PN ABD-577

8.051

PROGRESS REPORT

Title: Utilization of Hydrocarbon Producing Plants Native in Arid Areas.
Project N°: 936-5542
Grant N°: DPE-5542-G-SS-8029-00
Project Office: S & T/EY
Project Officer: Alberto Sabadell
Principal Investigator: Sara Gnecco
Period of report: October, 1, 1988 to March, 30, 1989.

1. Preparation of main components of plant extracts.

a. Collection of vegetal material

Fresh plants could not be collected, because when this project started, the suitable season for collecting was over. Therefore, for obtaining the main components, we worked with CH_2Cl_2 extracts, previously obtained, from the following species: Euphorbia lactiflua, Euphorbia copiapina, Colliguaja odorifera and Colliguaja salicifolia.

Samples of latex from Euphorbia lactiflua were collected by tapping wild plants (November, 1988) in Copiapó (III Region, Chile).

b. Fractionation and analysis.

CH_2Cl_2 extracts from the above species were fractionated with acetone to obtain acetone-soluble and acetone-insoluble fractions (1,2). The yield of each fraction was determined gravimetrically, after complete removal of solvent, and is given in percent of dry weight (Table 1). Representative fractions were characterized by quantitative analysis, infrared spectroscopy (IR, Perkin Elmer 757), carbon-13 and proton nuclear magnetic resonance spectroscopy (^{13}C NMR, Varian CFT-20 and ^{1}H NMR, Varian T-60-A). $CDCl_3$ or C_6D_6 were the solvents and TMS the internal standard for both NMR spectra.

Analysis of CH_2Cl_2 extracts from different species by IR, ^{13}C and ^{1}H NMR showed that the main components were cis-1,4-polyisoprene (natural rubber) and waxes (1,2). In ^{13}C NMR spectra the chemical shifts for cis-1,4-polyisoprene in parts per million (ppm) were: 23,6 (methyl carbon); 27,0 and 32,6 (cis-methylene carbons); 125,3 and 135,5 (olefinic carbons). In ^{1}H NMR spectra the respective resonances in ppm were: 1,2 (methyl hydrogens); 2,0 and 2,1 (cis-methylene hydrogens) and 5,2 (olefinic hydrogen (3). Chemical shifts at 29,7 ppm in ^{13}C NMR spectra and at 1,2 ppm in ^{1}H NMR spectra were assigned to methylene groups in waxes (4). This was corroborated in the IR spectra which revealed a sharp, medium intensity, absorption peak at 720 cm^{-1}, typical of $(CH_2)_n$ (n>4) rocking (5). In the corresponding IR, ^{13}C and ^{1}H NMR spectra of acetone-insoluble fractions of these species, the intensity of the above signals were enhanced, and the relative intensity of lines or peaks

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arising from resonances or vibrations of >C=O, -OH and >C-O groups was diminished. The inverse was true for acetone-soluble fractions.

The molar ratio C/H for representative fractions was calculated from quantitative analysis data and are given in Table 1. The lower values for acetone-insoluble fractions reflect higher hydrocarbon contents. (6). Extractions and determinations were repeated at least twice for each plant species.

TABLE 1

Yield and Molar Ratio C/H of Representative Fractions from some Chilean Euphorbiaceae species; Polymeric Hydrocarbon Type in these species.

Species	CH_2Cl_2 extract		Acetone-insoluble fraction		Polymeric hydrocarbon type[c]
	yield[a]	C/H ratio[b]	Yield[a]	C/H ratio[b]	
E. lactiflua	10.80	0.52	2.90	0.48	NR, waxes
E. copiapina	11.70	0.57	3.10	0.51	NR[d], waxes
C. odorifera	4.50	0.54	2.20	0.48	NR[d], waxes
C. salicifolia	5.30	0.55	1.60	0.49	NR, waxes

a. given as a percentage of plant dry weight; average value of extracts from 2 ó 3 plant samples.

