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LATEXES FROM *EUPHORBIA CADUCIFOLIA* - ISOLATION AND CHARACTERISATION OF RUBBER HYDROCARBON. *PART - I*

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Latex was collected by incising the stem of *E.caducifolia* plant which contains 26.90 - 28.60% solid material. The chemical composition of solid material shows resinous mass 68.30 - 72.70%, where as rubber hydrocarbon is around 6.20 - 7.60 and inorganic matters lie in the range 19.00 - 22.90% and 1.50 - 1.90%, respectively. The rubber hydrocarbon was characterised by different chemical and instrumental methods. Iodine value of hydrocarbon (310.91 - 350.80%) percentage of unsaturation (83.40 - 94.10%), elemental analysis (C = 87.48 - 88.04%, H = 11.20 - 11.82%), solubility, IR spectrum (840 cm^{-1}), ^{1}H-NMR spectrum (olefinic proton at 5.15 - 5.20%), ^{13}C-NMR spectrum (olefinic region 120 - 140 ppm), molecular weight (15275 - 88405), the value of T_g (- 63.02 - 60.81°C), refractive index (1.49200 to 1.49325) and specific gravity (0.93102 to 0.93628) identify rubber hydrocarbon as polyisoprene. The material is sticky and poor in strength and burning gives a smoky flame.

Key words: Latex, *Euphorbia caducifolia*, Hydrocarbon, ^{13}C-NMR spectrum.

Introduction

The chief source of natural rubber is the milky latex obtained by secretion from the bark of certain type of plants like *Hevea*, *Manihot giaziievii*, *Castillea elastica*, *Ficus elastica*, *Landolphia*, *Euphorbia* etc. One of the plant *Euphorbia* has been found in the lower region of Sindh, Pakistan. It is a widely grown plant abounding in a milky latex, a source of rubber. Until the synthetic material became reality, rubber had been obtained only from such plants/trees.

Euphorbia is a tropical and warm temperature genus of the world mainly grown in dry places and resemble with *Cacti* in appearance but are distinguished from others by the presence of milky latex. About 68 species, including few exotics are found in India (Sastri 1953). Giner *et al* (2000) have studied nonpolar components in the latex of *Euphorbia peplus*. In Pakistan, a large number of latex producing species occur but potentially tappable are *Euphorbia neriifolia* Linn, *Euphorbia nivulia* Bush Ham, *E. royleane* Hosia, *E. caducifolia*, *E. antiguorum* etc. But *E. caducifolia* rather is the only wild tree among the tall shrubby species of this genus in southern Pakistan. Some biological activity of latex of *Euphorbia sp* were also studied (de Vasconcellos and de Amorim 2003) It is a tall, armed, dense and stout bush with thick cylindrical leafless green branches. Leaves, when present are ovate or broadly elliptic. *E.caducifolia* grows abundantly. On rocky and sandy grounds from Karachi to Jungshahi and Hyderabad. Coagulated latex of this plant contains terpene, resins, rubber hydrocarbon and proteins alongwith inorganic matter.

The present work deals with the isolation and characterisation of rubber hydrocarbon from *E. caducifolia* latex.

Experimental

The latex of the plant was collected by incising the stem of the plant in sterilized bottles already containing preservative like formaline solution ammonia or acetone (Mc Gavack 1959). The preservation made by first two methods did not show any deterioration even after month whilst in acetone coagulation takes place within 2-3 days. Ammonia was finally chosen for preservation of latex. It makes the system alkaline which prevents putrefaction. Ammonia not only makes the system alkaline but also hydrolyzes the fatty acids esters, naturally occuring in the latex and form soaps. These soaps act as stabilizer.

The latexes were first strained to remove dirt, diluted with water (20%) and then coagulated with 2% formic acid. After filteration, the coagulated material was vaccum dried. It was first soxhelated with acetone for 14 to 15 h to remove resin contents of the latex and the soxhelated with hexane for 13 h to separate rubber hydrocarbons. Residual portions were estimated for proteins and inorganic material. Solid contents of the latexes were determined by heating at 105°C to a constant weight. Results of various estimates are shown in respective Tables.

