution concentration, 10 mg/ml; injection time, 2 min. The calibration was performed by use of NDGA. The elution volume is given in counts, each count corresponding to 5 ml. The proton nuclear magnetic resonance (NMR) spectra were taken in a Varian EM-360 spectrometer with 0.5% tetramethylsilane as internal reference and acetone-d_6 as the solvent. Number-average molecular weights were determined by vapor pressure osmometry (VPO) in a Hewlett–Packard apparatus Model 302B. The calibration standard was NDGA and the solvent was reagent-grade dimethylformamide at 75°C for all samples. The infrared spectra were taken in a Perkin–Elmer infrared spectrophotometer Model 297 by means of the KBr pellet technique and using polystyrene as the calibration standard.

RESULTS AND DISCUSSION

It has been reported that lignans and flavonoids are the two main types of phenolic compounds present in the *Larrea* resin. Their chemical structures have been elucidated although their weight ratio was not reported.[2] Figure 1 shows the chemical structures of the reported lignans. *Larrea* resin is soluble in aqueous sodium hydroxide but insoluble in water or in aqueous sodium bicarbonate. Its

TABLE II
Nuclear Magnetic Resonance Spectrum of *Larrea* Resin (TMS as Internal Reference)

Position, ppm	Multiplicity	Area ratio[a]	Number of hydrogens[b]	Hydrogen type
0.75	complex	1.00	6	2 aliphatic methyls
1.27	singlet	—	—	wax (methylenes)[c]
1.2–2.8	complex	1.00	6	$-CH_2-$ and $-\underset{\vert}{C}H-$
3.3–3.9	complex	0.66	3.6	1.2 aromatic methoxyls
6.0–7.3	complex	1.00	6	aromatic
7.3–8.3	broad	0.53	3.2	phenolic (—OH)[d]

[a] Normalizing the aliphatic methyl area to 1.00.
[b] Assuming an average of two methyl groups per mole.
[c] After Seigler et. al.[5]
[d] Active hydrogens exchanged by deuterium (by deuterium oxide treatment).

infrared spectrum has a strong and broad band centered at 3400 cm^{-1} (O–H stretching vibration for phenols) and a band at 3025 cm^{-1} (aromatic C–H stretching vibration).[6] *Larrea* resin has a number-average molecular weight of 352 and contains 10% or less of wax which is insoluble in aqueous sodium hydroxide and presents an ester infrared absorption band at 1735 cm^{-1}. This wax was identified by its NMR spectrum.[5] The wax is reported to be a mix of high molecular weight aliphatic monoesters (C_{46}–C_{56}) of a number-average molecular weight of about 757 obtained by mass spectrometry.[2]

Tables I and II show that there is a close analogy between the NMR spectra of NDGA and *Larrea* resin. Therefore, based on the data presented we conclude that *Larrea* resin is composed mainly of lignans although the presence of relatively small amounts of flavonoids is not discarded.

Further fractionation and compound isolation and identification for *Larrea* resin has shown that lignans are its major components.[7]

Considering the phenolic composition of *Larrea* resin, a polymerization study with formaldehyde was undertaken. Table III shows the results of the bulk polymerization of *Larrea* resin with formaldehyde at three different molar ratios. It is interesting that the molecular weight of the soluble portion of the polymer being formed is relatively low for all cases studied when we consider that the parent monomer (*Larrea* resin) has a number-average molecular weight of 352 g/mole. Additionally, the M_n values of the polymers of Table III do not represent the upper limit found until now because values of M_n as high as 1068 have been encountered (Table IV). From Table III we conclude that the mentioned polymers become insoluble at a relatively low degree of polymerization, presumably due to crosslinking. This is consistent with the chemical structures shown in

TABLE III
Molecular Weights and Percent Insoluble Material Obtained During the Bulk Polymerization of *Larrea* Resin Catalyzed by Oxalic Acid (100°C)

Sample	*Larrea* resin/formaldehyde mole ratio	Reaction time, hr	% Insoluble	M_n of soluble polymer
A	1/1	8	22	640
B	1/1	24	28	600
C	1/2	8	37	710
D	1/2	24	61	880
E	1/4	8	18	610
F	1/4	24	71	640

TABLE IV
Acid-Catalyzed Suspension Polymerization of *Larrea* Resin. Relationship Between the Number-Average Molecular Weight and Reaction Time

Reaction time, hr	M_n
0	352
0.18	498
1.25	660
2.25	668
2.25	701
8.00	727 (soluble portion)
14.00	1068 (soluble portion)

Figure 1 which have more than two possible reactive sites per molecule, thus favoring crosslinking during the condensation with formaldehyde.

Selected samples from Table III and from other key experiments were characterized by GPC. The chromatograms are shown in Figures 2, 3, and 4. It can be seen that for each *Larrea* resin/formaldehyde molar ratio the main peak of *Larrea* resin centered at about 40.4 counts decreases to give place to a new set of peaks between approximately 32 to 39 counts which have been assigned to the polymerization products of *Larrea* resin. Additionally, *Larrea* resin has a small peak centered at about 37.5 counts. This peak could be assigned to the wax mentioned earlier which has a number-average molecular weight of 757.