b. C/H molar ratio calculated from quantitative analysis data.

c. NR = natural rubber (cis-1,4-polyisoprene) identified by spectroscopic data.

d. Traces

c. Isolation and characterization of n-paraffins, rubber and resins.

c.1. n-paraffins

Acetone-insoluble fractions were refluxed in a suspension of activated carbon, Johns-Manville celite (1 g each w/w) and hexane (200 ml), filtered and dried to obtain the fractions of refined hydrocarbons (7). The yield of each fraction was determined gravimetrically, after complete removal of solvent, and is given in percent of plant dry weight (Table 2).

Refined hydrocarbons fractions were analyzed by IR, ^1H NMR, ^{13}C NMR, and GC.

NMR and IR spectra of refined hydrocarbons from different species revealed almost exclusively the presence of n-paraffins. The ^{13}C NMR spectra showed chemical shifts at 14.07, 29.7 and 31.95 ppm, corresponding to a straight chain saturated hydrocarbon $CH_3(CH_2)_n-CH_3$, with $n>5$(3). The IR spectra showed the peaks arising from Csp^3-H vibrations and rocking from $(CH_2)_n$, $n>4$.

The identification of hydrocarbons was carried out by the comparison of RR_t data with those of authentic standards. The results revealed the presence of n-alkanes mixtures of chain lenghts varying from n-nonadecane ($n-C_{19}$) to n-tritriacontane ($n-C_{33}$); n-heptaeicosane ($n-C_{27}$), n-nonaeicosane ($n-C_{29}$) and n-hentriacontane ($n-C_{31}$) were the dominant alkasanes. The quantitative results are given in Table 2; they were obtained by measurement of peak areas and are expressed as a percentage of the sum of the peak areas of all compounds lying between $n-C_{19}$ and $n-C_{33}$. Our GC analysis revealed some minor peaks between those representing the n-alkanes which might be due to branched, saturated hydrocarbons. However, they occurred in amounts too small to allow reliable determination.

c.2. Rubber

c.2.1. From acetone-insoluble fractions

The acetone insoluble fraction from E.lactiflua was dissolved in CH_2Cl_2. The solution was treated with CH_3OH, and the resulting precipitate washed with acetone. The precipitate was treated twice in the same way: dissolved in CH_2Cl_2, reprecipitated with CH_3OH and washed with acetone. The final precipitate (rubber) was characterized by IR and ^{13}C NMR spectroscopy. The yield was 1.3% on dry weight basis. Spectral analysis revealed slight contamination with polymethylene compounds. Samples are now being treated in order to eliminate the contamination.

c.2.2. From latex

Fresh latex from E.lactiflua was mixed with C_2Cl_4. After removing the azeotrope, the solid was dried at 50°C for 12 hours. The yield of dry latex was 53.5% (w/w) of the fresh latex.

Dry latex was treated with CH_2Cl_2, CH_3OH and acetone, in the same way that the acetone-insoluble fraction (section c.2.1). The final precipitate was dried in a vacuum oven at 50°C for 2 hours and weighed. The yield was 4.2% in dry latex weight basis. The characterization was done by IR; NMR spectroscopy (^{13}C and ^1H) and TLC. All the data obtained agreed with those given in literature for cis-1,4-polyisoprene.

TABLE 2.- Yield and Molar Ratio C/H of refined hydrocarbons fractions from some chilean Euphorbiaceae species. N-alkanes found in these fractions.