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Table 1
Composition of various constituents of latexes obtained from *Euphorbia caducifolia*

Sample	pH	Coagd mass	Solid content	Compostion of coagulated mass			
				Resin	Rubber	Protein	Inorg. matter
		(g)	%	%	Hyc	%	%
R1	6.9-7.0	700	28.60	72.70	6.50	19.00	1.80
R2	6.9-7.0	330	27.20	68.90	6.90	22.50	1.70
R3	6.9-7.0	285	26.90	69.10	6.20	22.50	1.90
R4	6.9-7.0	338	27.40	68.30	7.60	22.60	1.50
R5	6.9-7.0	340	27.10	68.60	7.20	22.70	1.50
R6	6.9-7.0	255	27.20	68.50	6.90	22.90	1.70
R7	6.9-7.0	350	28.00	68.90	6.80	22.70	1.60
R8	6.9-7.0	350	28.00	69.60	6.60	22.10	1.70
R9	6.9-7.0	202	28.20	72.10	6.90	19.20	1.80
R10	6.9-7.0	128	27.90	69.50	6.60	22.30	1.60
Literature value			27.65	69.62	6.82	21.85	1.68

Characterization of rubber hydrogen of latex. All samples of rubber hydrocarbon were softened at room temperature. Rubber hydrocarbons were characterised by determining unsaturation, elemental analysis, solubility, molecular weight, refractive index etc. Instrumental techniques like IR, NMR, DSC, GPC were also used for this purpose.

Iodine value was determined by Wij's method (Kemp 1927). Elemental analysis were carried out on Carto Erba Mod.1106 analyser. Molecular weight (M) was determined by measuring viscosities of dilute solutions at 30°C using an Ostwald type viscometer. Molecular weight was calculated by following relation, (Carter and Magat 1946; Scott *et al* 1949; Marks 1989).

$$[\eta] = 5.02 \times 10^{-4} M^{-0.667}$$

The intercept of the plot η_{sp} Vs C determined the value of intrinsic viscosity $[\eta]$ in dl/g, where η_{sp} is the specific viscosity and C is the concentration of solution.

Results and Discussion

Table 1 includes composition of various constituents of latex obtained form *Euphorbia caducifolia*. These results indicate that solid content obtained was found in the range 26.90 - 28.60%. The chemical composition of the solid content shows resinous mass as 68.30 - 72.70%, whereas rubber hydrocarbon is around 6.20 - 7.60%. The proteins and inorganic matters lie in the range 19.00 - 22.90% and 1.50 - 1.90%, respectively. It shows that the latex contain major quantity of resinous material and rubber contains are low. Besides, the proteinous material is also higher 19.00 - 22.90% than rubber hydrocarbon which causes putrefaction, if preservative is not added at the time of collection of latexes. pH of the latexes at the time of tapping was found to be 6.90 - 7.00% whilst on standing in open air it becomes 5.45% resulting in spontaneous coagulation. The dropping of pH from neutral to acidic is the action of lactic acid bacteria. Latex particles carry negative electronic charges and coagulation usually occurs when the pH reaches about 4.50 - 4.20%. The charged particles repel each other but below to the iso-electric charge approaches zero and coagulation takes place. To prevent coagulaion of latex at the time of collection, the pH may be increased from 6.90 to 11.00 by the addition of ammonia which not only enhance the pH of system but also hydrolyse the fatty acid esters and form soaps. These soaps act as stabilizing bodies.

Table 2
Iodine values and % unsturation of rubber hydrocarbon obtained from the latexes of *E. caducifolia* at 25°C (Reaction time one hour)

Sample no.	Iodine value	Unsaturation (%)
R1	313.33	84.05
R2	350.80	94.10
R3	310.91	83.40
R4	336.28	90.20
R5	349.80	83.83
R6	348.98	93.61
R7	250.00	93.88
R8	349.90	93.86
R9	348.00	86.80
R10	323.59	86.80
Literature value	350.90	94.12

The rubber hydrocarbon was characterised by different chemical and instrumental methods. These studies reveal the following findings:

Iodine value of rubber hydrocarbon. Rubber hydrocarbon extracted with toluene/hexane from the latexes of *E. caducifolia*, was characterised from extent of unsaturation by determination of iodine value of ten samples of rubber hydrocarbon which are summarized in Table 2. Iodine value of these hydrocarbon samples were determined which lies in the range 313.33 - 350.80%. Percentage of unsaturation has been calculated from the iodine value of rubber hydrocarbon which were found to be 83.40 - 94.10%. The determined value of unsaturation is in the vicinity of literature value for poly-isoprene as 94.12% (Kemp 1927; Kemp and Mueller 1934).