The aqueous suspension polymerization of *Larrea* resin with formaldehyde was also studied. Table IV shows the relationship between the number-average molecular weight of the polymer obtained and the reaction time to form this

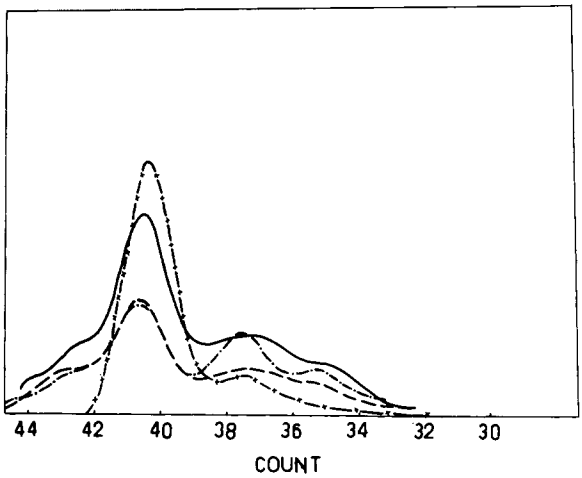

Fig. 2. GPC chromatograms of the soluble polymer from a *Larrea* resin/formaldehyde 1/1 molar ratio composition at 100°C and at different reaction times with oxalic acid as the catalyst: (-x-) *Larrea* resin; (—) 8 hr; (- - -) 24 hr; (-·-) 48 hr.

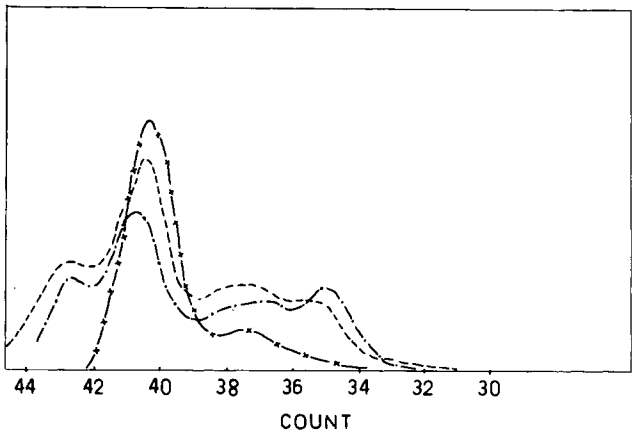

Fig. 3. GPC chromatograms of the soluble polymer from a *Larrea* resin/formaldehyde 1/2 molar ratio composition at 100°C and at different reaction times with oxalic acid as the catalyst: (-x-) *Larrea* resin; (- - -) 24 hr; (-·-) 48 hr.

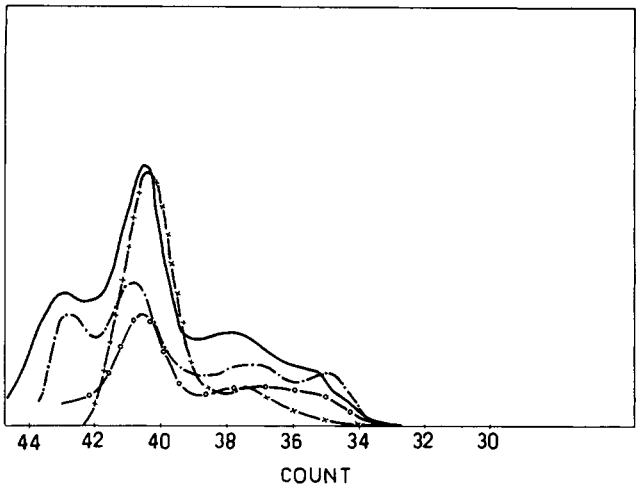

Fig. 4. GPC chromatograms of the soluble polymer from a *Larrea* resin/formaldehyde 1/4 molar ratio composition at 100°C and at different reaction times with oxalic acid as the catalyst: (-x-) *Larrea* resin; (-o-) 8 hr; (—) 24 hr; (-·-) 48 hr.

polymer. The *Larrea* resin/formaldehyde molar ratio was 1/3 with hydrochloric acid as the catalyst. From Table IV we can see that under the reaction conditions used there is a moment in which the M_n levels off at a value close to 700 at about 2.25 hr of reaction time. The polymer formed is totally soluble until a reaction time of 8 hr or higher is reached after which a considerable amount of insoluble product appears (above 15%).

An NMR spectroscopic characterization was done for the polymers mentioned in Table IV. Table V shows the main physical and NMR data for the totally soluble polymer of M_n of 668. NDGA was used as comparison reference. The introduction of methylene bridges by formaldehyde is evident from these data.

TABLE V
Larrea Resin and its Formaldehyde Condensation Polymer. Main Physical and NMR Data as Compared with NDGA

	Larrea resin	Polymer	NDGA
Number-average molecular weight	352	668	302
—OCH_3/mole[a]	1.3	2.6	0
Aromatic hydrogens (AH)[a]	6.0	8.6	6
Active hydrogens[b]	3.2	6.4	4
Methylene bridges[a,c]	0	0.9	0
Total substitution (TS)[d]	4.5	10.8	4
AH + TS	10.5	19.4	10

[a] By NMR spectroscopy.

[b] They were exchanged by deuterium by D_2O treatment.

[c] Introduced by reaction with formaldehyde. Signal centered at 3.70 ppm. In comparison, methylene signal of diphenylmethane occurs at 3.92 ppm.

[d] The sum of the measured amounts of methoxyl groups, active hydrogens, and methylene bridges.

CONCLUSIONS

Resin of *Larrea* and formaldehyde can be polymerized in bulk or in suspension to obtain phenolic-type resins that may find use in applications of the typical phenolic resins. These possible applications are at present under intensive study.

The VPO molecular weights were determined by F. Muñoz, and J. L. Angulo obtained the GP chromatograms.

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