Conversion of D-Galactose Diethyl Mercaptal into Ethyl β-D-Galactofuranoside with Mercuric Chloride and Cadmium Carbonate.—A mixture of D-galactose diethyl mercaptal (5.0 g., 1 mole) cadmium carbonate (6.0 g., excess) and mercuric chloride (9.2 g., 2 moles) in 100 cc. of absolute ethanol was stirred vigorously for two hours at room temperature and the product isolated as described above for the isolation of ethyl β-D-galactofuranoside. The crystalline material was found to be a mixture of D-galactose diethyl mercaptal and ethyl β-D-galactofuranoside. When the reaction time was extended to six hours at room temperature, only ethyl β-D-galactofuranoside was isolated, in approximately 50% yield.

Summary

1. D-Glucose S-ethyl O-methyl monothioacetal exhibited a simple mutarotation at 25° in methanol containing 0.05% hydrogen chloride and exhibited a complex mutarotation in 0.05% aqueous hydrochloric acid. Ethyl α-thio-D-glucofuranoside was isolated as a final product in both cases.

2. Similar mutarotation phenomena were exhibited by D-galactose diethyl monothioacetal. D-Galactose was isolated as a final product in the aqueous medium.

3. Ethyl β-D-galactofuranoside was not detectably hydrolyzed by 0.05% hydrochloric acid at 25°.

4. Mercuric chloride and cadmium carbonate in absolute ethanol reacted with D-galactose diethyl monothioacetal to yield ethyl β-D-galactofuranoside and with D-galactose diethyl monothioacetal pentaacetate to yield D-galactose diethyl acetal pentaacetate.

5. Mercuric chloride and yellow mercuric oxide in methanol reacted with D-glucose S-ethyl O-methyl monothioacetal to give a practically quantitative yield of the sirupy methyl β-D-glucofuranoside of Haworth and co-workers, herein characterized by a crystalline tetracarbanilate.

6. Mercuric chloride and yellow mercuric oxide in ethanol reacted with D-galactose diethyl monothioacetal to give a practically quantitative yield of the crystalline ethyl β-D-galactofuranoside. D-Galactose diethyl acetal was stable toward these reaction conditions.

7. The above data indicate that D-glucose S-ethyl O-methyl monothioacetal, at least in this anomeric form, is not the probable intermediate in the formation of ethyl α-thio-D-glucofuranoside from D-glucose diethyl mercaptal but that the mixed acetal is the probable intermediate in the formation of ethyl β-D-galactofuranoside from D-galactose diethyl mercaptal. These deductions are in accord with the postulations of Pacsu and Green.

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Chemical Investigations in Guayule. I. Essential Oil of Guayule, Parthenium argentatum, Gray

BY A. J. HAAGEN-SMIT AND R. SIU[1]

Aside from the identification of α-pinene by Alexander,[2] very little is known about the essential oil of the guayule rubber plant. This meager chemical knowledge could not furnish a sound basis for the understanding of the injurious effects of the oil on rubber, of its role in the plant, and of its possibilities as a by-product in the guayule rubber industry. The following investigation was carried out to fill this gap in the chemical knowledge of the oil.

The oil was obtained from the steam distillation of fresh guayule plants. Two-thirds of the total oil was obtained after one and one-half hours of steam distillation. About 25% more was obtained with an additional one and one-half hours. After four and one-half hours further steam distillation gave only a negligible amount of oil. The oil obtained after three hours of steam distillation emitted an odor suggestive of decomposition. For this reason later steam distillations were carried out for only two and one-half hours, yielding about 80% of the total oil.

According to Table I, the leaves possess the highest essential oil content on a fresh weight basis (1.04%), followed next by the flowers, then the bark. Only a small amount of oil can be obtained from the wood.

TABLE I

ESSENTIAL OIL CONTENT OF DIFFERENT PARTS OF THE GUAYULE PLANT

Part of plant	Fresh wt. of tissue in g.	Wt. of oil in g.	% of oil on fresh wt. basis
Leaves	6,870	71.2	1.04
Flowers	890	6.7	0.75
Bark	10,265	24.7	.24
Wood	5,910	6.3	.11
Total	23,935	108.9	.45

When the entire guayule plant was steam distilled, the oil separating from the steam distillate

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[1] The authors greatly appreciate the hearty coöperation and keen interest of Dr. A. C. Hildreth and Dr. H. Traub during the course of this work. The help of Dr. J. Kirchner is also gratefully acknowledged.

[2] Alexander, *Ber.*, **44**, 2320 (1911).

was light yellow in color. It was slightly *levo*-rotatory and contained only a small amount of acids and saponifiable matter. Some constants determined for the total oil from two-year old guayule plants (variety 593) from Salinas, California, are: $d^{27.4}_4$ 0.8648, n^{25}D 1.4774, $[\alpha]^{25}$D $-2.70°$, saponification no. 10, acid no. 0.3, and Wijs iodine no. 153.

This oil was carefully fractionated into 45 fractions, on which different physical measurements were made. The data are plotted in Fig. 1.[3]

TABLE II

BOILING POINT OF A SESQUITERPENE OIL FRACTION AT DIFFERENT PRESSURES[a]

Pressure	B. p., °C.
20 μ	60
250 μ	63
600 μ	67
3 mm.	87
17 mm.	120
143 mm.	182
746 mm.	234

[a] Interpolation among these figures gave a boiling point of 60° at 20–25 μ pressure and 125° at 20–22 mm. pressure. The difference of 125 − 60 or 65°, therefore, was adopted as the abscissa spacing in Fig. 1 between 51° at 20–25 μ and 51° at 20–22 mm.