Species	Ref.Hydroc. yield[a]	C/H ratio[b]	Composition (%)[c]								
			C_{21}	C_{23}	C_{25}	C_{27}	C_{29}	C_{30}	C_{31}	C_{32}	others
E.lactiflua	1.8	0.45	11	2	6	26	4	1	-	-	C_{19} = 22 C_{20}=20
E.copiapina	1.1	0.44	-	-	1	1	7	1	85	1	C_{19} = 2
C.odorifera	1.4	0.45	-	-	-	58	41	-	-	-	-
C. salicifolia	1.3	0.44	-	-	-	98	-	-	-	-	-

a: Percent on dry plant weight basis

b: C/H molar ratio calculated from quantitative analysis data

c: Percent obtained by measurement of peak areas, expressed as a percentage of the sum of the peak areas of all compounds lying between n-C_{19} and n-C_{33}. Compounds detected in percentage less than 1% are not given.

c.3 Resins

Acetone-soluble fractions from CH_2Cl_2 extracts and dry latex were fractionated with CH_2Cl_2 and MeOH. These fractions are now being analyzed.

2.- Preparation and characterization of catalysts

a. Preparation and activation

A series of HNaY, Pt NaY and PtHNaY zeolites were prepared by partial sodium exchange of a Y type sodium zeolite (Linde SK-40) with ammonium and/or platinium ions. The zeolite, faujasite type, NaY with a 2.4 Si:Al ratio and a formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{36}] \cdot 240\ H_2O$ was used

a_1. H(40) NaY and H (64) NaY

H(40) NaY was prepared by ionic exchange at 30°C for 6 hours, using a solution 1.3 M of ammonium acetate. The degree of exchange was determinated by atomic absortion sodium analysis in the filtrate. The solid obtained was dried at 110°C for 12 hours. For H(64) NaY the procedure was repeated 2 times.

The quantitative results are given in Table 3. The degree of the NH_4^+ exchanged (equivalents of Na^+ in the filtrate) are indicated in parenthesis. Both catalysts were activated in N_2 atmosphere for 8 hours at 480°C. Previously it was determinated that dehydration, deamination and dehydroxilation take place at 110°C, 250°C and 480°C respectively (8).

a_2. Pt (0.5) NaY

Pt(0.5) NaY was obtained by ionic exchange of the NaY zeolite with an aqueous solution of $Pt(NH_3)_4\ Cl_2$ at 25°C. The exchanged zeolite was filtrated, washed and dried at 110°C for 12 hours. The Na^+ removed was analyzed by atomic absorption in the filtrate. (9). The weight percentage of platinium exchanged is indicated in parenthesis (Table 3)

The dried solid was heated at 300°C in air flow for 3 hours, and then reduced by H_2 at 530°C for 2 hours (10).

a_3. Pt(2.0) H (40)-NaY

Pt (2.0) H(40)-NaY was obtained first by ionic exchange of sodium with ammonium ion as in a.1 for H(40)NaY. After drying at 110°C, the solid was treated with $[Pt(NH_3)_4]Cl_2$ solution as in a.2 for Pt(0.5)NaY. Drying, activation and reduction were performed as in a.2. The degree of ionic exchange in each step was determined as in a.1 and a.2 respectively. Quantitative results are given in Table 3.

TABLE 3

Characteristics of the prepared of Zeolites and ZSM-5

Preparation Method	Degree of ionic exchange	Solid Denomination	Crystallinity	$S_{BET}(m^2g^{-1})$
I.E.	40% NH_4^+	H(40)-NaY	Yes	726
I.E.	64% NH_4^+	H(64)-NaY	Yes	713
I.E.	0.5 weight % Pt	Pt(0.5)-NaY	Yes	680
I.E.	40 NH_4^+; 2.0 weight % Pt	Pt(2.0)H(40)-NaY	Yes	638
Mobil Method*	-	ZSM-5	Yes	351

I.E. = ionic exchange

* ZSM-5 Catalyst was provided by Mobil Co.

b. Characterization

b.1 Crystallinity

The crystallinity of the activated zeolites was determined by X-ray diffraction using the powder method (11). The diffraction lines of the (331), (533) and (751) planes, characteristics of the NaY faujasite, were considered. The results indicated that the prepared catalysts kept their crystallinity (Table 3).

b.2. Specific areas

The specific areas of the prepared zeolites were determined by the absorption method of N_2 on the activated and degasificated samples. These analysis were performed in a volumetric BET conventional equipment at - 196°C (12). The value of 16.0 $(A°)^2$ was used as the cross sectional area of the N_2 molecule. The mass of dried sample was about 0.3 g in all the measurements. Results are given in Table 3.