Element analysis. The elemental analysis of 10 samples of rubber hydrocarbon alongwith standard sample of natural rubber were accomplished. The results are summarized in Table 3. The analysis of standard sample shows its composition as

Table 3
Elemental analysis of rubber hydrocarbon obtained from the latexes of *E. caducifolia*

Sample no.	%C	%H
Standard sample	88.02	11.75
R1	87.50	11.82
R2	88.01	11.20
R3	88.40	11.25
R4	87.92	11.80
R5	88.00	11.50
R6	87.90	11.85
R7	87.45	11.83
R8	87.90	11.82
R9	87.60	11.70
R10	87.90	11.80

C = 88.02% and H = 11.75%, whereas the composition of 10 rubber hydrocarbon samples inidicates the composition as C = 87.45 - 88.40% and H = 11.20 - 11.85%. Furthermore, the sample were also tested for oxygen and halogens. It shows that the samples do not contain either oxygen or halogens. The absence of oxygen and halogens indicates that these samples do not contain protein and other carboxyl and hydroxyl containing materials and are therefore, simple. They are simply hydrocarbons. By comparing the composition of standard samples of natural rubber with the samples of rubber hydrocarbon, it is suggested that the chemical nature of both samples is same. Hence, rubber hydrocarbon extracted from *E. caducifolia* may be natural rubber containing 5 carbon and 8 hydrogen units (C_5-H_8).

Solubility. It is an important tool which helps in the identification of elastomers and polymeric materials. Unvulcanized samples of rubber hydrocarbon (masticated) get dissolved in all the solvents of natural rubber like benzene, toluene, xylene, hexane, cyclohexanone ether, carbon tetrachloride and carbon disulfide. On the other hand, vulcanized samples were found insoluble in these solvents and swollen in some solvents bearing the solvent uptake (>100%) like cyclohexanone (15%), CS_2 (800%), $CC1_4$ (1810%), benzene (1967%), ether (252%) and mineral oil (145%). The samples of rubber hydrocarbons show little solvent uptake in water (17%), butyl alcohol (24%), MEK (57%), chloroform (45%), acetone (22%) etc. These observations support the assumptions and the rubber hydrocarbon extracted from the latexes of *E. caducifolia* is polyisoprene.

Infrared examination. IR spectra of standard sample of natural rubber (from *Hevea*) and rubber hydrocarbon were examined and shown in Table 4. In this spectrum for *Hevea* (*cis*-1,4), the CH stretching modes are found in the 3000 cm^{-1} region and methylene (CH, CH_2-) and methyl (CH_3-) bands fall at about 1450 and 1380 cm^{-1}, respectively. On the other hand, the spectra due to rubber hydrocarbon obtained from *E. caducifolia* show C-H stretching vibration at about 2900 or 2950 cm^{-1} and methylene and methyl absorption bands lie respectively at about 1440 or 1435 and 1370 cm^{-1}. In the region between 700 and 990 cm^{-1}, the *cis*-1,4 (*Hevea*) shows single medium strong band at about 840 cm^{-1}, whereas, in the spectra due to rubber hydrocarbon, a strong broad band lies at about 840 or 820-680 cm^{-1}. These bands speculated the material is *cis*-1,4 rubber hydrocarbon -C(CH_3)=CH-. Furthermore, the absorption bands in the spectra of both hydrocarbon obtained from *Havea* and *E. caducifolia* fall at 1650 and 1640, 1650 or 1675 cm^{-1} respectively, indicating the characteristic C=C stretching vibration. The broad band (820 - 680 cm^{-1}) might be due to impurities present in the sample of rubber hydrocarbon