The fractionation curve of Fig. 1 shows 4 large groups. Their differences are also reflected in the behavior of the curves for the various physical constants. From the boiling point ranges, the carbon–hydrogen, and the Zerewitinoff analyses these four groups were shown to represent terpenes, oxygenated terpenes, sesquiterpenes and sesquiterpene alcohols, respectively. These groups are present in the oil in the following proportions: 72.6% terpenes, 5.8% oxygenated terpenes, 9.3% sesquiterpenes, 6.3% sesquiterpene alcohols and 5.9% residue.

The physical constants for the different fractions suggest the absence of large amounts of known aliphatic terpene hydrocarbons and aliphatic sesquiterpene hydrocarbons in guayule essential oil. This is confirmed by the analyses of the separate fractions.

Fraction 2 was shown to be α-pinene from the carbon–hydrogen analyses, physical constants, and the mixed melting point of the nitrosochloride with the same derivative prepared from known α-pinene. Although Fraction 2 was *levo*-rotatory ($[\alpha]^{25}$D $-5.67°$), it produced a nitrosochloride with the melting point of that of *dl*-α-pinene nitrosochloride. This suggests that most of the α-pinene in guayule is *dl*-α-pinene, with a possible excess of the *l*-isomer. It is estimated from the fractionation curve that *dl*-α-pinene makes up 50 to 60% of the total essential oil of guayule.

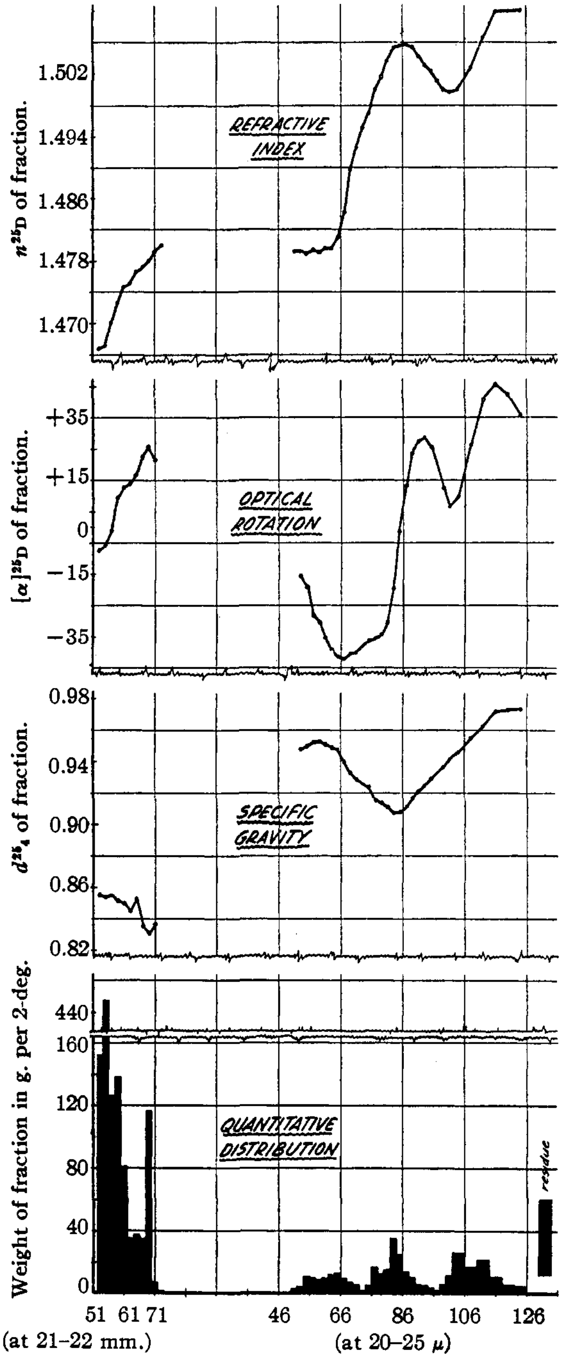

Fig. 1.—Quantitative distribution and physical properties of different boiling fractions of guayule essential oil.

Through the oxidation of Fraction 4 and the identification of the oxidation product as norpinic acid, β-pinene was identified.

The physical constants, the carbon–hydrogen analysis, and the melting point of the tetrabromide of Fraction 9 are identical with those from *dl*-limonene. Although the tetrabromide from Fraction 9 gave no melting point depression when

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(3) In order to establish the correct abscissa spacing in Fig. 1 between the boiling points of fractionations at different pressures, a sesquiterpene fraction was refluxed at various pressures. The results are given in Table II.

mixed with the tetrabromide from *dl*-limonene, Fraction 9 showed a dextro-rotation, $[\alpha]^{25}\mathrm{D}$ + 25.76°. This may be explained by an excess of the *d*-isomer in the guayule plant. About 10% of the weight of the oil was thus shown to be limonene.