The number of acid centers and their relative strengths are now being determined.

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Future Workplans

The analysis of the resins and the determination of the number of acid centers of prepared catalysts, and their relative strenghts, will be finished in April. Then, we will start with the calorimetric studies of the termochemical transformations, utilizing Differential Scanning Calorimetry (DSC).

Dr. Cid is preparing a new series of catalysts, faujasite-type MNaY (M= Ni, Co, Mo), not included in the original proposal . Therefore, we think we will be able to get more results that the previously proposed.

Now, we are waiting the final decision of AID about the purchase of a new Thermogravimetric Analyzer, before planning the trip of Dr. Gnecco to the Western Regional Research Center.

S. G.

Dr. Sara Gnecco
Principal Investigator

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FINANCIAL REPORT

Project N°936-5542
Grant N°DPE-5542-G-55-8029-00
Project Office S &T/EY
Obligation N°8361291

Federal funds authorized : US$30,500
Payment procedure: "Payment-Cost Reinbursement"
Internal Code: Project 20.10.08
Project Officer: Alberto Sabadell
Principal Investigator: Dr. Sara Gnecco
Period of report: October, 1, 1988 to January, 31, 1989
Exchange rate for local costs: US$1.00 = $250 (Chilean pesos)

Cash disbursements

Salaries

- Technician (Mrs.Caamaño) US$200 month x 4 months	US$800.00
- Part time secretary (Mrs.Sanhueza) US$1.50 hour x 47 hours.	US$ 70.00
Salaries total	US$870.00.-

Materials and supplies

- Platinum tetraamino dichloride x 1 g.	US$112.60.-
- Amonio heptamolibdato x 250 g.	US$ 70.45
- Cobalto (II) nitrato p.a. x 100 g.	US$ 40.05
- Niquel (II) nitrato p.a. x 250 g.	US$ 28.54
- Mixer with stand, double clamp.holder and rod	US$ 1030.50
Mat. & supplies total	US$ 1282.14

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Salaries total	US$ 870.00
Mat. & Supp.total	US$1282.14
Total	US$2152.14

Copies of documents were enclosed.

S. G.

Dr. Sara Gnecco D.
Principal Investigator

Marcelo Molina
Technical Assistance
Research Office

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FINANCIAL REPORT

Project N°936-5542
Grant N°DPE-5542-G-55-8029-00
Project Office S &T/EY
Obligation N°8361291

Federal funds authorized : US$30,500
Payment procedure: "Payment-Cost Reinbursement"
Internal Code: (Research Office, U. of Concepción): Project 20.10.08
Project Officer: Alberto Sabadell
Principal Investigator: Dr. Sara Gnecco
Period of report: February, 1, to March 30, 1989
Exchange rate for local costs: US$1.00 = $250 (Chilean pesos)

Cash disbursements

Salaries

- Technician (Mrs. Caamaño) US$200/mont x 2 month	US$ 400.-
- Graduate Student (Mrs. María Parra) US$ 200/month x 1 month	US$ 200
Salaries total	US$ 600.-

Materials and supplies

- Custom taxes and added value taxes for importation of Platinum Tetraamino Dichloride US$ 38.47

Salaries total	US$600.-
Mat & Supp. total	US$ 38.47
TOTAL	US$638.47

Copies of documents were enclosed

Comment:

We have not done any other expenses, because we are waiting the final decision of AID for additional funding to purchase a New Perkin Elmer Thermogravimetric Analyzer.

S. Gnecco

Dr. Sara Gnecco D.
Principal Investigator

Marcelo Molina
Technical Assistant
Research Office