Table 4
Infrared studies of the rubber hydrocarbon *Euphorbia caducifolia*

	C-H stretch (cm^{-1})	C=C strectch (cm^{-1})	C-H, CH_2 C-H_3 bands (cm^{-1})	C-H band specifically (cm^{-1})	CH_2 and C-C C-H bands (cm^{-1})	C-H band -C(CH_3) = CH (*cis* 1,4) (cm^{-1})
Heyea 1	3000	1650	1450	1380 - 1370	1130, 1325,1070,935	840
E. cad 1	2950	1660	1440	1370	1300, 1240, 1040, 1080, 1120	830
E. cad 3	2900	1660	1440	1370	1300, 1120, 1080, 1030	840
E. cad 4	2950	1660	1440	1380	1350, 1120, 1090, 1020	840
E. cad 5	2900	1650	1440	1375	1300, 1090, 1000	840-645
E. cad 6	2900	1640	1435	1360	1290, 1110, 1080, 1000	820-645
E. cad 7	2900	1650	1440	1375	1300, 1110, 1090, 1020	840-660
E. cad 8	2900	1660	1440	1375	1300, 1130, 1110, 1020	840-650
E. cad 9	2950	1675	1440	1350	1300, 1080, 980	820-680

Table 5
Intrinsic viscosity [η] and molecular weight of rubber hydrocarbon

Sample No.	[η]dl/g	Molecular weight (M)
R1	1.00	88405
R2	0.66	48980
R3	0.90	75490
R4	0.83	66860
R5	0.67	48500
R6	0.33	16773
R7	0.31	15275
R8	0.35	18320
R9	0.31	15275
R10	0.91	76750

from *E. caducifolia.* Dobholkar *et al* (1991) separated rubber hydrocarbon from *E. nivulia* and reported a broad and intense absorption bands at 838 - 840 and 1130 cm^{-1} respectively which identifies the material to be (*cis*-1,4) polyisoprene. IR examiantion of various polyisoprene and identified (*cis*-1,4) polyisoprene at 840 cm^{-1}. Hence, in the light of these findings, it can be safely assumed that the rubber hydrocarbon obtained from *E.caducifolia* may be *cis*-1,4 polyisoprene.

NMR spectra. Two of the samples of rubber hydrocarbon obtained from *Euphoribia caducifolia* have been selected for NMR examination. These samples were analysed by ^{1}H and ^{13}C-NMR spectra.

^{1}H-NMR spectra. In ^{1}H-NMR spectrum of one of the samples, most of the intensities lie in the saturation region (0 - 2.85). The peak apprears at δ 1.20 - 1.30 and relates to doublet from CH_3- C - C=CH at δ 1.60 - 1.80, corresponds to a multiplet for CH_3- C=C/CH_2- C=C- and at δ 1.90 - 2.20. There is a multiplet for CH_2- C=C/CH_2- C=C-. The olefinic proton (-C - CH=C/ CH=CH_2) appears at δ 5.10-5.20. In another samples, most of the intensities lie in the saturated region δ 0-2.40 (Chen 1962).

The peak appearing at δ 1.20-1.29 represents the doublet CH_3- C - C=CH, where as at δ 1.46-1.70, it corresponds to a multiplet for CH_3- C=C/CH_2- C=C-. The peak at δ 1.85-2.25 shows a multiplet for CH_2- C=C/CH_2- C=C -. The olefinic proton (- C-CH=C-CH=CH_2) appears at δ 5.15. The ^{1}H-NMR spectra clearly indicates that the rubber hydrocarbon is polyisoprene.

^{13}C-NMR spectra. In ^{13}C-NMR spectrum of one of the sample, the most of the intensities lie in the saturated region 0.80 ppm. The peaks at 23.1, 26.3 and 32.0 ppm corresponds to CH_3, CH_2 carbons, respectively. There are two peaks in the olefinic region 120-140 ppm. One is at 124.5 ppm correspondence to = CH olefinic carbon and other is at 134.5 ppm relates to = C-CH_3 olefinic carbon. In the spectrum of the other sample, the intensities lie in the saturated region 0.80 ppm. The peaks at 23.20, 26.50 and 32.10 ppm relates to CH_3 and CH_2 carbons, respectively. The olefinic peaks lie in the region 120-140 ppm which correspond to = CH and = C-CH_3 olefinic carbons. These evidences suggest that the samples are *cis*-1,4 polyisoprene.

Table 6
Molecular weight of rubber hydrocarbon by GPC method.