The largest sesquiterpene fraction, which makes up about 8% by weight of the total oil, was identified as cadinene. The chemical composition and the physical constants for Fraction 29 agree very closely with those given by Henderson and Robertson[4] for cadinene. The dihydrochloride gave the same melting point as that of cadinene dihydrochloride. Hydrogenation of Fraction 29 demonstrated the presence of two double bonds. This indicated a bicyclic structure for an empirical formula of $C_{15}H_{24}$. The ethylenic linkages were shown to be isolated by their non-reactivity toward sodium and alcohol and also toward maleic anhydride. Selenium dehydrogenation of the oil gave an aromatic hydrocarbon, the picrate of which had the same empirical formula and melting point as cadalene picrate, which is obtained from cadinene under similar conditions.

Selenium dehydrogenation of Fraction 26 produced S-guajazulene, which was identified by its picrate, m. p. 120–121.5°, its styphnate, m. p. 105.5–106.5°, and its absorption spectrum. The melting points recorded in literature[5] for the picrate and the styphnate are 106–107° and 121–122°, respectively. According to Plattner[6] the absorption spectrum of S-guajazulene is characterized by 3 strong bands at 603, 661 and 732 mμ, and weak bands at 556, 577, 631 and 699 mμ. The absorption spectrum of the azulene obtained from the dehydrogenation of Fraction 26 (Fig. 2), shows maxima at the same places. The formation of S-guajazulene in the selenium dehydrogenation of guayule oil is interesting in view of the work of Ruzicka and Haagen-Smit.[7] These workers obtained a blue S-guajazulene on dehydrogenation of guajol with sulfur and a violet Se-guazulene with selenium. Furthermore, picrates of the two azulenes gave distinctively different melting points of 121–122° and 114–115°, respectively. The fact that the physical constants of Fraction 26 agree very well with those for guajene, a sesquiterpene which can also be dehydrogenated to S-guazulene, suggests a guajene-like nucleus in Fraction 26. This fraction makes up 2% of the oil.

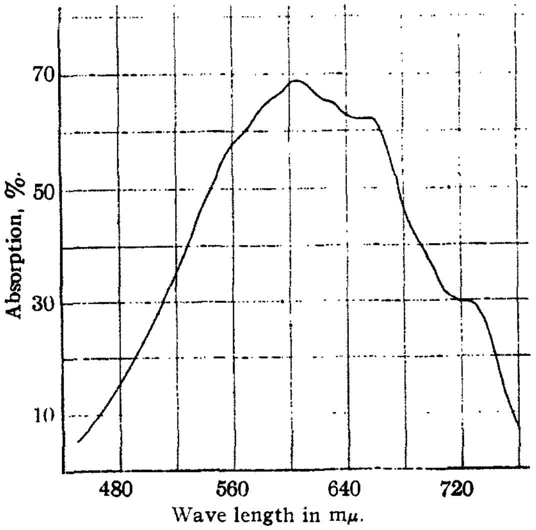

Fig. 2.—Absorption spectrum of guayule azulene.

A sesquiterpene alcohol, which is identical or closely related to elemol, $C_{15}H_{26}O$, was found in Fraction 39. The empirical formula and the physical constants agree very well. Fraction 39 gave eudalene upon selenium dehydrogenation, as is the case with elemol. One active hydrogen was shown by the Zerewitinoff analysis, thereby suggesting the presence of an alcoholic group. The failure of this group to react with phthalic anhydride and with carbon bisulfide to form a xanthogenate showed it to be a tertiary one. This is also the case with elemol. Further like elemol, there were found two ethylenic linkages in the guayule oil fraction. About 4% of the oil is made up of this compound.

One of the oxygenated terpene fractions was shown to be probably *l*-phellandral. Good agreement exists between the physical constants of Fraction 20 and those of *l*-phellandral. Also, the 2,4-dinitrophenylhydrazone prepared from Fraction 20 showed the same melting point as that recorded in the literature for phellandral.

Only 3 of the maxima in the fractionation curve of Table V remain unidentified at present. These are Fractions 7, 15 and 41. Inasmuch as this project had to be interrupted, the information obtained so far on these fractions will be given in this paper and conclusions as to their nature will be drawn, as much as available evidences permit.

Fraction 7.—This small maximum in the fractionation curve is probably caused by the presence of a small amount of an easily oxidizable terpene. Carbon–hydrogen analyses after different lengths of time of standing gave varying oxygen content. Immediately after fractionation, the oil fraction analyzed 86.84% carbon, 11.66% hydrogen and 1.50% oxygen.

Fraction 15.—The formation of a 2,4-dinitrophenylhydrazone showed this fraction to be a carbonyl compound. Its boiling point indicates a C_{10} compound. Molecular refractivity calculations suggest a monocyclic compound. This fraction makes up about 2% of the oil, experimental M_D, 46.0; calcd M_D for monocyclic $C_{10}H_{18}O$, 46.2.

Fraction 41.—Combustion analyses suggest an empirical formula of $C_{15}H_{26}O$. The oxygen is present as an alcoholic group, as shown by the

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(4) Henderson and Robertson, *J. Chem. Soc.*, **125**, 1992 (1924).

(5) Ruzicka and Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).

(6) Plattner, *ibid.*, **24**, 290E (1941).

(7) Ruzicka and Haagen-Smit, *ibid.*, **14**, 1101 (1931).

Zerewitinoff active hydrogen analysis. Failure of the hydroxyl group to react with phthalic anhydride and with carbon bisulfide to form xanthogenate indicates a tertiary alcoholic group. The compound in question is, therefore, a tertiary sesquiterpene alcohol. Furthermore, selenium dehydrogenation of the oil resulted in the formation of an azulene. The presence of such a carbon skeleton in the sesquiterpene alcohol is thereby indicated. This alcohol makes up about 3% of the total oil.

Thus, about 90% of the essential oil of guayule is identified as cyclic compounds. This is in support of the belief that the terpenaceous compounds are not intermediates in the formation of rubber in the plant.[8] If the terpene compounds are considered as rubber precursors, it is hardly to be expected that these intermediary compounds would be cyclic in nature, which would necessitate the difficult task of breaking the carbon-to-carbon bonds so that they can again polymerize in a straight chain manner into rubber.

While both terpenes and rubber can be resolved into isopentane units, which indicates a similarity in their mode of formation in the plant, it has never been demonstrated that these originate from a common precursor. The often irregular build up and the cyclization tendencies of the terpene precursor as contrasted to the aliphatic regularity of the rubber molecule speak against a common precursor. It may be that rubber has its origin in polyoses like starch and inulin, while the terpenes are derived in a similar way from simpler sugars as postulated by Emde.[9]

Experimental Part

Fractionation of Guayule Essential Oil.—The essential oil was obtained from the steam distillation for two and one-half hours of two-year old guayule plants (*Parthenium argentatum*, Gray, variety 593). These had been grown in the William Bryan tract of Salinas, California, and were harvested in the fall. The oil was separated from the water of the steam distillate and dried over anhydrous sodium sulfate. The oil was first fractionated by means of an 8-inch helices column into the 11 fractions given in Table III–IV.

TABLE III–IV

PRELIMINARY FRACTIONATION OF GUAYULE ESSENTIAL OIL

Fraction	Pressure	Distn. temp., °C.	Wt. in g.
1	21 mm.	54–58	1018.6
2	21 mm.	58–62	137.1
3	21 mm.	62–66	67.5
4	21 mm.	66–70	117.5
5	8 μ	<50	33.3
6	8 μ	50–60	39.0
7	8 μ	60–70	53.4
8	8 μ	70–80	57.6
9	8 μ	80–90	64.1
10	8 μ	90–110	51.3
11	Residue		112.4
Total			1751.8

A careful fractionation into 2-degree fractions was then made on the crude fractions listed in Table III–IV. A modified total condensation, variable-take-off still-head[10] was used, together with an 8-inch helices fractionating column for the lower boiling fractions and a 3-inch helices fractionating column for fractions boiling above 50° at 20 μ pressure. The final fractions together with their respective physical constants are given in Table V. The density was determined with a 1-cc. and a 5-cc. pycnometer at 25°. An Abbe refractometer was used for the refractive index measurements at 25°, while the optical rotations were measured at 25° by means of a Winkel–Zeiss polarimeter. The A. O. A. C. methods[11] were used for the determination of the saponification, iodine and acid numbers.

TABLE V

PHYSICAL CONSTANTS AND QUANTITATIVE DISTRIBUTION OF DIFFERENT BOILING FRACTIONS OF GUAYULE ESSENTIAL OIL

Fraction	Distillation range Temp. in °C.	Distillation range Pressure	Weight, g.	d^{25}_4	$[\alpha]^{25}_D$	n^{25}_D
1	52-54	22 mm.	152.5	0.8553	− 7.20	1.4668
2	54-56	22	447.0	.8542	− 5.67	1.4671
3	56–58	22	126.3	.8549	− 1.15	1.4702
4	58-60	22	138.3	.8521	+ 9.03	1.4728
5	60–62	22	80.7	.8501	+12.56	1.4746
6	62–64	22	35.2	.8464	+14.05	1.4751
7	64–66	21	37.7	.8536	+16.82	1.4766
8	66–68	21	35.2	.8354	+22.67	1.4772
9	68–70	21	116.5	.8322	+25.76	1.4780
10	70–72	21	6.9	.8374	+21.54	1.4793
11	72–74	21	0.9	....	.....	1.4800
12	.....	..	0.0	....	.....	....
13	50-52	20 μ	2.3	....	.....	1.4791
14	52–54	20	4.1	.9489	−15.24	1.4791
15	54–56	20	11.0	.9510	−19.07	1.4789
16	56–58	20	10.5	.9525	−28.09	1.4792
17	58–60	20	8.3	.9530	−30.57	1.4790
18	60–62	20	9.5	.9519	−35.25	1.4797
19	62–64	20	12.0	.9499	−39.01	1.4798
20	64–66	20	13.0	.9473	−41.07	1.4810
21	66–68	20	9.8	.9409	−41.85	1.4843
22	68–70	20	7.0	.9331	−40.96	1.4898
23	70–72	25	5.9	.9292	−40.79	1.4927
24	72–74	25	0.8	....	.....	1.4952
25	74-76	25	4.4	.9237	−36.08	1.4969
26	76–78	25	17.1	.9166	−35.96	1.5000
27	78-80	25	12.2	.9144	−34.45	1.5018
28	80–82	25	15.4	.9116	−30.98	1.5037
29	82–84	25	35.0	.9088	−19.85	1.5054
30	84–86	25	25.2	.9097	− 1.10	1.5057
31	86 88	25	14.0	.9118	+13.53	1.5058
32	88-90	25	10.4	.9165	+23.39	1.5050
33	90–92	25	5.2	.9229	+27.36	1.5042
34	92–94	25	4.3	.9247	+28.86	1.5030
35	94–96	25	3.2	.9293	+25.61	1.5022
36	96-98	25	1.9	....	.....	1.5010
37	98–100	25	5.5	.9366	+12.32	1.5003
38	100–102	25	11.5	.9426	+ 6.64	1.4998
39	102-106	25	26.0	.9451	+ 9.48	1.5005
40	106–110	25	17.4	.9562	+26.40	1.5029
41	110–114	25	21.0	.9635	+40.89	1.5066
42	114-118	25	10.5	.9719	+45.44	1.5098
43	118–122	25	4.9	.9722	+42.35	1.5099
44	122–126	25	4.1	.9731	+35.99	1.5100
45	Residue	..	96.0	....	.....	....
Total			1616.6			