Sample No.	Mn	Mw	Mw/Mn	Mn by viscosity
R1	150488	427547	2.84	88405
R2	52350	834978	15.95	48980
R3	64034	39684	6.20	75490
R7	11234	38183	3.40	15275
R8	15592	79728	5.11	18320

Mn, is number average molecular weight; Mw, is weight average molecular weight

$$- CH_2 - CH = C(CH_3) - CH_2 -$$

Both ^{1}H and ^{13}C NMR spectra suggests the rubber hydrocarbon of the polyisoprene.

Molecular weight. Intrinsic viscosities [η] in dl/g for rubber hydrocarbons were determined at 30°C in Ostwald type viscometer using toluene as solvent. Each sample showed different intrinsic viscosity (Table 5). It ranges from 0.31 to 1.00 dl/g, which determine molecular weight as 15275 - 88405. The difference in molecular weight and [η] show that as the stem of the plant is incised the hydrocarbon present in the latex starts polymerization and with the passage of time chain length of the resulting polymer gets increased. Isoprene molecules present in the latex in the prepolymer stage (Yousufzai and Khan 1984), on contact with atmospheric oxygen, it starts polymerizing, resulting in polyisoprene of different chain length. Besides, the molecular distribution of samples were determined by means of GPC. The chromatograms of rubber hydrocarbons show more than one peak which suggests that the samples should be fractionated for getting more dispersed polymers. The values of M obtained by GPC methods are found higher than those obtained by viscosity method. For sample R1 of rubber hydrocarbons, the value of Mn and Mw are 150488 and 427547, respectively. The value of Mw/Mn = 2.84 indicates a narrow molecular weight distribution. On the other hand, the value of M for this sample determined by viscosity method was found as 88405 (Table 6).

Similarly, the samples R2 , R3, R7 and R8 show the values of M by GPC as 52350, 64034, 11234 and 15592, whilst the values of Mw are 834978, 39684, 38183 and 79728 respec-

Table 7
Some physical parameters of rubber hydrocarbon obtained from the plants of *E. caducifolia*

Sample No.	Refractive index	Specific gravity	Consistency	Strength	Combustion
R 1	1.49281	0.93240	Sticky	Poor	Smooky flame
R 2	1.49300	0.39102	Sticky	Poor	Smooky flame
R 3	1.49282	0.39420	Sticky	Poor	Smooky flame
R 4	1.49250	0.93628	Sticky	Poor	Smooky flame
R 5	1.49325	0.93108	Sticky	Poor	Smooky flame
R 6	1.49250	0.93240	Sticky	Poor	Smooky flame
R 7	1.49200	0.93246	Sticky	Poor	Smooky flame
R 8	1.49282	0.93240	Sticky	Poor	Smooky flame
R 9	1.49325	0.93108	Sticky	Poor	Smooky flame
R 10	1.49288	0.93428	Sticky	Poor	Smooky flame

tively. On the other hand intrinsic viscosity for R2, R3, R7 and R8 samples determines Mn as 48980, 75490, 15275 and 18320, respectively. The values of Mw/Mn for R2, R3, R7 and R8 samples are calculated as 15.95, 6.20, 3.40 and 5.11% respectively. The sample R2 show broad molecular weight distribution, whereas rest of the samples, show narrow molecular weight distribution.

Differential scanning calorimetry (DSC). DSC studies of rubber hydrocarbon from *E. caducifolia* latex was also carried out.

The samples R2 and R5 were selected for this study. The sample R2 was heated from - 80 to - 10˚C/min. Glass transition temperature (T_g) appears to be an initial heating scale. The curve shows T_g as - 63.02˚C . Sample R5 was first quenched from 100 to - 100˚C and then heated from -100 to +100˚C at the rate of 10˚C/ min, the curve obtained shows the region of T_g as - 66.96 to 57.11 and middle point is - 60.81˚C. The values of T_g obtained for these samples are very close to literature value of polyisoprene i.e. - 67˚C which clearly evidences that the samples are polyisoprene.

Refractive index of various samples of rubber hydrocarbon are measured. It was found in the range 1.49200 to 1.49325. This value of refractive index is very close to literature value 1.5919 for confirms polyisoprene. It means the rubber hydrocarbons separated from latexes of *E.caducifolia* is polyisoprene. Specific gravity of rubber hydrocarbon samples were measured, which ranges from 0.93102 to 0.93628 and it is in the vicinity of literature value (0.92). Besides, all samples of rubber hydrocarbons are poor in strength and sticky. On flame, these samples are first converted into fluid and then are ignitiated. They burns freely with a smoky flame. These physical parameters also confirmed that the extracted material was natural rubber (Table 7).