Identification of α-Pinene.—The evidences for the identification of α-pinene are summarized in Table VI.

The α-pinene nitrosochloride was prepared in the following way: 7 cc. of oil, 10 cc. of amyl nitrite and 15 cc. of

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(8) Prokofieff, *Izvest. Akad. Nauk. S. S. S. R.*, 589 (1940).

(9) H. Emde, *Helv. Chim. Acta*, **14**, 881 (1931).

(10) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

(11) Skinner, Official Methods of A. O. A. C., 4th ed., pp. 412–413 (1935).

TABLE VI

IDENTIFICATION OF α-PINENE IN GUAYULE ESSENTIAL OIL

Property	Pure α-pinene	Fraction 2
Boiling point	156–156.3 at 760 mm.[12]	54–56° at 22 mm.
% carbon	88.16 (calcd.)	88.40[14]
% hydrogen	11.84 (calcd.)	11.65
Density	d^{20}_4 0.8582[13]	d^{25}_4 0.8542
Index of refraction	n 1.4658[13]	n^{25}_D 1.4671
M. p. of nitrosochloride, °C.	106–107	106–107
Mixed melting point, °C.	106–107	

glacial acetic acid were mixed and cooled in an ice–salt-bath. A cooled mixture of 5.5 cc. of glacial acetic acid and 5.5 cc. of concentrated hydrochloric acid was gradually added with stirring. The blue color which appeared upon the addition of a portion of the acid mixture was allowed to disappear before another portion was added. The resulting white crystals were purified six times from chloroform solution by the addition of methanol. The mixed melting point of this nitrosochloride and a nitrosochloride prepared from known *dl*-α-pinene gave no depression.

Identification of β-Pinene.[15]—In Table VII are summarized the evidences for the presence of β-pinene.

TABLE VII

IDENTIFICATION OF β-PINENE IN GUAYULE ESSENTIAL OIL

Property	β-Pinene[16]	Fraction 4
Boiling point, °C.	164–166 at 760 mm.	58–60 at 22 mm.
% carbon	88.16 (calcd.)	88.37
% hydrogen	11.84 (calcd.)	11.73
Density	d^{15} 0.8650	d^{25}_4 0.8521
Index of refraction	n^{20}_D 1.4755	d^{25}_D 1.4728
Nopinic acid		
Crystallinity	White needles	White needles
% carbon	65.19 (calcd.)	65.07
% hydrogen	8.75 (calcd.)	8.53
Melting point, °C.	126–127	126–127

The nopinic acid was obtained by Wallach's[17] method; 20 g. of Fraction 4 was added to a solution of 47 g. of potassium permanganate in 600 cc. of water; 10 g. of sodium hydroxide was then added and the mixture was shaken vigorously on a shaking machine for thirty minutes, during which time the temperature rose to about 60°. The unreacted hydrocarbon was removed by steam distillation and the manganese dioxide filtered off. The clear tan colored filtrate was distilled under reduced pressure in an atmosphere of carbon dioxide. Upon cooling of the solution sodium nopinate precipitated out. The crude product was recrystallized from hot water and 810 mg. of crystalline material was obtained.

In order to obtain the free acid, the sodium nopinate (810 mg.) was dissolved in 33 cc. of water and 6.6 cc. of 0.6 *N* sulfuric acid was added. The free nopinic acid thus released was extracted with ethyl ether. After evaporation of the ether it was recrystallized from benzene.

Identification of Limonene.—Table VIII summarizes the evidences for the presence of limonene in guayule essential oil.

TABLE VIII

IDENTIFICATION OF LIMONENE IN GUAYULE ESSENTIAL OIL

Property	*dl*-Limonene	Fraction 9
Boiling point, °C.	176 at 76 mm.[18]	68–70 at 21 mm.
% carbon	88.16 (calcd.)	88.11
% hydrogen	11.84 (calcd.)	12.05
Density	d^{20} 0.845[16]	a^{25}_4 0.8322
Index of refraction	n^{20}_D 1.4764[19]	n^{25}_D 1.4780
Tetrabromide		
% bromine	70.12 (calcd.)	70.05
Melting point, °C.	123–123.5	123–124
Mixed m. p., °C.	123–123.5	

The tetrabromide was prepared in the following manner: A sample of oil was dissolved in 8 volumes of a 1:1 ethanol-diethyl ether solution. The mixture was cooled in an ice-salt-bath and 0.6 volume of bromine added dropwise with shaking. After all of the bromine was added the reaction mixture was poured into an open crystallizing dish. White crystals of the tetrabromide appeared upon evaporation of the solvent. The crystals were subsequently recrystallized six times from diethyl ether. They gave no depression in melting point when mixed with known *dl*-limonene tetrabromide.

Identification of Cadinene.—The evidences for the presence of cadinene in the essential oil of guayule are summarized in Table IX.

TABLE IX

IDENTIFICATION OF CADINENE IN GUAYULE ESSENTIAL OIL

Property	Cadinene	Fraction 29
Boiling point, °C.	134–136 at 11 mm.[20]	82–84 at 25 mm.
Density	d^{20}_4 0.9189[20]	d^{25}_4 0.9088
Index of refraction	n^{20}_D 1.5079[20]	n^{25}_D 1.5054
% carbon	88.16 (calcd.)	87.83
% hydrogen	11.84 (calcd.)	12.02
Number of double bonds	2.0	1.9
Reaction with maleic anhydride	None	None
Reaction with sodium and alcohol	None	None
Dehydrogenation product		
M. p. of picrate, °C.	115[21]	114–115
% nitrogen in picrate	9.83 (calcd.)	10.16
Dihydrochloride:		
Melting point, °C.	117[21]	117–118
% chlorine	25.58 (calcd.)	25.66

The chemical and the physical properties of Fraction 29 agree very closely with those given in literature for cadinene. The number of ethylenic linkages was determined through the hydrogenation of Fraction 29 in glacial acetic acid solution in the presence of platinum black as a catalyst: 11.553 mg. of oil absorbed 2.375 cc. of hydrogen at N. T. P. in the presence of 5.695 mg. of catalyst. This revealed the presence of 2 double bonds and 2 rings in Fraction 29 with the empirical formula of $C_{15}H_{24}$. The same number of double bonds and rings are present in cadinene.

The two double bonds in question were shown to be isolated, as is the case with cadinene, by their non-reactivity toward maleic anhydride. Three grams of Fraction 29, 1.5 g. of maleic anhydride and 15 cc. of benzene were refluxed for ten hours. The benzene was then removed

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(12) Huntress and Mulliken, "Identification of Pure Compounds," 1941, p. 573.

(13) "Handbook of Chemistry and Physics," 22nd ed., p. 722.

(14) Analyses reported in this paper were done by Dr. G. Oppenheimer, Mr. H. Tomlin and Mr. G. Swinehart.

(15) The help of Mr. Victor Schocken during this phase of the work is gratefully acknowledged.

(16) *Beil.*, **5**, 155; **10**, 32 (1922).

(17) Wallach, *Ann.*, **356**, 228 (1907).

(18) "Handbook of Chem. and Physics," 22nd Ed., p. 678.

(19) Wallach, *Ann.*, **246**, 197 (1888).

(20) Henderson and Robertson, *J. Chem. Soc.*, **125**, 1992 (1924).

(21) Ruzicka and Stoll, *Helv. Chim. Acta*, **7**, 84 (1924).

through vacuum distillation. No addition of the maleic anhydride was found to have occurred. Heating maleic anhydride and Fraction 29 directly over a flame also gave no reaction.

Further experiments on the treatment of Fraction 29 with sodium and alcohol confirmed the negative results with maleic anhydride. Five grams of Fraction 29 was mixed with 25 cc. of amyl alcohol and 12 g. of sodium was added. This mixture was heated in an oil-bath at 180°. Amyl alcohol was added in small portions until all of the sodium was dissolved. The reaction mixture was cooled and shaken four times with water. The alcohol layer was separated and the alcohol distilled off. The resulting oil was refractionated two times. Most of the oil distilled over at approximately 125° at 12 mm. pressure. Hydrogenation of this fraction showed that the two original double bonds had not been attacked by the sodium and alcohol treatment.

Selenium dehydrogenation of Fraction 29 gave an aromatic hydrocarbon, the picrate of which had the same melting point and the same empirical formula as cadalene picrate. The latter can also be obtained from the dehydrogenation of cadinene; 2.7 g. of Fraction 29 and 5.2 g. of selenium powder was heated in a 100-cc. test-tube fitted with a reflux glass tubing 3 feet long. The end of the reflux tubing was bent back and led into a saturated solution of sodium hydroxide, which served as a trap. The reaction mixture was heated in a Wood's metal bath at 208° for sixteen hours, then at 315° for thirty hours. The thick fluid was decanted into a 10-cc. Claissen flask and distilled at 17 mm. pressure: 1.5 g. of oil distilled over between 95 and 120°. The picrate was made from this fraction and was recrystallized 6 times from ethanol. The resulting long, dark orange crystals melted at 114–115°, as compared to 115° for cadalene picrate. The nitrogen content was the same in both cases.

The dihydrochloride from Fraction 29 showed the same melting point and percentage chlorine as that from cadinene. Three grams of Fraction 29 was diluted with 18 cc. of absolute ethyl ether. Dry hydrogen chloride gas was passed through the ice-cooled solution for thirty minutes. The flask was stoppered and placed in the refrigerator for three weeks, whereupon the dihydrochloride settled out. The long white needles were recrystallized 7 times from glacial acetic acid. They melted at 117–118° as compared to 117° recorded for cadinene dihydrochloride.