In brief, on incising the stem of the plant, the latex was collected in sterilized bottles already containing preservative. The preservative not only makes the system alkaline but also hydrolyses the fatty acids esters naturally occuring in the latex and form soaps. These soaps serve as stabilizer. The latex was coagulated with formic acid and this coagulated material was first soxhelated with acetone to remove resin contents of the latex and then with hexane to separate rubber hydrocarbons. The rubber hydrocarbons was obtained and characterised by different chemical and instrumental methods. Iodine value of hydrocarbon (310.91-350.80) percentage of unsaturation (83.40-94.10%), elemental analysis (C = 87.48 - 88.04%), H = 11.20 - 11.82%). Solubility (soluble in the solvents of natural rubber), IR spectrum (840 cm^{-1}), ^{1}H-NMR spectrum (olefinic proton at δ 5.15-5.20), ^{13}C-NMR spectrum (olefinic region 120-140 ppm), molecular weight (15275 - 88405), molecular weight distribution (both broad & narrow molecular weight distribution), value of T_g (- 63.02/-60.81˚C), refractive index (1.49200 to 1.49350), specific gravity (0.93102 to 0.93628), consistency (sticky), strength (poor) and combustion (smoky flame) identify the rubber hydrocarbon to be certainly *cis*-1,4 polyisoprene.

References

Carter W C, Magat M 1946 The viscosity molecular weight relation for natural rubber. *J Am Chem Soc* **68** 1480.

Chen H Y 1962 Determination of *cis*-1,4 and *trans*-1,4 contents of polyisoprenes by high resonance nuclear magnetic resonance. *Analytical Chemistry* **34**(13) 1793-1795.

Dobholker D A, Kaicker P K, Diwan R K 1991 *Euphorbia* latex - its chemistry and industrial applications. *Part-I Research & Industry* **36** 126-131.

Giner J L, Berkowitz J D, Andersson T 2000 Nonpolar components of the latex of *Euphorbia peplus*. *J Nat Prod* **63**(2)

267-269.

Kemp A R 1927 Direct determination of hydrocarbon in raw rubber, Gutta-Percha and related substances. *Industrial and Engineering Chemistry* **19**(4) 43.

Kemp A R, Mueller G S 1934 Iodine value of rubber and Gutta-Parcha hydrocarbon. *Industrial and Engineering Chemistry* **6**(1) 52-55.

Marks J E 1989 *Comprehensive Polymer Science*. eds, Booth C, Price C, Pergammon, vol **2** pp 286.

Mc Gavack J 1959 Natural latex as a colloidal system. The preservation and concentration of *Hevea* latex. *Rubber Chemistry and Technology* XXX II, 1627-1673.

Richard H W, Brauer G M 1949 Specific refractivity temperature data for polyvinyl acetate and poly butyl acrylate. *J Polym Sci* **4** 351-357.

Sastri B N 1953 *The Wealth of India*. Vol III, CSIR, India.

Scott R L, Carter W C, Magat M 1949 Viscosity molecular weight relations for various synthetic rubbers. *J Am Chem Soc* **71** 220.

de Vasconcellos M C, de Amorin A 2003 Molluscicidal action of the latex *Euphorbia splendens* var hislopic N.E.B. ("Christ's Crown") (*Euphorbiaceae*) against *Lymnaea columella* (Say, 1817) (*Pulmonata lymnaeidae*) intermediate host of *Fasciola hepatica* Linnaeus 1758 (*Trematode. fasciolidae*): 1-test-in laboratory. *Mem Inst Oswaldo Cruz* **98**(4) 557-563.

Yousufzai A H K, Khan A Rasheed 1983 A new vulcanisable rubber from caster oil prepolymer (COP). *Proc Poly Sci Symp* **2** 17.

Yousufzai A H K, Khan A Rasheed 1984 Copolymers from caster oil prepolymer. Part-IV Copolymerization of MMA with Cop. *J Macromole Sci Chem* A **21**(3) 282.