Identification of Guajene-like Sesquiterpene.—One hundred and fifty-nine grams of a sesquiterpene fraction, b. p. 76–80° at 20 μ, was heated with 300 g. of selenium powder at 250–270° for eight hours, then at 170° for eleven hours, and finally at 250° for twenty-eight hours. The thick reaction mixture was distilled at 200 μ pressure. One hundred and thirty grams of a blue distillate was collected between 65 and 110°. The distillate was dissolved in thrice its volume of petrol ether (b. p. 30–60°), chilled in ice and shaken with about 20 cc. of concentrated phosphoric acid. The blue ether solution was gradually decolorized with the concomitant formation of the red phosphoric acid addition product. The acid layer was then washed three times with petrol ether. The addition product was decomposed with the addition of ice and the regenerated azulene taken up in petrol ether. This solution was immediately washed thoroughly with sodium carbonate solution and finally with water. After drying over anhydrous sodium sulfate the ether was distilled off, leaving 3.7 g. of crude deep-blue azulene.

The crude azulene was purified through the formation of its picrate. After recrystallization ten times the picrate, m. p. 120–121.5, was decomposed on an alumina (Alcoa activated brand) column with 1:1 benzene–cyclohexane as the solvent.

Analysis of regenerated azulene: Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 91.18; H, 9.19.

Analysis of picrate of regenerated azulene, m. p. 120–121.5°: Calcd. for $C_{21}H_{21}N_3O_7$: C, 59.01; H, 4.95; N, 9.83. Found: C, 59.24; H, 5.04; N, 10.03.

Analysis of styphnate of regenerated azulene, m. p. 105.5–106.5°: Calcd. for $C_{21}H_{22}N_3O_8$: C, 56.88; H, 4.97; N, 9.48. Found: C, 56.93; H, 4.89; N, 9.26.

The absorption spectrum of the azulene from guayule was taken by means of a Beckman Photoelectric Spectrophotometer, with the slit width varying from 0.03 to 0.24 mm. A 0.025% benzene solution of the azulene was used. The results are plotted in Fig. 2.[22]

Identification of Elemol-like Sesquiterpene Alcohol.—Although conclusive evidence is still necessary, the experimental results summarized in Table X indicate the presence of an elemol-like sesquiterpene alcohol in guayule oil.

TABLE X

IDENTIFICATION OF ELEMOL-LIKE SESQUITERPENE ALCOHOL IN GUAYULE ESSENTIAL OIL

Property	Elemol	Fraction 39
Empirical formula	$C_{15}H_{26}O$	$C_{15}H_{26}O$
Boiling point, °C.	141–142 at 12 mm.	102–106 at 25 μ
Density	d^{18}_4 0.9345	d^{25}_4 0.9451
Refractive index	n^{18}D 1.4980[23]	n^{25}D 1.5005
Active hydrogen	1	1
Primary and secondary alcohol test		
(a) Phthalic anhydride	Negative	Negative
(b) Xanthogenate	Negative	Negative
Unsaturation	2.0 double bonds	1.8 double bonds
Dehydrogenation product		
Picrate, color	Bright yellow-orange	Bright yellow-orange
Picrate, m. p., °C.	Eudalene, 92.8	92.5-93
Picrate, % nitrogen	$C_{20}H_{19}O_7N_3$, 10.16	9.83

Identification of *l*-Phellandral.—The evidences presented in Table XI point to the probable presence of this compound in the essential oil of guayule.

TABLE XI

IDENTIFICATION OF PHELLANDRAL IN GUAYULE ESSENTIAL OIL

Property	Phellandral	Fraction 20
Boiling point, °C.	89 at 5 mm.	64–66 at 20 μ
Density	d^{20} 0.9412	d^{25}_4 0.9473
Index of refraction	n^{20}D 1.4912	n^{25}D 1.4810
Optical rotation	αD −130.85°	α^{25}D −41.07
Molecular refractivity	45.72 (calcd.)	45.73
2,4-Dinitrophenylhydrazone		
Color	Dark orange	Dark orange
Melting point, °C.	204[24]	203.5–205

Summary

The physical and chemical properties, the composition, and the distribution of the essential oil of the guayule rubber plant, *Parthenium argentatum*, Gray, have been investigated.

The leaves contain the highest essential oil content on the fresh weight basis (1.04%), followed next by the flowers (0.75%), then the bark (0.24%), and finally the wood (0.11%). The average yield for the whole plant is 0.45%.

The oil was separated by distillation into 45 fractions, and in this way could be divided into 5 large groups, *viz.*: 72.6% terpenes, 5.8% oxygenated terpenes, 9.3% sesquiterpenes, 6.3% oxygenated sesquiterpenes, and 5.9% residue.

The following compounds were identified and their approximate amounts in the oil are listed:

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(22) The spectrophotometric readings were made by Mr. Earl Malmberg, for which the authors are grateful.

(23) Ruzicka and Pfeiffer, *Helv. Chim. Acta*, **9**, 850 (1926).

(24) Berry, MacBeth and Swanson, *J. Chem. Soc.*, 1449 (1938).

60%, α-pinene; 9%, dipentene; 8%, cadinene; 6%, di-, tri- and higher terpenaceous compounds; 4%, elemol-like sesquiterpene alcohol; 4%, phellandral (probably); 3%, sesquiterpene alcohol with an azulene nucleus; 2%, guajene-like sesquiterpene; 2%, terpene ketone or aldehyde; 2%, β-pinene and small amounts of an easily oxidizable terpene.

The significance of these compounds in relation to the formation of rubber in the plant has been discussed.

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[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

The Chlorination of Certain Long Chain Esters

BY HERBERT H. GUEST AND CHARLES M. GODDARD, JR.[1]

Normal aliphatic acids with more than seven carbon atoms undergo almost exclusively alpha bromination when treated according to Hell–Vollhard–Zelinsky.[2] Upon chlorination of such acids by the same procedure, we have found that a much larger amount of by-products, particularly products of disubstitution, is formed. As the acids decompose readily upon distillation, the methyl esters were investigated as possibly being more suitable starting material.

Methyl caprylate, laurate, myristate and stearate were treated with chlorine in the presence of various catalysts. Chlorination took place readily and fractional distillation of the products was effected without decomposition. It was possible to obtain a fraction from which unaltered and dichloro ester were removed but this fraction was not resolvable into isomers by further distillation. Isomers were present, however, because derivatives prepared from this highly purified fraction differ from those prepared in a similar manner from authentic α-chloro or α-bromo esters.

Experimental

Chlorination of Methyl Laurate.—The ester used as starting material was obtained from commercial acid which had been fractionally distilled on a large scale. After esterification, very careful distillation through a Stedman[3] fractionation column further purified it to the desired degree. It had the characteristics: b. p. (8 mm.) 136–139°; saponification equivalent 214; calcd. for $C_{13}H_{26}O_2$: 214.

It was found that the methyl esters were preferable, not only on account of their lower boiling point, but also because they reacted more readily with chlorine than the other alkyl esters.

Twenty-five experiments were conducted in which the average amount of ester used was 200 g. The time of chlorination ranged between one-half and seventeen hours. The temperature also was varied between 7 and 130°, the optimum being 30°. As catalysts, sulfur, phosphorus chlorides, and chloroacetyl chloride were used. In every case it was found that there was unaltered ester, ranging from 13 to 54%; the amount of dichloro ester correspondingly varying from 40 to 8%.

Experiments 1 to 12 were carried out in a dark hood, and 13 to 24 with illumination from 120-watt electric light bulb.

In Experiment 5, the cold reaction mixture (7°) held enough unreacted chlorine in solution to cause such rapid evolution of gases upon warming to room temperature that more than half the ester was lost from the reaction flask.

Experiment 6 showed the effect of washing out the dissolved chlorine before it could react completely. There was only 3.7% chlorine in the portion washed with ice-water as compared to 8.4% chlorine in the remainder which had been allowed to reach room temperature.

In Experiment 19 the flask was coated with wax, to determine whether glass acted as a catalyst. The result was negative.

In Experiments 22, 23 and 24, the cold ester containing dissolved chlorine was dropped slowly through a glass tower loosely packed with glass wool which was kept at 70°. It was hoped that the shortened time of reaction allowed the dissolved chlorine would prevent the formation of polychloro ester.

Data on Purified Fractions of Monochloro Esters

	B. p., °C.	Mm.	n_D	Analyses, % Cl Found	Calcd.
$C_7H_{14}ClCOOCH_3$	100	4	1.4435	18.9	18.4
$C_{11}H_{22}ClCOOCH_3$	158–164	7	1.4505	14.2	14.3
$C_{13}H_{26}ClCOOCH_3$	167–174	6	1.4531	12.5	12.9

Chlorination of Methyl Myristate using Phosphorus Pentachloride as Catalyst.—Methyl myristate (412 g.) to which 20 g. of phosphorus pentachloride was added, was treated with dry chlorine for one hour when increase in weight was 40 g. After standing at room temperature for thirty-six hours a further quantity of chlorine was added until final weight had increased by 82 g.; temperature was held between 25 and 32°. Distillation at 3 mm. gave the following fractions.

	Boiling range, °C.	% of total	Chlorine content, %	Sap. equiv.
1	135–150	26	4.7	195
2	150–160	20	9.3	169
3	160–170	24	14.5	132
4	170–185	20	19.6	114
5	Residue	10	23.3	105

Direct Chlorination of Methyl Stearate.—The methyl ester of stearic acid, substantially free from palmitic acid, was prepared and distilled carefully. It was chlorinated at 35° for six and one-half hours until the chlorine content was 10.9%. After washing and drying it was distilled. A fraction b. p. (10 mm.) 203–210° was collected.

Anal. Calcd. for $C_{19}H_{35}O_2Cl$: Cl, 10.7. Found: Cl, 10.6.

Preparation of α-Chlorostearic Acid.—α-Bromostearic acid was converted into α-hydroxystearic acid by heating with potassium hydroxide. By the action of thionyl chloride at 100° for sixteen hours, the hydroxyl group was replaced with chlorine. Distillation at 6 mm. pressure gave an ester with b. p. 190–200.

Anal. Calcd. for $C_{19}H_{35}O_2Cl$: Cl, 10.7; sap. equiv., 167. Found: Cl, 11.8; sap. equiv., 159.

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(1) In active service U. S. N. R.

(2) "Organic Syntheses," Coll. Vol. 1, p. 108.

(3) U. S. Patent 2,047,444 (1936), *cf.* L. B. Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).